Theoretical Investigation on the Structure-Property Relationship of Nitropyrazoles. Nitrodeiodination of Iodopyrazoles and Environmentally Friendly Synthesis of Nitropyrazoles by Impregnated Bismuth Nitrate

A Thesis Submitted for the Degree of

DOCTOR OF PHILOSOPHY

by

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June 2011

To

Prof. Seyed E. Hasnain

Former Vice Chancellor, University of Hyderabad

Contents

Statement

I hereby declare that the matter embodied in this thesis entitled "**Theoretical Investigation on the Structure-Property Relationship of Nitropyrazoles. Nitrodeiodination of Iodopyrazoles and Environmentally Friendly Synthesis of Nitropyrazoles by Impregnated Bismuth Nitrate"** is the results of investigations carried out by me in the Advanced Centre for Research in High Energy Materials (ACRHEM), University of Hyderabad under the supervision of **Prof. Surya P. Tewari** and **Dr. Arun K. Sikder**.

In keeping with the general practice of reporting scientific observations due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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Certificate

This is to certify that the work embodied in this thesis entitled **"Theoretical Investigation on the Structure-Property Relationship of Nitropyrazoles. Nitrodeiodination of Iodopyrazoles and Environmentally Friendly Synthesis of Nitropyrazoles by Impregnated Bismuth Nitrate"** has been carried out by **Pasupala Ravi** under our supervision and the same has not been submitted elsewhere for Degree or Diploma.

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Acknowledgements

I thank almighty God who is unto me wisdom, righteousness, sanctification and redemption.

I would like to thank my supervisor ***Prof. Surya P. Tewari*** *for his guidance and personal motivation throughout my research work.*

I wish to express my deep sense of gratitude to ***Dr. Arun K. Sikder****, Joint Director, High Energy Materials Research Laboratory, Pune for useful discussions, constant encouragement, personal motivation and help. I will always be indebted to him for this.*

I thank ***Shri. Girish M. Gore****, Joint Director for his generous help in many ways throughout my stay at EMR Division, High Energy Materials Research Laboratory. I also thank all EMR family members for creating a pleasant atmosphere.*

I would like to thank Prof. Ananta Krishnan, Prof. Kishore, Prof. Givind, Prof. Om Prakash, Prof. A. K. Choudhary, Dr. Kishore, Dr. Kranthi, Dr. Rajendra, Dr. Anand, Dr. Munenna, Dr. Ravenna, Dr. Sivanna, Dr. Bhusenna, Dr. Sivabalan, Dr. Venkatesan, Dr. Dilip, Dr. Aniyappan, Shri. Agawane, Shri. Soman, Shri. Bhatewara, Shri. Waani, Mrs. Wagh, Ms. Suman, Saikia, Lingala, Sreekantha Reddy, Sujit, Sekhar and Bhemmanna for their help and extreme cooperation during my research work.

I thank Bro. Joseph Kurion (HEBRONE), Mary, Showraiah, Suseelakka, Siluvamma, Peddaiah, Sudheer, Pushpa Raju, Savithree, Dr. Jhansi, Dr. Sunitha, Rekha, Viswasanna (IITB) and Yesupadam for their constant prayers and support. I also thank Manikyamanna, Chandaih, Jagadeesh, Vasanthanna, Bheesanna, Mark, Shyam, Ramana, Masthan, Jaya Raju, Jaya Ram, Santhosh, Nageswara Rao and Suresh for their prayers.

I thank all the staff members and the research scholars of ACRHEM for their moral support.

I should recall here, the kind of training I received from my beloved teachers Dr. Venkata Narsu (Chemistry), Dr. Ramachandrudu (Telugu), Shri. Madhavaiah (English), Dr. Siraj (Chemistry), Dr. Ramana (Chemistry), Dr. Balasundara Reddy (Zoology), Shri. Obula Reddy (Botany), Fr. S. Emmanuel (Botany), Dr. Chandra Sekhar (Botany) and Shri. Suresh Babu (Zoology) that laid a very strong foundation to be peculiar and I thank them all.

Finally, I would like to thank Defence Research Development Organization (DRDO), India for sustaining financial support through Advanced Centre for Research in High Energy Materials (ACRHEM), University of Hyderabad.

Pasupala Ravi

Abbreviations

Ac	acetyl
aq.	aqueous
Ar	aromatic
Bn	benzyl
Bu	butyl
cat.	catalytic
D	detonation velocity
$E_{(ES)}$	electric spark sensitivity
E	electrophile
EI	electron impact
eq.	equation
equiv.	equivalent
Et	ethyl
HOMO	highest occupied molecular orbital
$h_{50\%}$	impact sensitivity
liq.	liquid
LUMO	lowest unoccupied molecular orbital
Me	methyl
mp	melting point
n-	primary
P	Detonation pressure
Ph	phenyl
Py	pyrazole
Q	heat of detonation

R	alkyl
r.t	room temperature
sec	secondary
t-	tertiary
THF	tetrahydrofuran
TMS	tetramethylsilane
X	halide

Abstract

This thesis describes **"Theoretical Investigation on the Structure-Property Relationship of Nitropyrazoles. Nitrodeiodination of Iodopyrazoles and Environmentally Friendly Synthesis of Nitropyrazoles by Impregnated Bismuth Nitrate"** comprises of four chapters. First chapter is subdivided into three sections namely **Introduction**, **Applications** and **Motivation and Objectives** along with **References**. Second chapter is subdivided into four sections namely **Introduction**, **Computational Detail**, **Results and Discussion** and **Conclusions** along with **References**. Third and fourth chapters are subdivided into four sections namely **Introduction**, **Results and Discussion**, **Conclusions** and **Experimental Section** along with **References**. The work described in this thesis is exploratory in nature.

First chapter describes a brief survey on nitropyrazoles and their use for explosive applications. Second chapter describes the structure-property relationship of nitropyrazoles. Density functional theory (DFT) calculations at the B3LYP/aug-cc-pVDZ level were performed to explore the structure, band gap, heat of detonation (Q), density (ρ), detonation velocity (D), detonation pressure (P), impact sensitivity ($h_{50\%}$) and electric spark sensitivity (E_{ES}) of amino-, methyl- and nitro substituted pyrazoles for explosive applications. The molecular structures of nitropyrazoles are shown in Figure 1. The heats of detonation are obtained for the gas phase compounds and in the reality they should be for the solid phase which would diminish the magnitude of Q values. The higher densities of pyrazole-2-oxides are due to the intra- and intermolecular hydrogen interactions or the layered packing in the crystal lattice. The absolute errors in the computed densities are believed to be less than 0.03 g/cm^3 thus known to be fairly good to evaluate the performance properties. Kamlet-Jacob semi-empirical equations were used to determine the detonation velocity (D) and detonation pressure (P) of model compounds. The substituent groups NO_2 and NH_2 and also N-oxide bond of model compounds have increased Q, ρ, D and P tremendously.

The performance properties of nitropyrazol-2-oxides are appearing to be higher compared with 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and octanitrocubane (ONC) presumably due to their higher densities. The explosive properties of nitropyrazoles are summarized in Table 1.

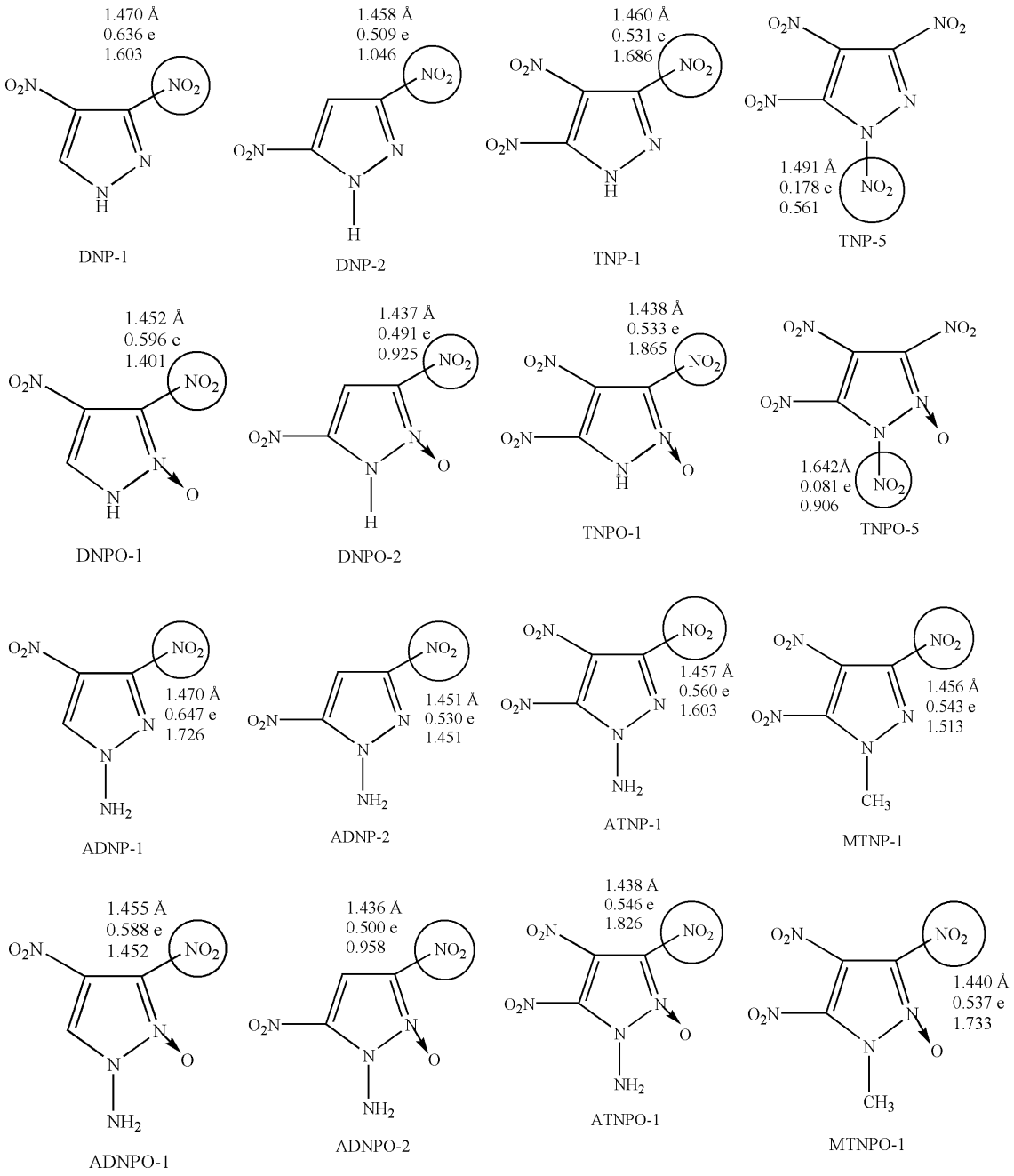


Figure 1 Molecular structures of nitropyrazoles with trigger bond *encircled*; *the list of the values beside each structure shows* the trigger length (in Å), nitro group charge (in e) and midpoint electrostatic potential.

We have chosen the Mulliken charges of nitro groups ($-Q_{NO2}$) to evaluate the stability/ or sensitivity of nitropyrazoles. The presence of NO_2 group at 1-position decreased the sensitivity. The more sensitive compounds have smaller charges on nitro groups. TNP-1 (-0.531 e) is more insensitive compared with TNP-5 (-0.178 e). It is also true for the midpoint

electrostatic potential values. Figure 1 shows the molecular structures of nitropyrazoles with trigger bond length, nitro group charge and midpoint electrostatic potential. The electric spark sensitivity of model compounds have also been predicted from the nitro group ($-Q_{NO_2}$) charge and the lowest unoccupied molecular orbital (LUMO).

Table 1

HEM	**Mw (g mol^{-1})**	**ρ (g cm^{-3})**	**Q (kcal g^{-1})**	**D (km s^{-1})**	**P (GPa)**
DNP-1	158	1.798	0.98	8.34	30.82
DNP-2	158	1.820	0.95	8.33	30.98
TNP-1	203	2.002	1.51	9.40	41.60
TNP-5	248	2.062	1.25	9.24	41.27
DNPO-1	174	2.272	1.34	10.42	54.76
DNPO-2	174	2.245	1.30	10.24	52.54
TNPO-1	219	2.398	1.56	10.75	59.84
TNPO-5	264	2.498	1.15	10.27	55.74
ADNP-1	178	1.810	1.38	9.02	36.20
ADNP-2	178	1.784	1.50	9.07	36.27
ATNP-1	218	1.934	1.47	9.31	40.13
MTNP-1	217	1.842	1.12	8.68	33.90
ADNPO-1	189	2.176	1.30	10.20	51.33
ADNPO-2	189	2.195	1.28	10.24	52.00
ATNPO-1	234	2.337	1.71	10.92	61.04
MTNPO-1	233	2.210	1.37	10.26	52.31
CL-20	438	2.042	1.85	9.20	42.02
ONC	464	1.979	2.20	10.26	48.45

In the third chapter, synthesis, characterization and explosive properties of promising nitropyrazoles (DNP-1, DNP-2, TNP-1 and MTNP-1) are described. Figure 2 shows the possible routes to synthesize nitropyrazoles. Refluxing 1-methylpyrazole (**9**) with nitric acid-sulfuric acid mixture at 110 °C for 1 h gave polynitropyrazole (**8**) in 12% yield. We also have obtained **8** starting from pyrazole via dinitropyrazole (**12**) using nitric acid-sulfuric acid mixture (Scheme 1).

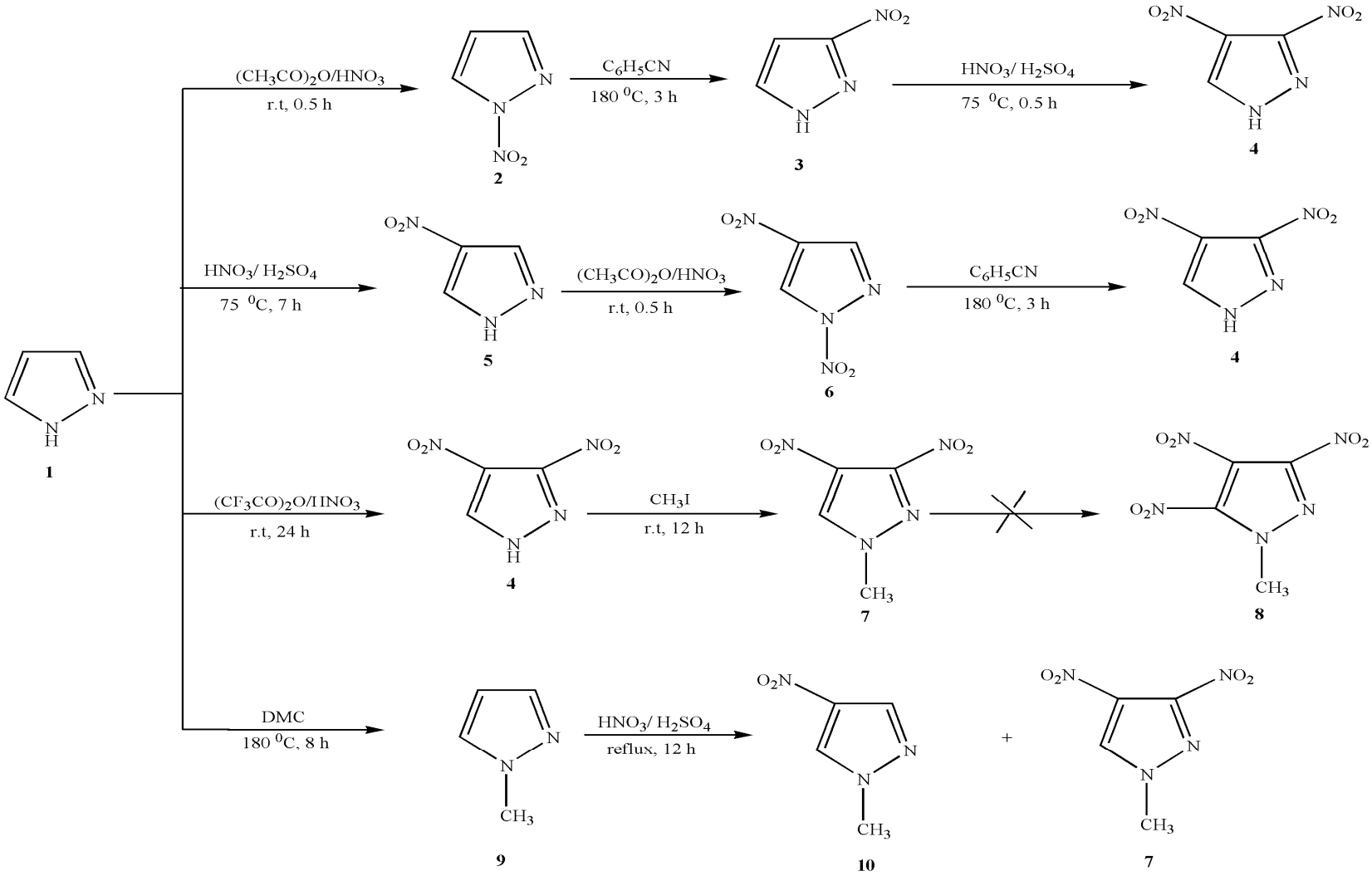
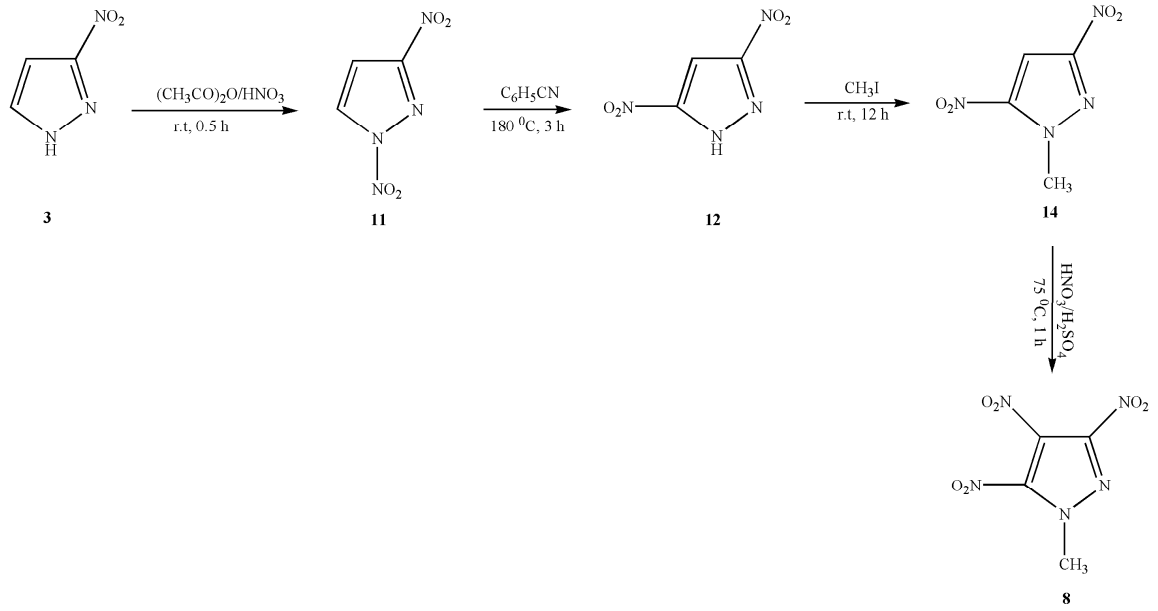


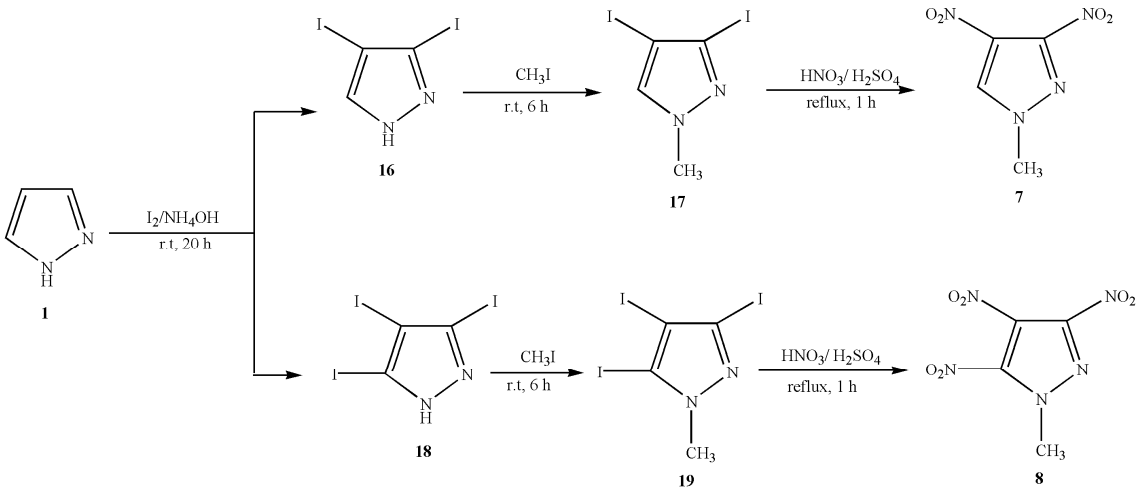
Figure 2 Synthesis of nitropyrazoles using conventional nitration methodologies.

Scheme 1



Our attempts were failed to nitrate nitropyrazoles (**5**,**4**,**7**,**10**) using nitronium tetrafluoroborate, fuming nitric acid or a mixture of fuming nitric acid-sulfuric acid. Iodination and nitrodeiodination methodologies have been used to obtain nitropyrazoles in quantitative yields. Polyiodopyrazoles (**16**-**19**) were nitrodeiodinated using fuming nitric acid or nitric acid- sulfuric acid mixture into polynitropyrazoles (**4**,**7**,**8**,**13**) in good yields (Scheme 2 & 3).

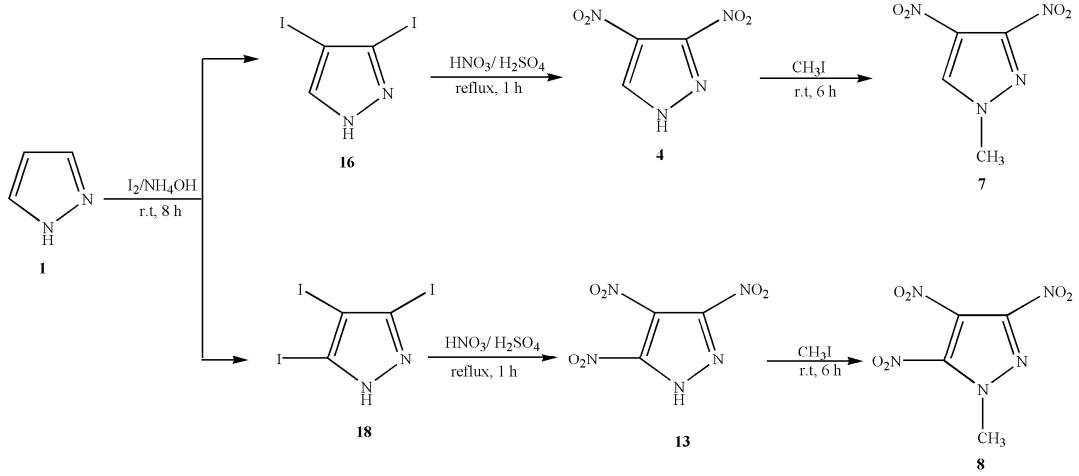
Scheme 2



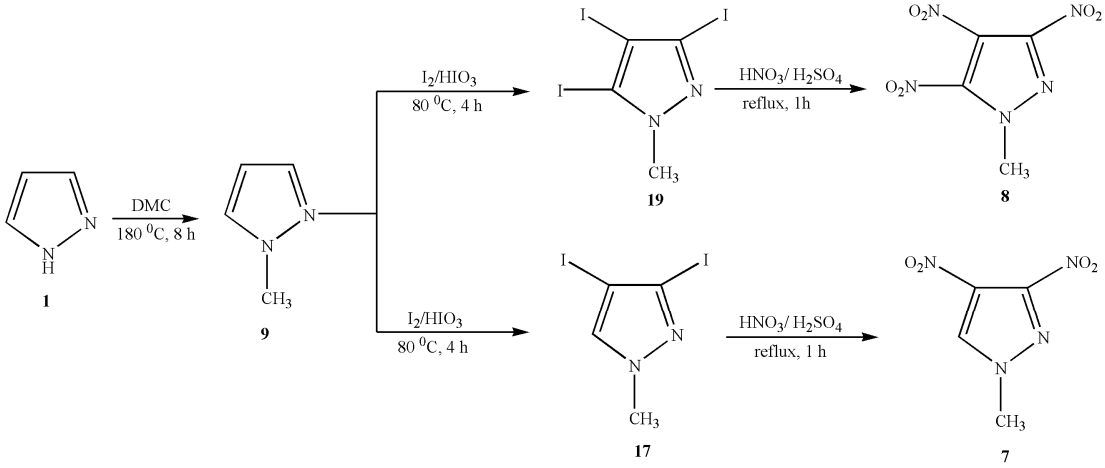
3,4-Diiodo- (**16**) and triiodopyrazoles (**18**) were methylated using methyl iodide and dimethyl sulfate in DMF into diiodo-1-methyl- (**17**) and triiodo-1-methylpyrazoles (**19**) respectively in higher

yields. Dinitro- (**4**,**12**) and trinitropyrazoles (**13**) were also methylated using methyl iodide and dimethyl sulfate into methyl substituted dinitro- (**7**,**14**) and trinitropyrazoles (**8**) respectively.

Scheme 3



Methylating pyrazole with dimethyl carbonate (DMC) prior to oxidative iodination using I_2-HIO_3 has been found to be preferred route to synthesize **8** in higher yields (Scheme 4). Both DMC and I_2-HIO_3 have several advantages such as cost-effectiveness, low-toxicity to humans, exceedingly simple and clean workup of products. Polyiodopyrazoles are preferred to synthesize dinitro-(**4**) and trinitropyrazoles (**8**,**13**) in good yields to avoid denitrations at ambient temperatures.



Thermal decomposition kinetics of trinitropyrazole (**8**) has been investigated using TG-DTA technique under nitrogen atmosphere to determine the weight loss and activation energy. The compound **8** showed good thermal stability with exothermic decomposition peak at 248 °C on DTA. Kinetic parameters were calculated from the DTA peak temperatures at different heating rates. The

activation energy required for the thermal decomposition of **8** according to Flynn-Wall-Ozawa method and Friedman method have been found to be 240.5 kJ mol^{-1} and 241.8 kJ mol^{-1} respectively. The weight loss of trinitropyrazole (**8**) with increasing temperature at heating rate 10 ^{0}C per minute is shown in Figure 3. A linear relationship of activation energy with the conversion rate indicates the possibility of single reaction mechanism or the unification of multiple-reaction mechanisms. However, **8** showed non-linear relation indicating the involvement of multi-step decomposition pathway. The stability of **8** has been proved by the E_α versus α relation experimentally.

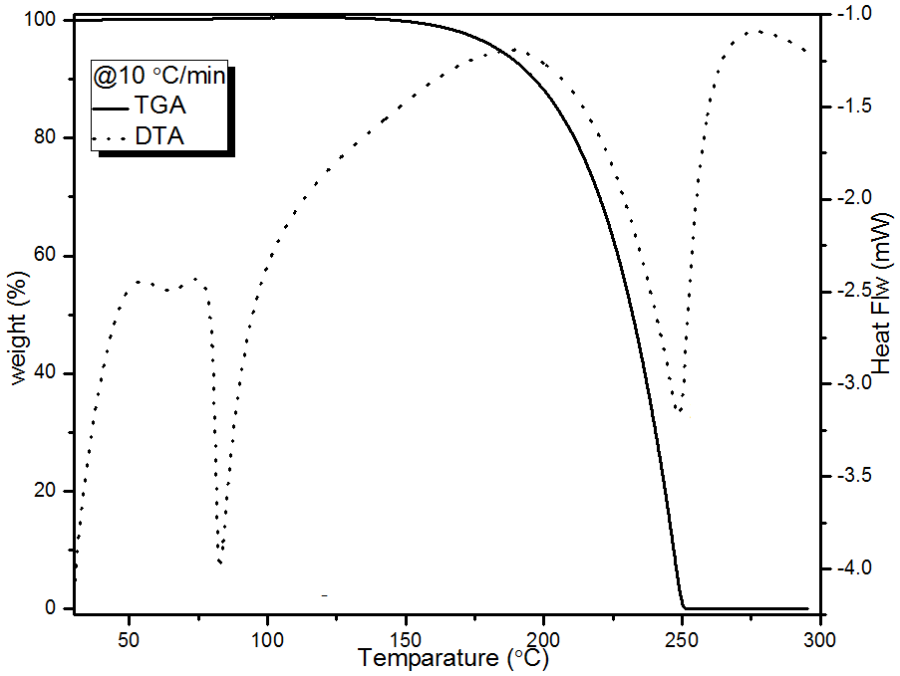
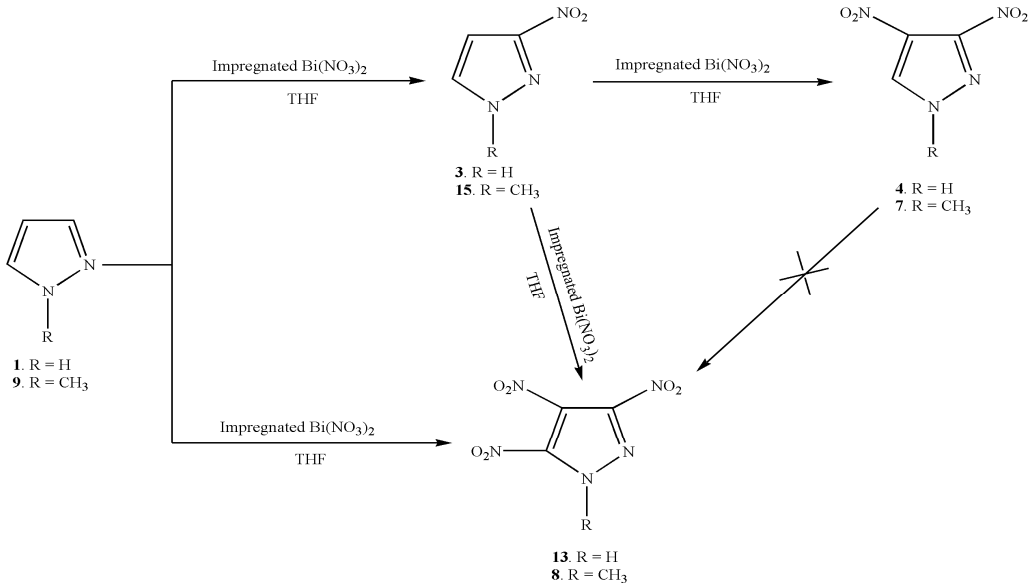


Figure 3 The Effect of temperature on the weight loss of 1-methyl-3,4,5-trinitropyrazole (**8**).

3-Nitropyrazoles, 3,4-dinitropyrazoles and 3,5-dinitropyrazoles have been obtained in good yields heating 1-nitropyrazoles at 140-190 ^{0}C in anisole, benzonitrile, chlorobenzene, *n*-decane, mesitylene, nitrobenzene, xylene, *N*-methylformamide, propylene glycol for 3-7 h. Normally, these C-nitropyrazoles are formed quantitatively and in some instances denitrations of 1-nitropyrazoles were observed. The problems associated with conventional methods tedious work up procedures and denitrations of 1-nitropyrazoles have prompted us to search for the alternative methodologies. Synthesis of nitropyrazoles using such methodologies has been described in fourth chapter. We have synthesized **3**, **4**, **7**, **8**, **12**, **13** and **19** in higher yields starting from pyrazole (**1**) under microwave irradiation. A series of iodopyrazoles were nitrodeiodinated using nitric acid over silica sulfuric acid

(SSA) into the corresponding nitropyrazoles in higher yields. We also have discussed a facile, rapid and environmentally friendly synthesis of nitropyrazoles in good yields using silica-bismuth nitrate, silica-sulfuric acid-bismuth nitrate and montmorillonite-bismuth nitrate at room temperature (Scheme 5). The relatively non-toxic nature, ease of handling, easy availability and low cost make the present procedure is attractive for the nitration of a wide variety of diazoles in the drug and pharmaceutical industries.

Scheme 5



The density functional theory calculations at B3LYP/aug-cc-pVDZ level were performed to explore the structure and detonation properties of pyrazoles substituted by amino, methyl and nitro groups for explosive applications. The mono-, di- and trinitropyrazoles (DNP-1, DNP-2, TNP-1 and MTNP-1) were synthesized using conventional and alternative methodologies. Thermal decomposition kinetics of trinitropyrazole (**8**) has also been investigated to determine the weight loss and activation energy. Nitropyrazole-2-oxides (DNPO, TNPO, ADNPO, DADNPO, MTNPO and ATNPO) are also possible to synthesize for high explosive applications in near future.

Chapter 1

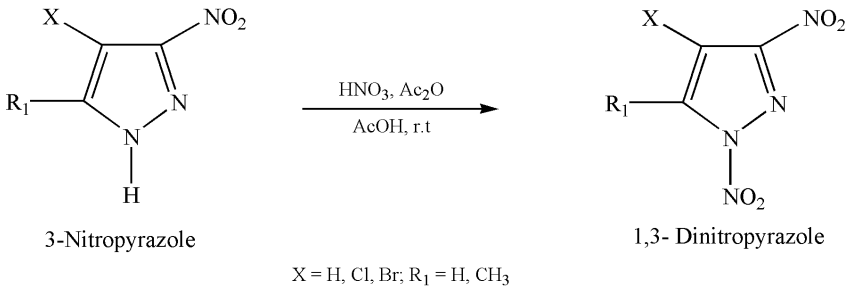
1.1 Introduction

Nitropyrazoles have been used as biologically active compounds including antibiotics or their analogues, agrochemicals, dyestuffs, phosphores, non-linear optical materials and recently as energetic materials.[1-3] The presence of nitro group in the pyrazole ring considerably enlarges the possibility of functionalization of various types of pyrazole derivatives. The methods to synthesize nitropyrazoles are diverse and depend upon the nature of substituent groups in the pyrazole ring, the electron density distribution in it, nitration mixtures, nitration conditions, etc. Pyrazoles are nitrated with nitric acid-sulfuric acid,[4-6] nitric acid-acetic anhydride,[4,5] nitric acid-trifluoro acetic anhydride[7] or nitromethane-nitronium tetrafluoroborate.[8-10] In many cases, it is impossible to introduce NO_2 group into the desired position of the pyrazole ring and therefore indirect methods are used. Hüttel and Büchele[4] described the rearrangement of N-nitropyrazoles into 4-nitropyrazoles in cold sulfuric acid solution. However, N-nitropyrazoles in anisole, xylene, benzonitrile, chlorobenzene, nitrobenzene, n-decane, mesitylene, N-methylformamide, or propylene glycol at 120-190 ^{0}C for 3-7 h were rearranged into 3-nitropyrazole, 3,4-dinitro pyrazole and 3,5-dinitropyrazole.[5] In this chapter we review the literature reports of such nitropyrazoles.

1.1.1 1,3-Dinitropyrazoles and 1,5-Dinitropyrazoles

It is known that many 3- and 5- substituted NH-pyrazoles exist in solution as mixture of unseparable tautomers.[1] The positions 3 and 5 of the pyrazole ring often possess very similar reactivity. 1,3-Dinitropyrazole or its halo- and alkyl derivatives were obtained by the nitration of 3-nitropyrazoles with acetyl nitrate in acetic acid (Scheme 1).[5,11,12]

Scheme 1



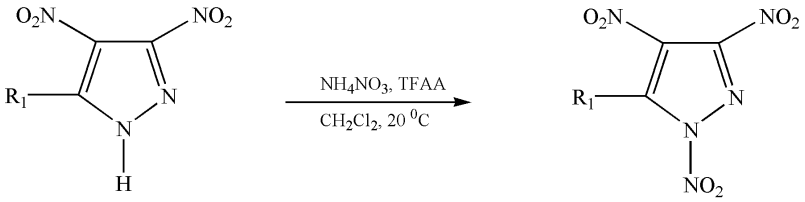
3-Nitropyrazole

1,3- Dinitropyrazole

X = H, Cl, Br; R_1 = H, CH_3

3-Nitropyrazole-5-carboxylic acid was nitrated to 1,3-dinitropyrazole-5-carboxylic acid using copper nitrate-acetic anhydride.[13] For the nitration of 3,4-dinitropyrazole and 5-methyl-3,4-dinitropyrazole to 1,3,4-trinitropyrazole and 5-methyl-1,3,4-trinitropyrazole respectively acetyl nitrate and trifluoroacetyl nitrate (ammonium nitrate and trifluoracetic anhydride) were used (Scheme 2).[14] The nitration of 3-nitroindazole with acetyl nitrate gave 2,3-dinitroindazole. Dinitroindazole and trinitroindazoles were nitrated to tetranitroindazoles using nitric acid-sulfuric acid.[5,15,16]

Scheme 2



3,4-Dinitropyrazole 1,3,4-Trinitropyrazole

R_1 = H, CH_3

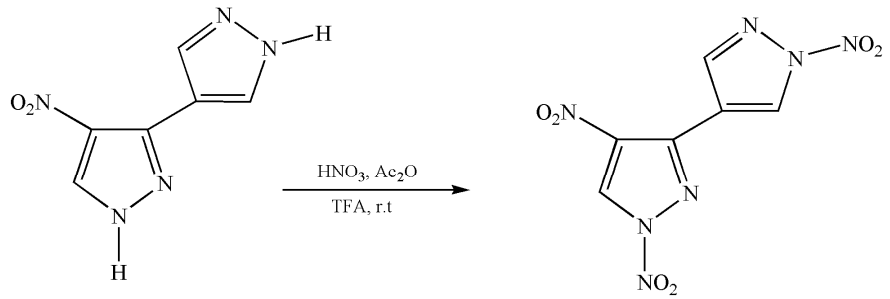
The thermolysis of 1,3-dinitropyrazole in benzonitrile gave 3,5-dinitropyrazole in high yield accompanied by an insignificant amount of 3-nitropyrazole, a denitrated product.[5] The key step in the rearrangement of N-nitropyrazoles to C-nitropyrazols is a concerted intramolecular [1,5] sigmatropic shift of NO_2 group. The intermediate 3,5-dinitro-3H-pyrazole undergoes fast aromatization to form C-dinitro-1H-pyrazole. The treatment of 1,3-dinitropyrazole or dinitro-indazoles with secondary amine brings about denitration of N-NO_2 group which is characteristic of N-nitroazoles.[16,17]

1.1.2 1,4-Dinitropyrazoles

1,4-Dinitropyrazoles were synthesized by the nitration of 4-nitropyrazoles using acetyl nitrate in acetic acid.[5] Trifluoroacetic acid (TFA) have also been used for the N-nitration.[14,18] Upon the nitration of 4-nitro-3,4-bipyrazole and 3-(4-nitropyrazol-3-yl)-1,2,3,4-oxatriazol-3-ium-5-olate, the corresponding 1,4-dinitro derivatives were synthesized (Scheme 3 & 4). In several cases, the classical nitration using acetyl nitrate in acetic acid or trifluoroacetic acid gave N-nitrated products. 1,4-Unsubstituted pyrazoles were nitrated to the corresponding 1,4-dinitro

derivatives using NH_4NO_3-TFAA in TFA.[19] The presence of trifluoroacetic acid is essential for the preparation of dinitropyrazoles. In the absence of acetic acid or trifluoroacetic acid, NH_4NO_3-TFAA nitrated 3-methylpyrazole to 1-nitro derivative.

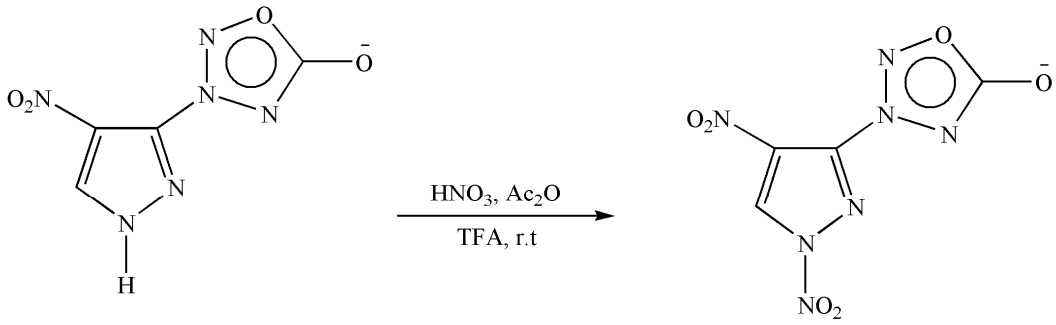
Scheme 3



4-Nitro-3,4'-bipyrazole

1,4- Dinitro-3,4'-bipyrazole

Scheme 4



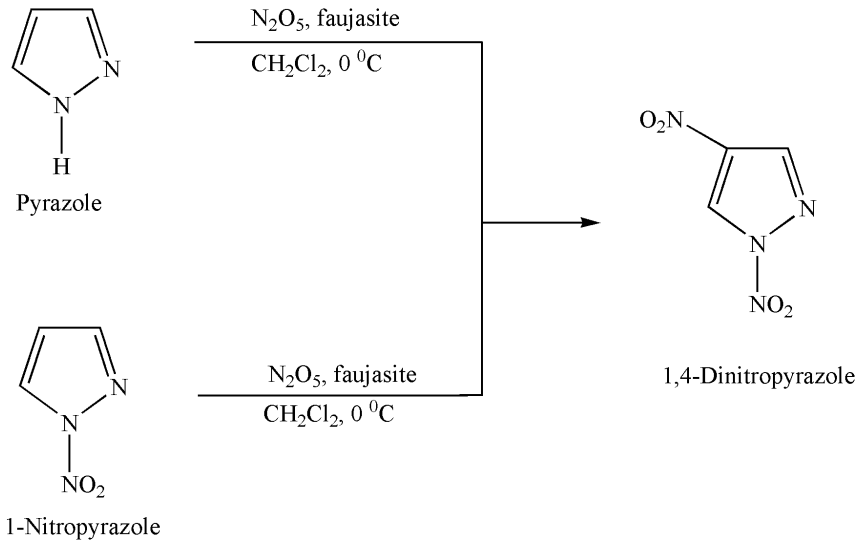
3-(4-Nitropyrazol-3-yl)-1,2,3,4-oxatrizol-3-ium-5-olate

3-(1,4-Diitropyrazol-3-yl)-1,2,3,4-oxatrizol-3-ium-5-olate

It is only in the system NH_4NO_3-TFAA in CH_2Cl_2, 3-amino-4-nitropyrazole can be converted to the corresponding 3-amino-1,4-dinitropyrazole.[20] 4-Nitropyrazole was converted to 1,4-dinitropyrazole in high yield using nitrogen (IV) oxide in the presence of ozonated oxygen (Kyodai nitration).[21] It was demonstrated that nitrogen (IV) oxide in the presence of faujasite nitrates both pyrazole and 1-nitropyrazole (Scheme 5).[22] Like the majority of N-nitropyrazoles, 1,4-dinitro derivatives undergo thermal rearrangement into 3,4-dinitropyrazoles.[5] The simplest 1,4-dinitropyrazole produces 3,4-dinitropyrazole in low yield accompanied by the formation of a significant amount of 4-nitropyrazole, a denitrated product. The presence of a substituent at the

3-position of the pyrazole ring increases the yields of rearrangement products. Several terpyrazoles were also synthesized for various applications.[23]

Scheme 5

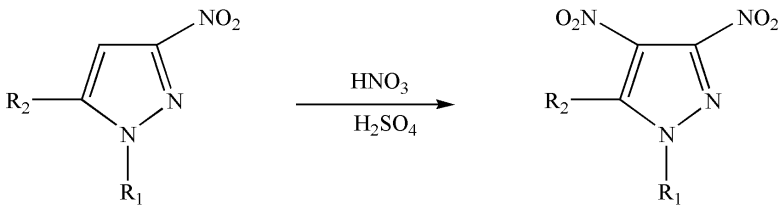


1.1.3 3,4-Dinitropyrazoles and 4,5-Dinitropyrazoles

NH-Pyrazoles bearing two nitro groups at 3,4- and 4,5-positions are annular tautomers and in solution they exist as unseparable equilibrium mixtures.[1] 3,4-Dinitropyrazole, 1-alkyl-3,4-dinitropyrazole and 5-alkyl-3,4-dinitropyrazole were synthesized by the nitration of 3-nitro pyrazole, 1-alkyl-3-nitropyrazole and 5-alkyl-3-nitropyrazole respectively using nitric acid-sulfuric acid mixture (Scheme 6).[6] Katrizky et al[7] obtained 3,4-dinitropyrazole in moderate yield upon the nitration of pyrazole using nitric acid-trifluoro acetic anhydride at room temperature. However, 1-methylpyrazole under same nitration conditions gave a mixture of 1-methyl-3,4-di nitropyrazole, 1-methyl-3-nitropyrazole and 1-methyl-4-dinitropyrazole.[7] Grimmett et al[6] have obtained a mixture containing 1-methyl-4-nitropyrazole and 1-methyl-3,4-dinitropyrazole using nitric acid in 80% sulfuric acid at 100 ^{0}C for 18 h. 1,4-Dinitropyrazole undergo thermal rearrangement into 3,4-dinitropyrazole in lower yield.[5] 3,4-Dinitropyrazole is formed from the corresponding 3-nitropyrazole in higher yields rather than from 4-nitropyrazole. The nitration of 4-nitropyrazole and 1-alkyl-l-4-nitropyrazoles does not result into 3,4-dinitropyrazole and 1-alkyl-3,4-dinitropyrazoles respectively.[6,24,25] 1-Alkyl-3-nitropyrazole obtained by other methods was nitrated to 1-alkyl-3,4-nitropyrazole using nitric acid-sulfuric acid mixture. The

intermediate formation of an abnormal 3-nitration product presumably by the [1,5] sigmatropic shift of the NO_2 group in the transient 2-nitropyrazolium cation.

Scheme 6



3-Nitropyrazole

3,4-Dinitropyrazole

R_1, R_2 = H, CH_3

The nitration of 1,5-dimethylpyrazole with nitric acid-20% oleum at 75 ^{0}C gave 1,5-di methyl-4-nitropyrazole.[26] Under more drastic conditions, 1,5-dimethyl-3,4-dinitropyrazole was the only product. The nitration of 1-methylpyrazole-5-carboxylic acid with nitric acid in 20% oleum at 140 ^{0}C produced 1-methyl-3,4-dinitropyrazole-5-carboxylic acid.[27] The only difference is that the introduction of the second nitro group into the pyrazole ring require more drastic conditions.1-Methyl-3,4-dinitropyrazole and 5-iodo-1-methyl-3,4-dinitropyrazole were obtained by the ipso nitration of 4-iodo-1-methyl-3-nitropyrazole and 4,5-diiodo-1-methyl-3-nitropyrazole respectively using nitric acid-sulfuric acid.[28,29] 1-(Dimethylamino)-3-phenylpyrazole under mild conditions was nitrated to 1-(dimethylamino)-3-phenyl-4,5-dinitropyrazole.[30] The oxidation of 5-amino-4-nitropyrazoles gave the corresponding dinitropyrazoles.[31] 3,4-Dinitropyrazoles were also obtained by the diazotization of aminopyrazoles followed by the substitution of nitro groups for the diazo group with an excess of sodium nitrite.[32] The oxidation of 3,4-dinitropyrazoles with potassium or sodium dichromate gave 3,4-dinitropyrazole-5-carboxylic acid and 1-methyl-3,4-di nitropyrazole-5-carboxylic acid.[33,34] 1-Hydroxy-3,4-dinitropyrazoles was prepared by the oxidation of NH-pyrazoles using potassium perxomonosulfate in buffer solution.[35]

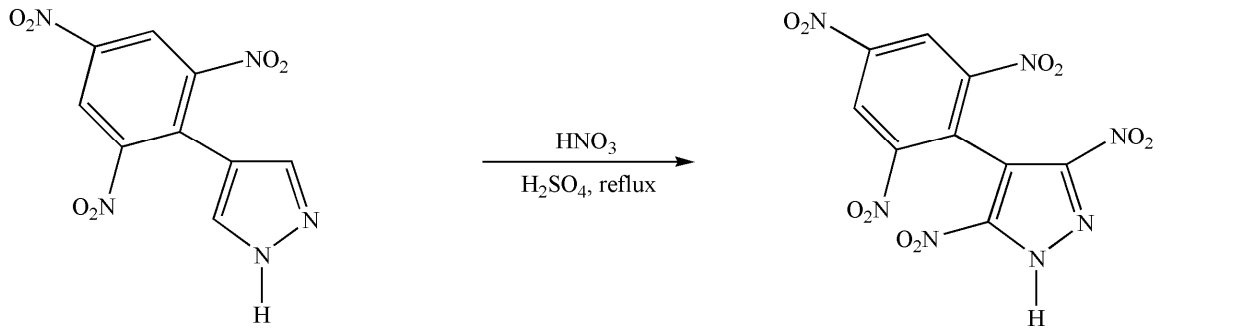
The nitro groups in 3,4-dinitropyrazoles can be reduced by classical methods.[1] 5-(p-Nitrophenyl)-3,4-dinitropyrazole treated with sodium hydrogen sulfite gave diaminopyrazole.[36] The use of an equivalent amount of reductant allows the reduction of 3-nitro group of pyrazole. 1,5-Dimethyl-3,4-diaminopyrazole was obtained from 1,5-dimethyl-3,4-dinitropyrazole with hydrazine hydrate in the presence of the Raney Nickel.[26,34] 1,5-Dimethyl-3,4-diaminopyrazole

can also be prepared from dinitropyrazole by nucleophilic substitution. It was found that 3-NO_2 group in 1,5-dimethyl-3,4-dinitropyrazole is replaced by the NH_2 group on the treatment with aqueous ammonia under drastic conditions (autoclave at 190 ^{0}C).

1.1.4 3,5-Dinitropyrazoles

The thermolysis of 1,3-dinitropyrazole in benzonitrile gave 3,5-dinitropyrazole in high yield.[5] 1-Methyl-4-(2,4,6-trinitrophenyl)-3,5-dinitropyrazole was synthesized by the nitration of 1-methyl-4-(2,4,6-trinitrophenyl)-pyrazole with nitric acid-sulfuric acid mixture (Scheme 7).[37] In the absence of sulfuric acid, 1-methyl-4-(2,4,6-trinitrophenyl)-pyrazole gave 1-methyl-4-(2,4,6-trinitrophenyl)-3-nitropyrazole. It was established that the nitration with 70% HNO_3 for 5 h does not lead to a complete conversion of the initial pyrazole, the products being 1-methyl-4-(2,4,6-trinitrophenyl)-3-nitropyrazole and 1-methyl-4-(2,4,6-trinitrophenyl)-5-nitropyrazole. Increase in the nitric acid concentration to 90% results in full conversion of the starting pyrazole and thus 1-methyl-4-(2,4,6-trinitrophenyl)-3,5-dinitropyrazole appears among the reaction products. It was demonstrated that the nitration of a mixture of 1-methyl-4-(2,4,6-trinitrophenyl)-3-nitro pyrazole and 1-methyl-4-(2,4,6-trinitrophenyl)-5-nitropyrazole with nitric acid-sulfuric acid mixture produced 1-methyl-4-(2,4,6-trinitro phenyl)-3,5-dinitropyrazole.[37]

Scheme 7



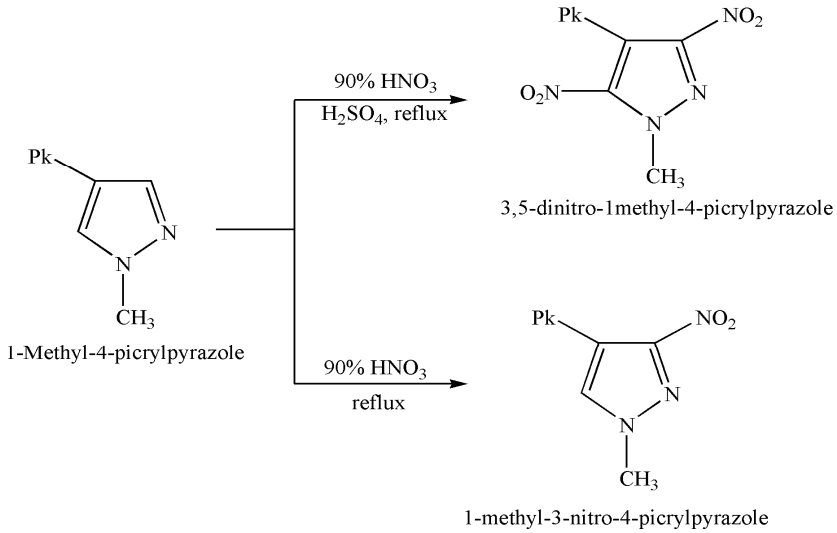
1-Methyl-4-(2,4,6-trinitrophenyl)-pyrazole

1-Methyl-4-(2,4,6-trinitrophenyl)-3,5-dinitropyrazole

4-Ethyl-3,5-dinitropyrazole can be synthesized by the nitration of 1-ethyl-3-nitropyrazole with nitric acid-sulfuric acid mixture.[5] 4-Methyl-1-(p-nitrophenyl)-3-nitropyrazole with nitric acid-sulfuric acid mixture produces 4-methyl-1-(2,6-dinitro phenyl)-3,5-dinitropyrazole in low yield. 4-Methyl-1-(2,6-dinitrophenyl)-3,5-dinitropyrazole was synthesized from 4-methyl-1-(2,6-

dinitrophenyl)-pyrazole in 64% yield. The condensation of pyrazole with picryl chloride gave 1-picrylpyrazole.[37,38] 1-Picrylpyrazole was nitrated to 4-nitro-1-picrylpyrazole. 3-Aminopyrazole reacted with one molecule of picryl chloride to form 3-picrylaminopyrazole and with two molecules of picryl chloride to give a mixture of 1-picryl-3-picrylaminopyrazole and 1-picryl-5-picrylaminopyrazole.[39] 5-Amino-1-methylpyrazole gave 1-methyl-5-nitropyrazole-1-oxide under similar conditions. Coburn[40] reported the nitration of 1-methyl-4-picrylpyrazole to 1-methyl-3-nitro-4-picrylpyrazole and 3,5-dinitro-1methyl-4-picrylpyrazole (Scheme 8). 4-(2,4-Dinitrophenyl)-1-methylpyrazole was nitrated with 90% nitric acid gave a mixture containing 4-(2,4-dinitrophenyl)-1-methyl-3-nitropyrazole, 4-(2,4-dinitrophenyl)-1-methyl-5-nitropyrazole and 3,5-dinitro-(2,4-dinitrophenyl)-1-methyl-3-nitropyrazole.[37]

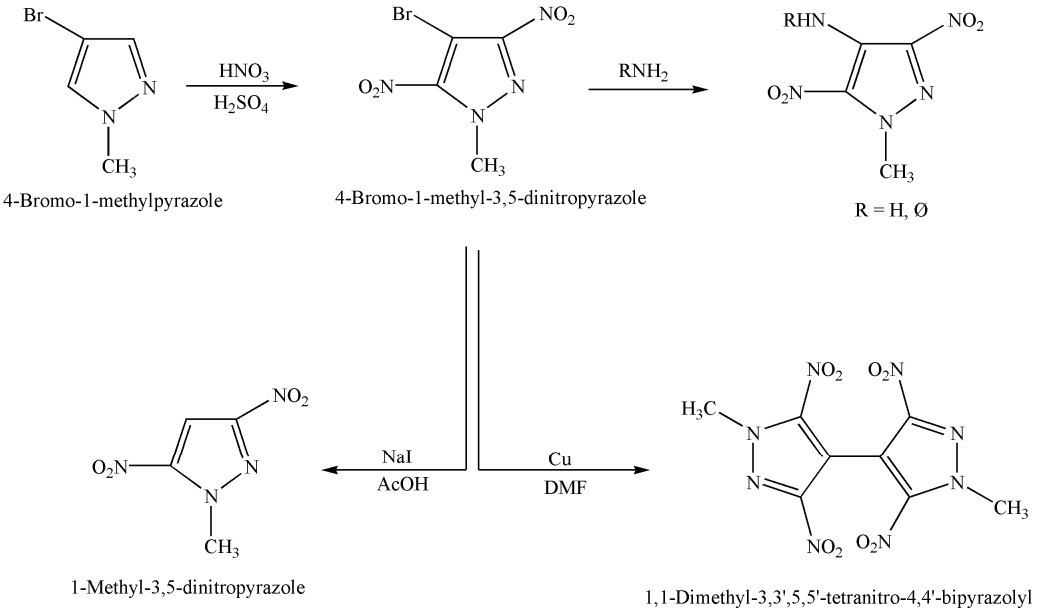
Scheme 8



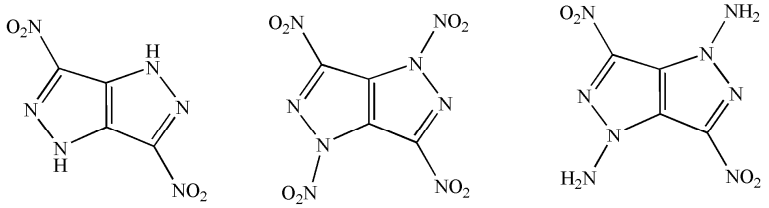
4-Bromo-1-methylpyrazole could be nitrated to 4-bromo-3,5-dinitro-1-methylpyrazole, which is a useful intermediate in the synthesis of 3,5-dinitropyrazoles.[41] 4-Bromo-3,5-dinitro-1-methylpyrazole reacted gave 4-anilino-3,5-dinitro-1-methylpyrazole with ammonia. The treatment of 4-bromo-3,5-dinitro-1-methylpyrazole with sodium iodide in acetic acid produced 1-methyl-3,5-dinitropyrazole. 4-Bromo-3,5-dinitro-1-methylpyrazole underwent the Ullmann reaction in DMF to 1,1-dimethyl-3,3',5,5'-tetranitro-4,4'-bipyrazolyl (Scheme 9). 1-Methyl-4-nitropyrazole was hydrogenated to 4-amino-1methylpyrazole which reacted with picryl chloride

to form 1-methyl-4-picrylaminopyrazole. The nitration of 1-methyl-4-picrylaminopyrazole under mild conditions provided 3,5-dinitro-1-methyl-4-picrylaminopyrazole.

Scheme 9



The fused pyrazole anion and an amine cation are novel energetic compounds that are employed as ingredients in gun propellants.[1,2] Several fused nitroazoles have been suggested for synthesis as novel high explosive candidates. 3,6-Dinitropyrazolo[4,3-c]pyrazole (DNPP) and its salts have higher heat of formation, impetus and nitrogen content than the corresponding dinitro- and trinitrpyrazole salts.[1] DNPP was employed as a precursor to 1,4-diamino-3,6-dinitro pyrazolo[4,3-c]pyrazole (LLM-119). The further nitration of DNPP gave 1,4,3,6-tetranitro pyrazolo[4,3-c]pyrazole (LLM-121), a highly sensitive product. It is obvious that very high energy heterocycles are synthetically achievable but might not be stable for routine handling.

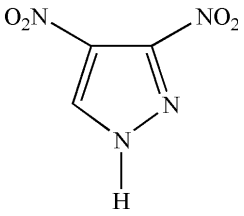
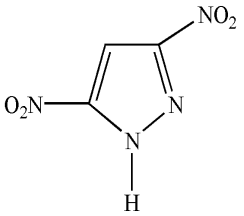
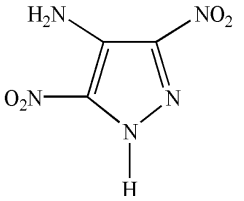
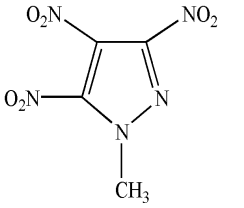
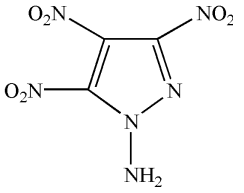
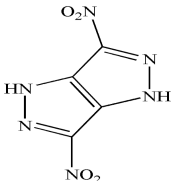


1.2 Applications of Nitropyrazoles

Several 3(5)- and 4-nitropyrazoles containing diverse substituents have been used as biologically active substances including antibiotics or their analogues. The nitration of pyrazoles, cine substitution of the N-nitro group and reduction of a C-nitro groups to amino groups have been used for the synthesis of formycin,[42-44] pyrazomycin,[44] araformycin,[45] xyloformycin,[46] azaformycin[47] and azapyrazofurin.[47] Halo- and methyl substituted 1,3-dinitropyrazoles posses the ability substantially to increase the ocular blood flow and restore the function of retina.[48] 1-Nitropyrazole, 1,3-dinitropyrazole and 1,4-dinitropyrazole have been used for the generation of nitrogen (II) oxide which acts as a regulator of the vasodilatory process.[49] These N-nitro pyrazoles have also been used for the treatment of prevention of macular degeneration.[50] 1,4-Di nitropyrazoles have been used for the suppression of ammonium nitrogen nitrification to nitrate ions in soil to prevent its fast removal from soil.[51] N-Unsubstituted 3-nitro-4(R)-pyrazoles (R = CN, CO_2H, $CONH_2$) and their derivatives have been used as bactericides, herbicides or intermediates for their preparation.[52-54] Aminonitropyrazoles have been served as the basis for the creation of azo dyes[32] and luminescent dyes.[55] Pyrazolo[4,3-c]pyrazole and dipyrazolo [3,4-b;4'3-e]pyrazines derivatives have been used as pharmacologically active and luminescent compounds.[2,51,56]

3,4-Dinitropyraole (3,4-DNP), 3,5-dinitropyrazole (3,5-DNP) and their nitrophenyl-, picryl- and picrylamino substituted compounds known to possess explosive properties.[1,3] The physical and explosive properties of nitropyrazoles are presented in Table 1.2.1. 4-Amino-3,5-di nitropyrazole (LLM-116) is known with the decomposition point of 184 $^{\circ}C$ and exhibits the highest density of 1.90 g/cm^3 in the five-membered heterocyclic compounds.[57] 3,4,5-Trinitro pyrazole melts at 188 $^{\circ}C$ and decompose from 260 to 350 $^{\circ}C$ and its heat of decomposition is 255 Jg^{-1}, which is extremely low for an explosive.[58,59] Shevelev et al[60] synthesized 3,6-dinitro pyrazolo [4,3-*c*]pyrazoles (DNPP) from 3,5-dimethylpyrazole. Pagoria et al[61] have developed an alternative route with several advantages such as easy synthesis scale up and improved the yield over Shevelev method. DNPP was used as a precursor to synthesize 1,4-diamino-3,6-dinitro pyrazolo[4,3-*c*] pyrazole (LLM-119). It is obvious that very high energy fused polynitroazoles are synthetically achievable but might not be stable for routine handling.[66-68]

Table 1.2.1 Physical and explosive properties of known nitropyrazoles.

Name	Structure	mp (^{0}C)	dec. point (^{0}C)	ρ (g/cm^3)	D (km/s)	P (Gpa)	$h_{50\%}$ (cm)	Ref
3,4-DNP		88	190	1.81	8.24	28.80	82	3,5
3,5-DNP		173	280	1.80	8.15	28.65	87	3,5
ADNP		177	184	1.90	8.00	28.57	167	62
MTNP		91	256	1.83	8.65	33.54	78	58,59
ATNP		130	239	1.93	9.31	40.13	-	58,63
DNPP		158	330	1.86	8.85	35.64	68	64,65

1.3 Motivation and Objectives

Nitropyrazoles due to their positive heat of formation, good thermal stability and higher density have recently drawn a considerable attention by several explosives chemists.[1,259] 3,4-Dinitropyrazole, 3,5-dinitropyrazole and 4-amino-3,5-dinitropyrazole have been known to possess explosives properties. The heat of decomposition of 3,4,5-trinitropyrazole (TNP) is 255 Jg^{-1}, which is extremely low to be an explosive. It is known that the increasing NO_2 and NH_2 groups on the pyrazole ring increases the energy of explosion, density and detonation performance. Furthermore, if nitration, amination or methylation at 1-position of TNP is possible, it will not only enhance the detonation performance but also may stabilize the compound chemically. To our knowledge, there were no such studies on the explosive properties of such nitropyrazoles. It would be desirable before attempting synthesis of these compounds to be able to predict the heat of explosion, density, detonation performance, stability and sensitivity. Following are the objectives of the present work:

- To explore the structure, stability, heat of explosion, density, detonation velocity, detonation pressure, impact sensitivity and electric spark sensitivity of amino- and methylnitropyrazoles.
- To synthesize 3,4-dinitropyrazole, 3,5-dinitropyrazole, 3,4,5-trinitropyrazole and 1-methyl-3,4,5-trinitropyrazole using conventional nitration and nitrodeiodination methodologies.
- To determine the density, heat of formation, performance properties, impact sensitivity and friction sensitivity of synthesized nitropyrazoles for explosive applications.
- To investigate the thermal decomposition mechanism of synthesized compounds using isoconversional methods.
- To synthesize nitropyrazoles using alternate methodologies (e.g. under microwave irradiation, silica-sulfuric acid catalyzed nitrodeiodination, silica-bismuth nitrate, silica sulfuric acid-bismuth nitrate and montmorillonite-bismuth nitrate).

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Chapter 2

2.1 Introduction

Nitropyrazoles due to their promising explosive properties have drawn renewed attention by explosives chemists.[1-4] 3,4-Dinitropyrazole,[5] 3,5-dinitropyrazole[5] and 3,4,5-trinitropyrazole[6-10] are non-hygroscopic, weakly acidic, insensitive and stable C-nitropyrazoles. 3,4-Dinitropyrazole is under consideration as melt cast explosive with its mp 88 ^{0}C, density 1.81 g/cm^3, detonation velocity 8.24 km/s and detonation pressure 28.8 GPa. However, the heat of decomposition of 3,4,5-trinitropyrazole is 255 J/g, which is extremely low to be used for explosive applications.[6,10] 4-Amino-3,5-dinitropyrazole is an insensitive explosive with its decomposition point 178 ^{0}C and exhibits the highest density 1.90 g/cm^3 in the five membered heterocyclic compounds.[11]

It is known that increasing NH_2 and NO_2 groups in the pyrazole ring increases the heat of explosion, density and thus detonation performance.[1-3,12,13] The substitution of acidic hydrogen at 1-position of C-nitropyrazole by CH_3 group decreases the melting point.[4] We have synthesized 1-methyl-3,4,5-trinitropyrazole and suggested for use as melt pour explosive.[10] It has mp 91 ^{0}C, density 1.83 g/cm^3, detonation velocity 8.65 km/s and detonation pressure 33.54 GPa. The presence of CH_3 group on the C-atom of the pyrazole ring increases the melting point and thus the molecule become stable to heat and mechanical stimuli. To our knowledge, there were no studies on the structure-property relationship of NH_2, NO_2 and CH_3 substituted pyrazoles. Therefore, it would be desirable before attempting synthesis of such nitropyrazoles to be able to predict the heat of detonation, density, detonation performance, stability and sensitivity.

In this chapter, we describe the geometry, band gap, density, heat of detonation, detonation velocity, detonation pressure, impact sensitivity and electric spark sensitivity of nitropyrazoles using density functional theory. Thermodynamic properties were determined working chemical reactions of model compounds computed from B3LYP/aug-cc-pVDZ level. The relationship between impact sensitivity and electronic structure of nitropyrazoles has been established by nitro group charge analysis. The electric spark sensitivity has been predicted from the nitro group charge and the lowest unoccupied molecular orbital of the molecule. The frontier molecular orbital energies and their gaps were used to determine the stability of model compounds.

2.2 Methods and Computational Detail

Density functional theory (DFT) calculations have been performed for the model compounds using Gaussian 03 program.[14] The structures were optimized at the B3LYP/aug-cc-pVDZ level knowing the method and basis set provide better approximations.[12,13,15] Vibrational frequencies have also been calculated for the optimized structures to characterize the nature of stationary points, zero-point energy and thermal correction to enthalpy. The stationary points have been identified as positive on the potential energy surface with no imaginary frequencies. All the correction terms were estimated by the following set of equations.[16]

$$\left[H(T) - H(0) \right]_{trans} = \frac{5}{2} RT \quad (1)$$

$$\left[H(T) - H(0) \right]_{rot} = \frac{3}{2} RT \quad (2)$$

$$\left[H(T) - H(0) \right]_{vib} = RT \sum_{i=1}^{f} \left(\frac{h\nu_i}{KT} \right) \frac{\exp \frac{-h\nu_i}{KT}}{\left(1-\exp \frac{-h\nu_i}{KT} \right)} \quad (3)$$

The heat of explosion (Q) can be calculated from the difference between sum of the energies for the formation of explosive components and sum of the energies for the formation explosive products.

$$\begin{aligned} Q &= \Delta E_{298.15K} + \Delta(PV) \\ &= \Delta E_0 + \Delta ZPE + \Delta_T H + \Delta nRT \end{aligned} \quad (4)$$

where ΔE_0 is the change in total energy between the products and reactants at 0 K; ΔZPE is the difference between the zero point energies of the products and reactants; $\Delta_T H$ is the difference between the thermal correction from 0 to 298.15 K of the products and reactants; $\Delta(PV)$ equals to ΔnRT. $\Delta n = 0$ for an ideal gases.

The optimized structures have been used to determine the densities (ρ) of nitropyrazoles using Materials Studio 4.1 package with CVFF force field and Ewald summation method.[17] Kamlet and Jacob semi-empirical equations[18] were used to determine the detonation

performance:

$$D = 1.029\ (NM^{1/2}Q^{1/2})^{1/2}\ (1+1.30\ \rho) \quad (5)$$

$$P = 15.58\ NM^{1/2}Q^{1/2}\rho^{2} \quad (6)$$

where D is the detonation velocity in km/s, P is the detonation pressure in GPa, N is the number moles of gaseous detonation products per gram of explosive, M is the average molecular weight of gaseous products, Q is the energy of explosion in kcal/g of explosive and ρ is the density in g/cm^3.

Oxygen balance (OB%) can be defined as the amount of oxygen liberated as a result of the complete conversion of the explosive with the general formula $C_aH_bN_cO_d$ to carbon monoxide, carbon dioxide, water and so on. In other words, oxygen balance represents the lack or excess of oxygen required to produce H_2O, CO and CO_2.

$$OB\% = \frac{[d - 2a - \frac{b}{2}]\ X\ 1600}{Mw} \quad (7)$$

where Mw is the molecular weight of explosive. It is related to Q, D and P and sensitivity. Generally, Q value reaches maximum for pyrazoles containing three NO_2 groups corresponds to the oxidation of carbon to more CO_2 and less CO and hydrogen to H_2O. Based on the composition of explosive, the main components of gaseous products may include CO, CO_2, N_2, H_2O with lesser quantities of other molecules and radicals such as H_2, NO, H, O, CHO and N_2O. The possible detonation products of designed compounds have been written based on the modified Kistiakowsky-Wilson rules.[19]

Mononitropyrazoles:

$$C_3H_3N_3O_2 \rightarrow 1\ ½\ H_2O + ½\ CO + 2\ ½\ C + 1\ ½\ N_2 \quad (8)$$

Dinitropyrazoles:

$$C_3H_2N_4O_4 \rightarrow H_2O + 3\ CO + 2\ N_2 \quad (9)$$

Dinitropyrazole-2-oxides:

$$C_3H_2N_4O_5 \rightarrow H_2O + CO_2 + 2\ CO + 2\ N_2 \quad (10)$$

Trinitropyrazoles:

$$C_3HN_5O_6 \rightarrow \tfrac{1}{2}\ H_2O + 2\tfrac{1}{2}\ CO_2 + \tfrac{1}{2}\ CO + 2\tfrac{1}{2}\ N_2 \quad (11)$$

Trinitropyrazole-2-oxides:

$$C_3HN_5O_7 \rightarrow \tfrac{1}{2}\ H_2O + 3\ CO_2 + \tfrac{1}{4}\ O_2 + 2\tfrac{1}{2}\ N_2 \quad (12)$$

Tetranitropyrazole:

$$C_3N_5O_8 \rightarrow 3\ CO_2 + O_2 + 2\tfrac{1}{2}\ N_2 \quad (13)$$

Tetranitropyrazole-2-oxide:

$$C_3N_5O_9 \rightarrow 3\ CO_2 + 1\tfrac{1}{2}\ O_2 + 2\tfrac{1}{2}\ N_2 \quad (14)$$

Aminodinitropyrazoles:

$$C_3H_3N_5O_4 \rightarrow 1\tfrac{1}{2}\ H_2O + 2\tfrac{1}{2}\ CO + \tfrac{1}{2}\ C + 2\tfrac{1}{2}\ N_2 \quad (15)$$

Aminodinitropyrazole-2-oxides:

$$C_3H_3N_5O_5 \rightarrow 1\tfrac{1}{2}\ H_2O + \tfrac{1}{2}\ CO_2 + 2\tfrac{1}{2}\ CO + 2\tfrac{1}{2}\ N_2 \quad (16)$$

Diaminodinitropyrazole-2-oxides:

$$C_3H_4N_6O_5 \rightarrow 2\ H_2O + 3\ CO + 3\ N_2 \quad (17)$$

Aminotrinitropyrazoles:

$$C_3H_2N_6O_6 \rightarrow H_2O + 2\ CO_2 + CO + 3\ N_2 \quad (18)$$

Aminotrinitropyrazole-2-oxides:

$$C_3H_2N_6O_7 \rightarrow H_2O + 3\ CO_2 + 3\ N_2 \quad (19)$$

Methyltrinitropyrazoles:

$$C_4H_3N_6O_6 \rightarrow 1\tfrac{1}{2}\ H_2O + \tfrac{1}{2}\ CO_2 + 3\tfrac{1}{2}\ CO + 2\tfrac{1}{2}\ N_2 \quad (20)$$

Methyltrinitropyrazole-2-oxides:

$$C_4H_3N_6O_7 \rightarrow 1\tfrac{1}{2}\ H_2O + 1\tfrac{1}{2}\ CO_2 + 2\tfrac{1}{2}\ CO + 2\tfrac{1}{2}\ N_2 \quad (21)$$

The relationship between impact sensitivity ($h_{50\%}$) and electronic structure of nitropyrazoles has been predicted by the nitro group charge analysis. The Mulliken charges were chosen to evaluate the stability/or sensitivity of designed molecules knowing the Mulliken charges are qualitatively correct and reproducible for the basis set.[13,20-22] The relationship between electric spark sensitivity and electronic structure of model compounds has been established by nitro group charge analysis and the lowest frontier molecular orbital energy.[23] The stability has been determined from the frontier molecular orbital energies and their gaps.[24-26]

2.3 Results and Discussion

2.3.1 Optimized Structures

We have optimized the structures of nitropyrazoles at the B3LYP/aug-cc-pVDZ level and their molecular frameworks are shown in Figure 2.3.1. All the model compounds belong to C_1 point group. The non-planarity or co-planarity of a molecule is due to the repulsion between the neighboring nitro groups, which rotate the oxygen atoms away from the molecular plane. Two nitro groups and one of the hydrogen atoms of methyl or amino group form the molecular plane and the oxygen atoms of other nitro group are either perpendicular or coplanar to the ring. The lowest frequency, total energy, zero-point energy, thermal correction to enthalpy and frontier molecular orbital energies and their gaps of nitropyrazoles are presented in Table 2.3.1.

The lowest frequencies varying from 8.337 to 101.2410 cm^{-1} are for the torsions of NO_2 groups.[13,15] The bond lengths, bond angles, total energies and frontier molecular orbital energies are varying with the relative positions and the nature of substituent groups. The C-NO_2 lengths of the optimized structures indicates that C3-NO_2 bond is longer in DNP-1 (1.469 Å), DNP-2 (1.458 Å), DNPO-1 (1.452 Å) and DNPO-2 (1.437 Å). However, the C4-NO_2 length is longer in DNP-3 (1.448 Å), DNPO-3 (1.456 Å), TNP-1 (1.466 Å) and TNPO-1 (1.470 Å). In all N-NO_2 containing compounds, N-NO_2 lengths are varying from 1.429 to 1.642 Å. DNPO-4, DNPO-5, DNPO-6, TNPO-2, TNPO-3, TNPO-4 and TNPO-5 have N-NO_2 distances 1.437, 1.441, 1.543, 1.587, 1.576, 1.461 and 1.642 Å respectively. The C3-NO_2 length is longer in ADNPO-1, ADNPO-10 and DADNPO-6 than ADNPO-2, ADNPO-4, ADNPO-7, ADNPO-12 and DADNPO-5. The C4-NO_2 length is longer in ADNPO-3 (1.453 Å) and ATNPO-1 (1.471 Å). The equal C-NO_2 lengths (1.427 Å) in DADNPO-4 are due to the presence of NH_2 group at 3-position. ATNPO-2, ATNPO-3 and ATNPO-4 have unusual N-NO_2 lengths 1.750, 1.592 and 1.467 Å respectively. Methyl-, amino- and tetranitropyrazoles have C…O (2.760 to 3.031 Å), N-H…O (2.720 to 2.990 Å) and N…O (2.6858 to 2.953 Å) interactions respectively that are shorter than sum of the vander Waals radii.[27-29] The discrepancies in the total and zero-point energies, thermal correction to enthalpy, frontier molecular orbital energies, trigger lengths and N2-O lengths are presumably due to relative positions of substituent groups in the pyrazole ring.

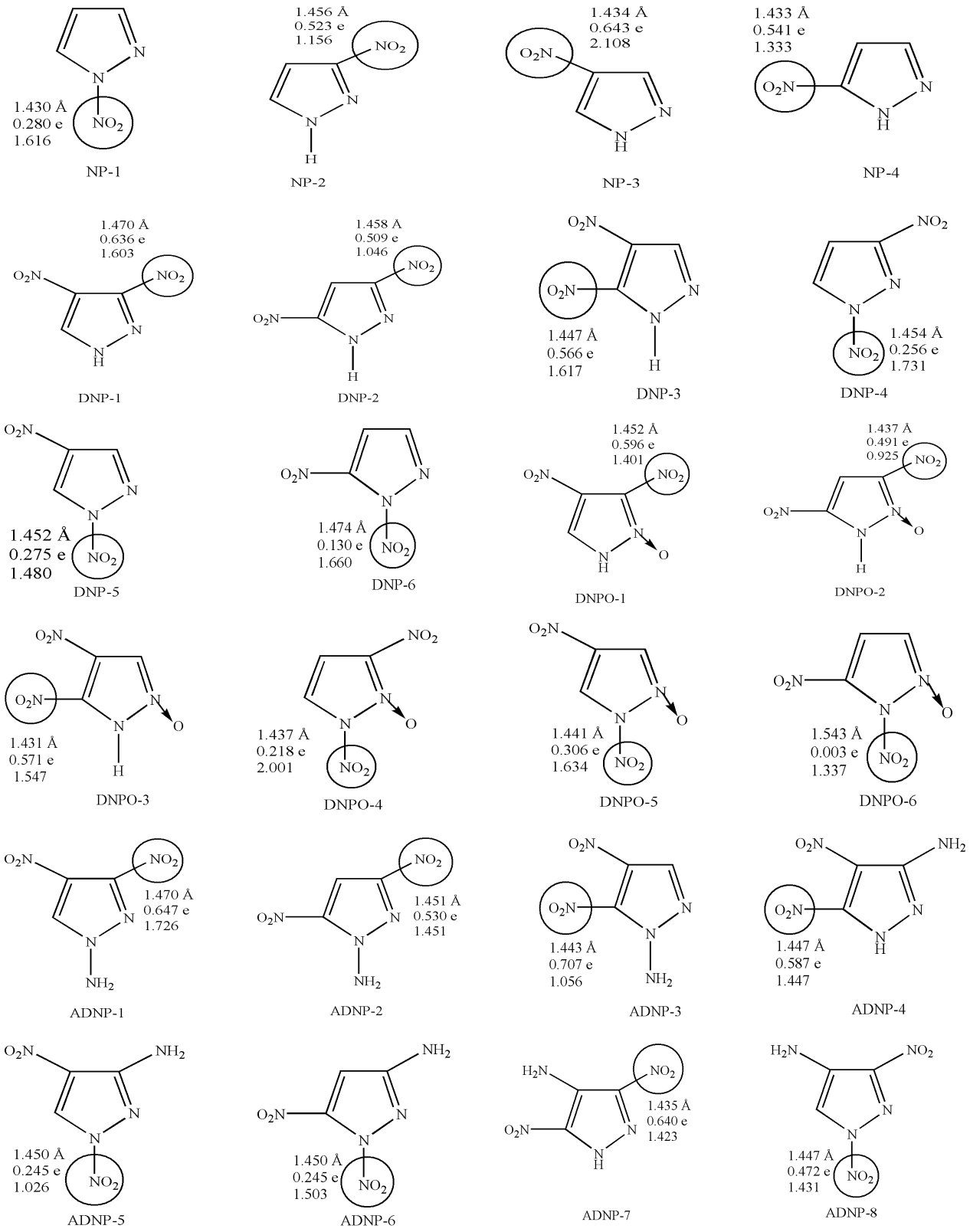
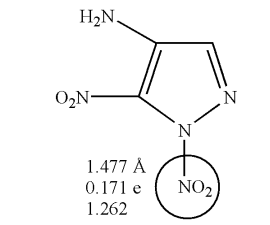


Figure 2.3.1 Molecular structures of nitropyrazoles with trigger bond *encircled*; *the list of the values beside each structure shows* the trigger length (in Å), nitro group charge (in e) and midpoint electrostatic potential (continued…).



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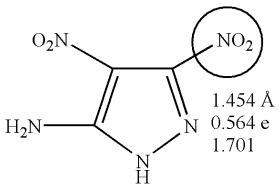
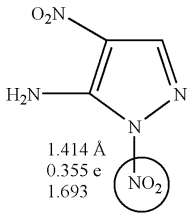


ADNP-10



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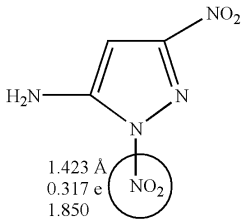

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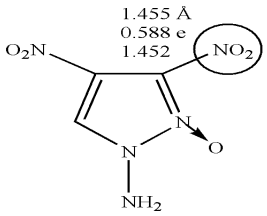

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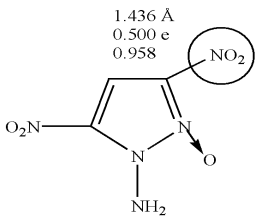

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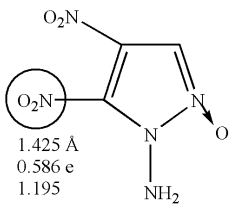

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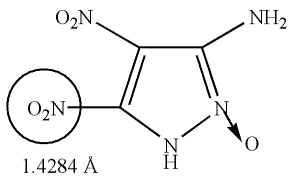

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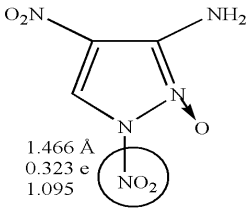

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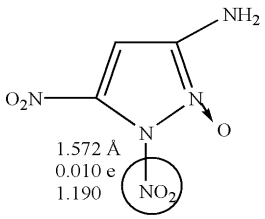

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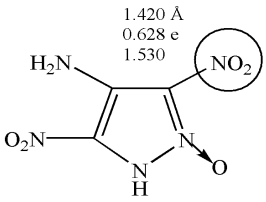

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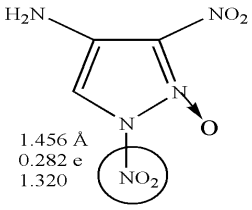

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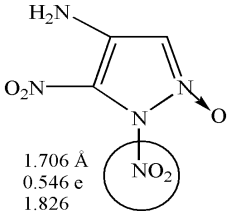

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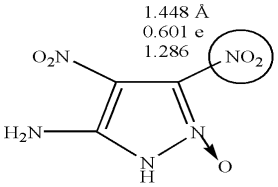

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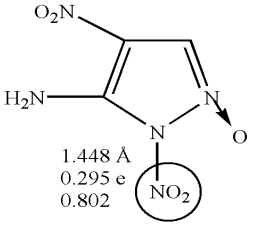

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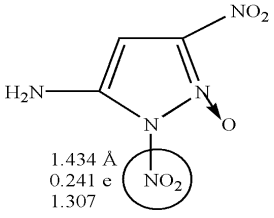

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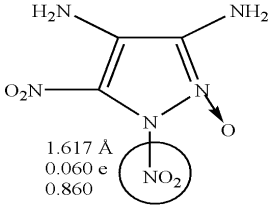

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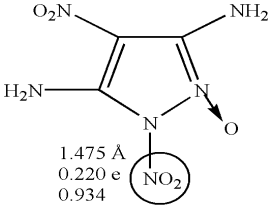

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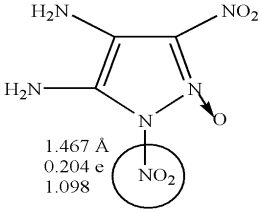

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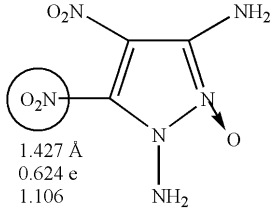

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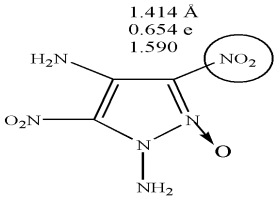

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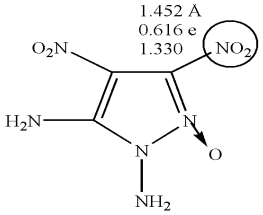

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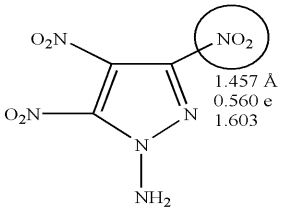

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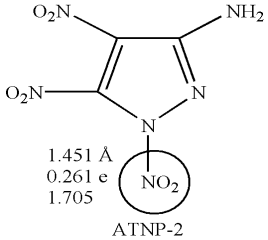

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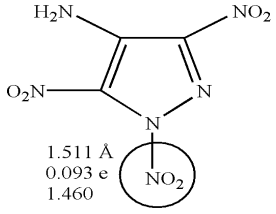

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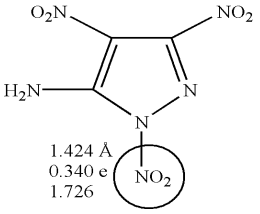

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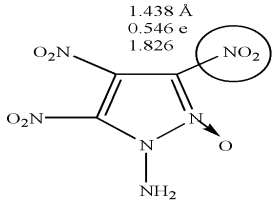

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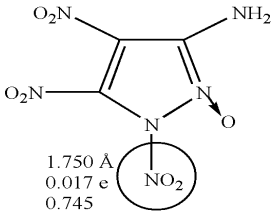

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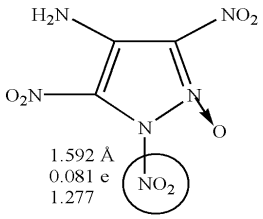

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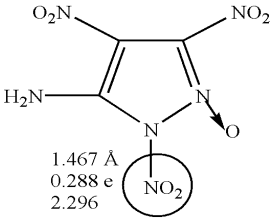

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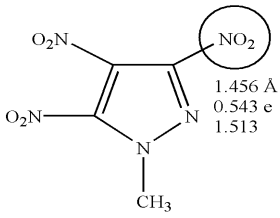

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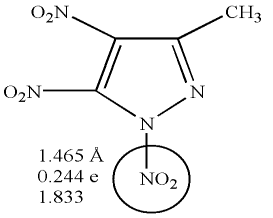

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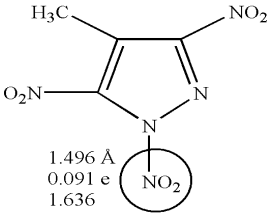

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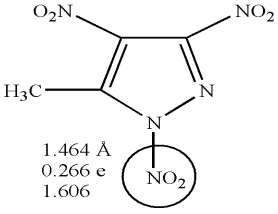

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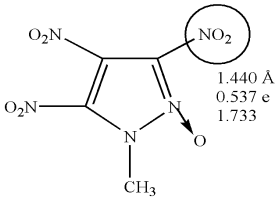

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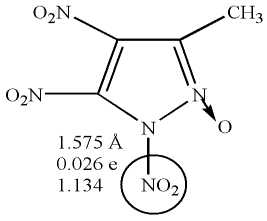

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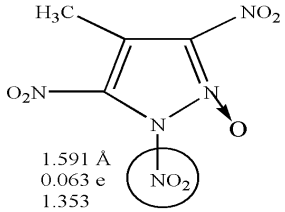

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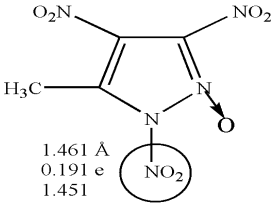

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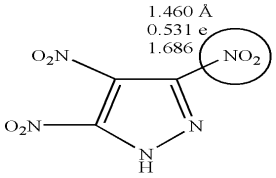
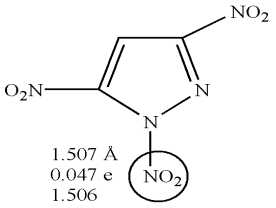


TNP-1



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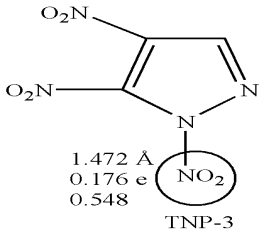

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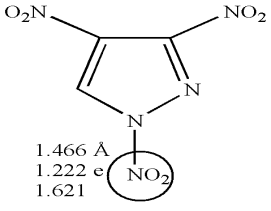

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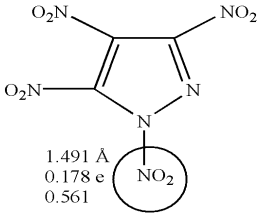
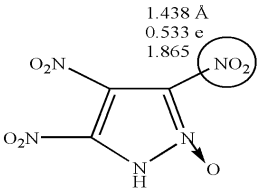
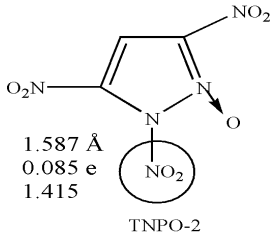


TNP-5



TNPO-1



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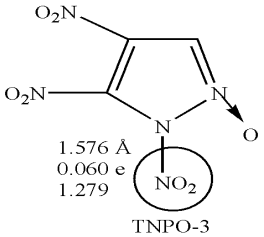

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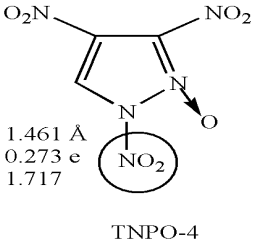

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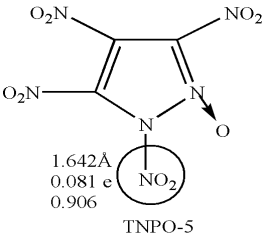

TNPO-5

Table 2.3.1 Lowest frequency (ω_L), total energy (E_o), zero-point energy (ZPE), thermal correction to enthalpy (H_T) frontier orbital energies of nitropyrazoles computed from the B3LYP/aug-cc-pVDZ level.

HEM	ω_L (cm^{-1})	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOMO (a.u.)	LUMO (a.u.)	$\Delta\varepsilon_{(LUMO-HOMO)}$
NP-1	86.4064	-430.732912	0.072557	0.103572	-0.11659	-0.31099	0.19440
NP-2	64.7703	-430.766153	0.073733	0.103218	-0.13931	-0.29331	0.15400
NP-3	87.2965	-430.769614	0.073986	0.103368	-0.13887	-0.29324	0.15437
NP-4	101.2409	-430.707101	0.073763	0.103633	-0.14071	-0.26737	0.12666
DNP-1	10.4071	-635.284297	0.076050	0.102608	-0.13546	-0.26810	0.13264
DNP-2	55.1172	-635.2929492	0.076130	0.102178	-0.13258	-0.27021	0.13763
DNP-3	45.1485	-635.2827794	0.076071	0.103955	-0.13049	-0.27220	0.14171
DNP-4	50.3953	-635.2591263	0.748280	0.102416	-0.13699	-0.26108	0.12409
DNP-5	63.5593	-635.2621334	0.075029	0.102252	-0.12472	-0.27149	0.14677
DNP-6	42.9411	-635.2441322	0.074490	0.102383	-0.12650	-0.27768	0.15118
DNPO-1	32.0251	-710.440743	0.078989	0.102867	-0.12547	-0.27587	0.15040
DNPO-2	48.0567	-710.4524609	0.079055	0.102293	-0.13158	-0.26576	0.13418
DNPO-3	39.7764	-710.4467171	0.079071	0.107849	-0.27074	-0.12730	0.14344
DNPO-4	26.0087	-710.4051722	0.077456	0.107590	-0.27947	-0.14036	0.13911
DNPO-5	35.1772	-710.4130086	0.077540	0.107450	-0.27219	-0.14757	0.12462
DNPO-6	31.5022	-710.4073434	0.077497	0.107808	-0.25075	-0.14921	0.10154
TNP-1	34.9047	-839.7988390	0.078177	0.106502	-0.23376	-0.14176	0.0920
TNP-2	34.9580	-839.7658247	0.076465	0.106364	-0.24614	-0.14202	0.16412
TNP-3	37.0249	-839.9628517	0.076797	0.108152	-0.26434	-0.13387	0.13047
TNP-4	20.0467	-839.772916	0.076878	0.106354	-0.24811	-0.13846	0.10965
TNP-5	23.1180	-1044.271009	0.078516	0.106550	-0.28515	-0.14533	0.13982
TNPO-1	31.7295	-914.9553671	0.081000	0.126065	-0.24589	-0.11587	0.13002
TNPO-2	39.9132	-914.9217603	0.079385	0.106620	-0.24268	-0.13227	0.11041
TNPO-3	22.0078	-914.9157624	0.079297	0.106362	-0.24735	-0.13597	0.11138
TNPO-4	21.1140	-914.9169173	0.079362	0.124907	-0.24749	-0.12365	0.12384
TNPO-5	36.1329	-914.4238387	0.081237	0.124746	-0.21397	-0.12397	0.09254

continued...

HEM	ω_L (cm^{-1})	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOMO (a.u.)	LUMO (a.u.)	$\Delta\varepsilon_{(LUMO-HOMO)}$
ADNP-1	15.1714	-690.618398	0.092317	0.103572	-0.11659	-0.31099	0.19440
ADNP-2	55.9645	-690.6218158	0.092331	0.103218	-0.13931	-0.29331	0.15400
ADNP-3	44.4385	-690.6217358	0.092332	0.103368	-0.13887	-0.29324	0.15437
ADNP-4	58.1361	-690.6617320	0.092601	0.103633	-0.14071	-0.26737	0.12666
ADNP-5	42.4181	-690.6431944	0.091327	0.102608	-0.13546	-0.26810	0.13264
ADNP-6	42.1023	-690.6186803	0.090978	0.102178	-0.13258	-0.27021	0.13763
ADNP-7	79.3360	-690.6747163	0.093195	0.103955	-0.13049	-0.27220	0.14171
ADNP-8	62.9717	-690.6297066	0.091433	0.102416	-0.13699	-0.26108	0.12409
ADNP-9	66.5077	-690.6225297	0.091234	0.102252	-0.12472	-0.27149	0.14677
ADNP-10	8.3373	-690.6286803	0.091222	0.102383	-0.12650	-0.27768	0.15118
ADNP-11	68.6226	-690.6463260	0.092189	0.102867	-0.12547	-0.27587	0.15040
ADNP-12	46.3191	-690.6306958	0.091123	0.102293	-0.13158	-0.26576	0.13418
ADNPO-1	29.4908	-765.7777837	0.095520	0.107849	-0.27074	-0.12730	0.14344
ADNPO-2	49.1366	-765.7815637	0.095526	0.107590	-0.27947	-0.14036	0.13911
ADNPO-3	39.9214	-765.7748352	0.095338	0.107450	-0.27219	-0.14757	0.12462
ADNPO-4	59.1141	-765.8250761	0.095628	0.107808	-0.25075	-0.14921	0.10154
ADNPO-5	34.4094	-765.7904323	0.094058	0.106502	-0.23376	-0.14176	0.0920
ADNPO-6	40.3549	-765.7819807	0.093929	0.106364	-0.24614	-0.14202	0.16412
ADNPO-7	60.7575	-765.8355691	0.096123	0.108152	-0.26434	-0.13387	0.13047
ADNPO-8	39.6723	-765.7750714	0.094054	0.106354	-0.24811	-0.13846	0.10965
ADNPO-9	38.0913	-765.7912222	0.094262	0.106550	-0.28515	-0.14533	0.13982
ADNPO-10	43.0402	-821.1601763	0.112186	0.126065	-0.24589	-0.11587	0.13002
ADNPO-11	48.8506	-765.700923	0.094660	0.106620	-0.24268	-0.13227	0.11041
ADNPO-12	50.4173	-765.7742598	0.094165	0.106362	-0.24735	-0.13597	0.11138
DADNPO-1	40.0617	-821.1652908	0.111133	0.124907	-0.24749	-0.12365	0.12384
DADNPO-2	42.0217	-821.1766787	0.110997	0.124746	-0.21397	-0.12397	0.09254

continued...

HEM	ω_L (cm^{-1})	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOMO (a.u.)	LUMO (a.u.)	$\Delta\varepsilon_{(LUMO-HOMO)}$
DADNPO-3	51.5157	-821.1391399	0.110826	0.124534	-0.23291	-0.13470	0.09821
DADNPO-4	65.7043	-821.1557409	0.112130	0.125729	-0.24940	-0.13988	0.10952
DADNPO-5	62.3734	-821.164356	0.112907	0.126191	-0.25842	-0.12811	0.13031
DADNPO-6	38.0913	-765.7912222	0.094262	0.106550	-0.24589	-0.11587	0.13002
ATNP-1	35.1787	-895.1282330	0.094385	0.108100	-0.15460	-0.30701	0.15241
ATNP-2	45.7231	-895.1445915	0.093181	0.107231	-0.14892	-0.28276	0.13384
ATNP-3	56.6169	-895.1507101	0.093757	0.107266	-0.15412	-0.29010	0.13598
ATNP-4	28.3781	-895.1587202	0.094100	0.107659	-0.14093	-0.29595	0.15502
ATNPO-1	35.0205	-970.2845909	0.097467	0.112399	-0.29483	-0.15483	0.1400
ATNPO-2	45.2785	-970.2948549	0.095971	0.111105	-0.26101	-0.17022	0.0908
ATNPO-3	24.2429	-970.3124378	0.096590	0.111462	-0.27885	-0.16998	0.10887
ATNPO-4	33.7391	-970.3011948	0.096562	0.111355	-0.26424	-0.14959	0.11465
MTNP-1	34.1451	-879.1135028	66.37395	0.119699	-0.15013	-0.32320	0.17307
MTNP-2	39.0547	-879.0904589	65.43678	0.118301	-0.15021	-0.32560	0.17539
MTNP-3	35.1440	-879.0905059	65.35148	0.117303	-0.15483	-0.32957	0.17474
MTNP-4	9.5030	-879.0972270	65.57833	0.118572	-0.14723	-0.32546	0.17776
MTNPO-1	31.2279	-954.2714586	0.108949	0.124082	-0.29307	-0.15172	0.14135
MTNPO-2	29.0710	-954.2724282	0.106754	0.122404	-0.28278	-0.15977	0.12301
MTNPO-3	41.3603	-954.246435	0.107091	0.122391	-0.29432	-0.16165	0.13567
MTNPO-4	31.0257	-954.2413458	0.107092	01.22458	-0.28489	-0.15508	0.12981

2.3.2 Theoretical Density

Density (ρ) continues to be one of the top priorities in the development of new energetic materials. It appears to a higher power in the Kamlet-Jacob[18] semi-empirical equations than does any variables. The detonation velocity (D) linearly increases with ρ for most of explosives. The detonation pressure (P) increases with the square of ρ, when ρ is greater than one. Several researchers have attempted to predict the densities with satisfactory accuracy.[30-32] We have taken

the optimized structures computed from the B3LYP/aug-cc-pVDZ level to predict the densities using Materials Studio 4.1 package with CVFF force field and Ewald summation method. This approach is based on the generation of possible packing arrangements in all reasonable space groups. Many organic compounds known to pack in C2/c, $P2_1$, $P2_1/c$, $P2_12_12_1$, P-1, Pbca, Pbcn, $Pna2_1$, CC and/or C2 space groups.[33-38] The calculated crystal characteristics of nitropyrazoles are shown in Table 2.3.2.

The densities of pyrazole, RDX, HMX, ONC and CL-20 computed from the B3LYP/aug-cc-pVDZ level are 1.242, 1.817, 1.910, 2.054 and 2.075 g/cm^3 that are comparable with the experimental values 1.22, 1.82, 1.92, 1.979 and 2.042 g/cm^3 respectively.[19,34-36,39] Pyrazole, DNP-1, DNP-2, DNP-3, DNP-5, DNPO-1, DNPO-5, DNPO-6, TNP-6 and TNPO-3 were packed in $P2_1/c$, NP-1, TNPO-4 and TNPO-5 in $P2_1$, DNP-4, DNPO-2 and TNP-2 in $P2_12_12_1$, NP-2 and NP-4 in Pbcn, TNP-4 and TNPO-1 in Pbca, NP-3, DNP-6, DNPO-3, DNPO-4, TNP-1 and TNP-5 in $Pna2_1$, TNPO-2 in P_{-1} space groups (triclinic system) with the densities varying from 1.542 to 2.351 g/cm^3. MTNP-1, MTNP-2, MTNP-3 and MTNP-4 have densities varying from 1.797 to 1.858 g/cm^3 comparable with RDX (ρ 1.82 g/cm^3).[39] Similarly, the predicted densities of ATNP-1, ATNP-2, ATNP-3 and ATNP-4 are varying from 1.900 to 1.934 g/cm^3 comparable with as HMX (ρ 1.92 g/cm^3).[39] Aminonitropyrazole-2-oxides such as ADNPO-2, ADNPO-3, ADNPO-7, ADNPO-9, ADNPO-10, ADNPO-11, DADNPO-1, DADNPO-5, DADNPO-6, ATNPO-1, ATNPO-2 and ATNPO-3 were packed in $P2_1/c$, ADNPO-1, ADNPO-5, ADNPO-6, ADNPO-8, DADNPO-4 and DADNPO-2 in $Pna2_1$, ADNPO-4 and ATNPO-4 in Pbca, DADNPO-6 in $P2_12_12_1$ space groups with the densities varying from 2.106 to 2.340 g/cm^3. ADNPO-12 and ADNPO-7 have highest and lowest densities 2.106 and 2.106 g/cm^3 respectively among the dintropyrazole-2-oxides. The crystal structures of TNP-1, TNP-5, MTNP-1, ATNP-1, MTNPO-1 and ATNPO-1 are presented in Figure 2.3.2. The higher densities of nitropyrazole-2-oxides are presumably due to the intramolecular hydrogen bonds as well as the layered structures in the crystal lattice. The absolute error in the predicted densities are believed to be less than 0.03 g/cm^3 and thus known to be fairly good to calculate the performance properties of designed compounds.[30-32]

Table 2.3.2 Crystal characteristics nitropyrazoles.

HEM	Cell volume Å^3	Total energy kJ mol^{-1}	Space group	Crystal system	a, b, c (Å) α, β, γ	Density g cm^{-3}
Pyrazole	363.60900241	0.9649011	$P2_1$	monoclinic	4.97, 7.70, 10.45 α = γ = 90º, β = 114º.6'	1.242
NP-1	238.31500417	-3.2451618	$P2_1$	monoclinic	7.23, 9.33, 3.72 α = γ = 90º, β = 107º.8'	1.578
NP-2	973.93634401	8.67575760	Pbcn	rhombic	12.54, 6.68, 11.81 α = β = γ = 90º	1.542
NP-3	473.06673454	-15.80413520	$Pna2_1$	rhombic	8.23, 10.06, 5.72 α = β = γ = 90º	1.587
NP-4	972.3561918	9.81229761	Pbcn	rhombic	10.36, 7.58, 11.82 α = β = γ = 90º	1.545
DNP-1	583.72699651	-40.73016121	$P2_1/c$	monoclinic	8.14, 7.50, 14.82 α = γ = 90º, β = 58º.6'	1.798
DNP-2	576.87020031	-3.76649924	$P2_1/c$	monoclinic	19.78, 9.33, 10.48 α = γ = 90º, β = 45º.8'	1.820
DNP-3	593.60580257	-39.35275350	$P2_1/c$	monoclinic	7.28, 8.45, 18.61 α = γ = 90º, β = 148º.8'	1.768
DNP-4	592.93954021	-12.82752461	$P2_12_12_1$	rhombic	9.06, 6.14, 10.65 α = β = γ = 90º	1.771
DNP-5	592.30462942	-36.87487452	$P2_1/c$	monoclinic	6.26, 9.30, 13.60 α = γ = 90º, β = 131º.6'	1.772
DNP-6	607.34881627	-23.40185152	$Pna2_1$	rhombic	10.01, 7.33, 8.28 α = β = γ = 90º	1.728
DNPO-1	508.96137442	-585.09958903	$P2_1/c$	monoclinic	6.00, 7.91, 13.78 α = γ = 90º, β = 128º.7'	2.272
DNPO-2	515.08080585	-585.47665270	$P2_12_12_1$	rhombic	5.86, 9.97, 8.82 α = β = γ = 90º	2.245
DNPO-3	508.72449344	-589.69836526	$Pna2_1$	rhombic	9.22, 6.72, 8.22 α = β = γ = 90º	2.273
DNPO-4	521.75188394	-561.144295621	$Pna2_1$	rhombic	8.77, 6.28, 9.50 α = β = γ = 90º	2.216
DNPO-5	516.8784297	-546.36629268	$P2_1/c$	monoclinic	6.08, 9.55, 10.60 α = γ = 90º, β = 122º.6'	2.237
DNPO-6	525.66604778	-572.98872972	$P2_1/c$	monoclinic	16.58, 8.82, 11.10 α = γ = 90º, β = 161º.1'	2.200
TNP-1	673.7598811	-81.88808250	$Pna2_1$	rhombic	8.10, 9.0, 9.23 α = β = γ = 90º	2.002
TNP-2	714.73724305	-50.30520473	$P2_12_12_1$	rhombic	8.86, 9.23, 8.73 α = β = γ = 90º	1.887
TNP-3	701.74645375	-85.90461455	$P2_1/c$	monoclinic	15.77, 6.45, 12.42 α = γ = 90º, β = 146.3º	1.922
TNP-4	1406.3310	-76.19767653	Pbca	rhombic	8.02, 19.37, 9.05 α = β = γ = 90º	1.918
TNP-5	800.5052	-141.7806026	$Pna2_1$	rhombic	11.84, 6.73, 10.04 α = β = γ = 90º	2.062
TNPO-1	14217.4020	-747.16317198	Pbca	rhombic	11.72, 9.70, 10.72 α = β = γ = 90º	2.398
TNPO-2	354.65184473	-14.52212309	$P\text{-}_1$	triclinic	6.66, 12.35, 8.67 α = 80.23 º, β = 52º.3', γ = 45 º.3'	2.351
TNPO-3	617.89536800	-713.52996820	$P2_1/c$	monoclinic	15.22, 10.63, 11.73 α = γ = 90º, β = 161º	2.355
TNPO-4	312.83257906	-700.78826520	$P2_1$	monoclinic	8.26, 8.60, 6.11 α = γ = 90º, β = 92º.7'	2.326
TNPO-5	350.15360014	-885.85323813	$P2_1$	monoclinic	8.57, 8.18, 6.37 α = γ = 90º, β = 52º.2'	2.498

continued..

HEM	Cell volume Å^3	Total energy kJ mol^{-1}	Space group	Crystal system	a, b, c (Å) α, β, γ	Density g cm^{-3}
ADNP-1	635.93527243	-57.85415170	$P2_12_12_1$	rhombic	10.99, 11.60, 4.96 α = β = γ = 90°	1.808
ADNP-2	646.74476883	-9.37242910	$P2_1/_C$	monoclinic	7.84, 8.42, 9.87 α = γ = 90°, β = 97°.3'	1.787
ADNP-3	1262.5260	-47.38590836	Pbca	rhombic	17.28, 9.16, 7.97 α = β = γ = 90º	1.816
ADNP-4	317.50065135	-40.91776086	$P2_1$	monoclinic	7.37, 7.85, 6.91 α = γ = 90°, β = 52°.7'	1.807
ADNP-5	669.93220870	-37.14080710	$P2_1/c$	monoclinic	13.58, 6.42, 9.76 α = γ = 90°, β = 128°.1'	1.798
ADNP-6	646.09112502	-35.94281074	$P2_12_12_1$	rhombic	11.69, 10.86, 5.12 α = β = γ = 90°	1.797
ADNP-7	644.45416010	-16.937091	$P2_1/c$	monoclinic	6.20, 9.63, 13.53 α = γ = 90°, β = 127°.1'	1.806
ADNP-8	647.15267924	-2.29083863	$P2_12_12_1$	rhombic	7.01, 9.42, 9.82 α = β = γ = 90º	1.769
ADNP-9	648.04333733	-14.11670145	$P2_1/c$	monoclinic	6.85, 8.43, 7.51 α = γ = 90°, β = 131°.6'	1.766
ADNP-10	646.0844254	-35.84321112	$P2_12_12_1$	rhombic	11.96, 10.68, 6.22 α = β = γ = 90º	1.797
ADNP-11	656.7571756	-37.22132852	$P2_1/c$	monoclinic	15.19, 9.57, 11.81 α = γ = 90°, β = 157°.5'	1.749
ADNP-12	644.32112374	-23.47546335	$P2_12_12_1$	rhombic	9.44, 9.75, 6.99 α = β = γ = 90°	1.798
ADNPO-1	577.18144858	-535.03036546	$Pna2_1$	rhombic	9.61, 7.22, 8.33 α = β = γ = 90°	2.176
ADNPO-2	572.22275212	-521.02906795	$P2_1/c$	monoclinic	15.55, 6.15, 10.55 α = γ = 90°, β = 145°.5'	2.201
ADNPO-3	580.63072956	-521.74288695	$P2_1/c$	monoclinic	15.55, 6.15, 10.55 α = γ = 90°, β = 145°.5'	2.157
ADNPO-4	1143.9450011	-433.75538927	Pbca	rhombic	12.13, 11.11, 8.48 α = β = γ = 90°	2.200
ADNPO-5	568.67218664	-511.88788054	$Pna2_1$	rhombic	13.73, 6.60, 6.28 α = β = γ = 90°	2.210
ADNPO-6	576.38728699	-447.98404141	$Pna2_1$	rhombic	11.18, 7.82, 6.60 α = β = γ = 90°	2.181
ADNPO-7	560.88855384	-577.99388511	$P2_1/c$	monoclinic	10.06, 9.90, 11.55 α = γ = 90°, β = 150°.8'	2.240
ADNPO-8	567.37191596	-558.90004135	$Pna2_1$	rhombic	8.57, 6.54, 10.13 α = β = γ = 90°	2.209
ADNPO-9	572.22271112	-521.02924562	$P2_1/c$	monoclinic	15.20, 6.12, 10.42 α = γ = 90°, β = 150°.8'	2.190
ADNPO-10	564.04750674	-571.75097100	$P2_1/c$	monoclinic	9.66, 10.97, 12.72 α = γ = 90°, β = 150°.8'	2.230
ADNPO-11	582.44993924	-523.90083310	$P2_1/c$	monoclinic	14.28, 8.68, 11.43 α = γ = 90°, β = 155°.7'	2.162
ADNPO-12	596.23746283	-548.18785463	$P2_1/c$	monoclinic	13.76, 5.93, 10.02 α = γ = 90°, β = 155°.7'	2.101
DADNPO-1	632.90129894	-428.5162146	$P2_1/c$	monoclinic	5.13, 10.77, 12.81 α = γ = 90°, β = 155°.7'	2.150
DADNPO-2	584.52044455	-485.92191347	$Pna2_1$	rhombic	15.53, 7.18, 5.25 α = β = γ = 90°	2.320

continued..

HEM	Cell volume Å^3	Total energy kJ mol^{-1}	Space group	Crystal system	a, b, c (Å)	Density g cm^{-3}
					α, β, γ	
DADNPO-3	647.4558479	-534.61368847	$P2_1/c$	monoclinic	10.73, 6.10, 9.96 α = γ = 90°, β = 96°.2'	2.094
DADNPO-4	620.42523118	-486.86008944	$Pna2_1$	rhombic	8.78, 12.08, 5.85 α = β = γ = 90°	2.181
DADNPO-5	618.22886778	-509.72664406	$P2_1/c$	monoclinic	8.97, 6.68, 10.56 α = γ = 90°, β = 77°.9'	2.200
DADNPO-6	629.93010206	-508.47269608	$P2_12_12_1$	rhombic	9.40, 6.23, 10.8 α = β = γ = 90°	2.152
ATNP-1	748.92681562	-89.94626855	$Pna2_1$	rhombic	8.95, 12.756.57 α = β = γ = 90°	1.934
ATNP-2	755.29761248	-92.11732472	$Pna2_1$	rhombic	9.10, 12.80, 6.48 α = β = γ = 90°	1.918
ATNP-3	760.2333301	-36.25893442	$P2_1/c$	monoclinic	12.13, 9.21, 9.75 α = γ = 90°, β = 135°.7'	1.905
ATNP-4	764.3019348	-82.32390034	$P2_1/c$	monoclinic	8.50, 9.18, 9.84 α = γ = 90°, β = 95°.9'	1.900
ATNPO-1	665.84444617	-684.13549750	$P2_1/c$	monoclinic	5.94, 10.11, 12.70 α = γ = 90°, β = 119°.7'	2.340
ATNPO-2	671.89686464	-576.33873302	$P2_1/c$	monoclinic	5.88, 9.33, 12.60 α = γ = 90°, β = 115°.5'	2.311
ATNPO-3	672.7857001	-677.6642221	$P2_1/c$	monoclinic	5.84, 9.25, 12.56 α = γ = 90°; β =118°.2'	2.273
ATNPO-4	1368.2861	-679.6531222	Pbca	rhombic	9.16, 20.48, 7.30 α = β = γ = 90°	2.268
MTNP-1	783.01890108	-77.99773717	$Pna2_1$	rhombic	8.52, 13.32, 6.90 α = β = γ = 90°	1.840
MTNP-2	1592.9411	-83.09096275	Pbca	rhombic	9.40, 10.82, 15.67 α = β = γ = 90°	1.811
MTNP-3	802.32786474	-40.38268150	$P2_1/c$	monoclinic	10.02, 8.98, 21.11 α = γ = 90°, β = 155°.3'	1.797
MTNP-4	387.88838311	-70.54307470	$P2_1$	monoclinic	6.78, 8.38, 6.90 α = γ = 90°, β = 81°.4'	1.858
MTNPO-1	702.22974222	-674.88763729	$P2_1/c$	monoclinic	6.07, 10.14, 13.34 α = γ = 90°, β = 148°.3'	2.211
MTNPO-2	705.32881296	-677.13767046	$P2_1/c$	monoclinic	10.44, 11.64, 11.05 α = γ = 90°, β = 148°.3'	2.200
MTNPO-3	702.61857027	-680.32711600	$P2_12_12_1$	rhombic	8.17, 9.55, 9.02 α = β = γ = 90°	2.200
MTNPO-4	695.56931242	-664.21838966	$P2_1/c$	monoclinic	9.82, 6.54, 13.53 α = γ = 90°, β = 126°.6'	2.230

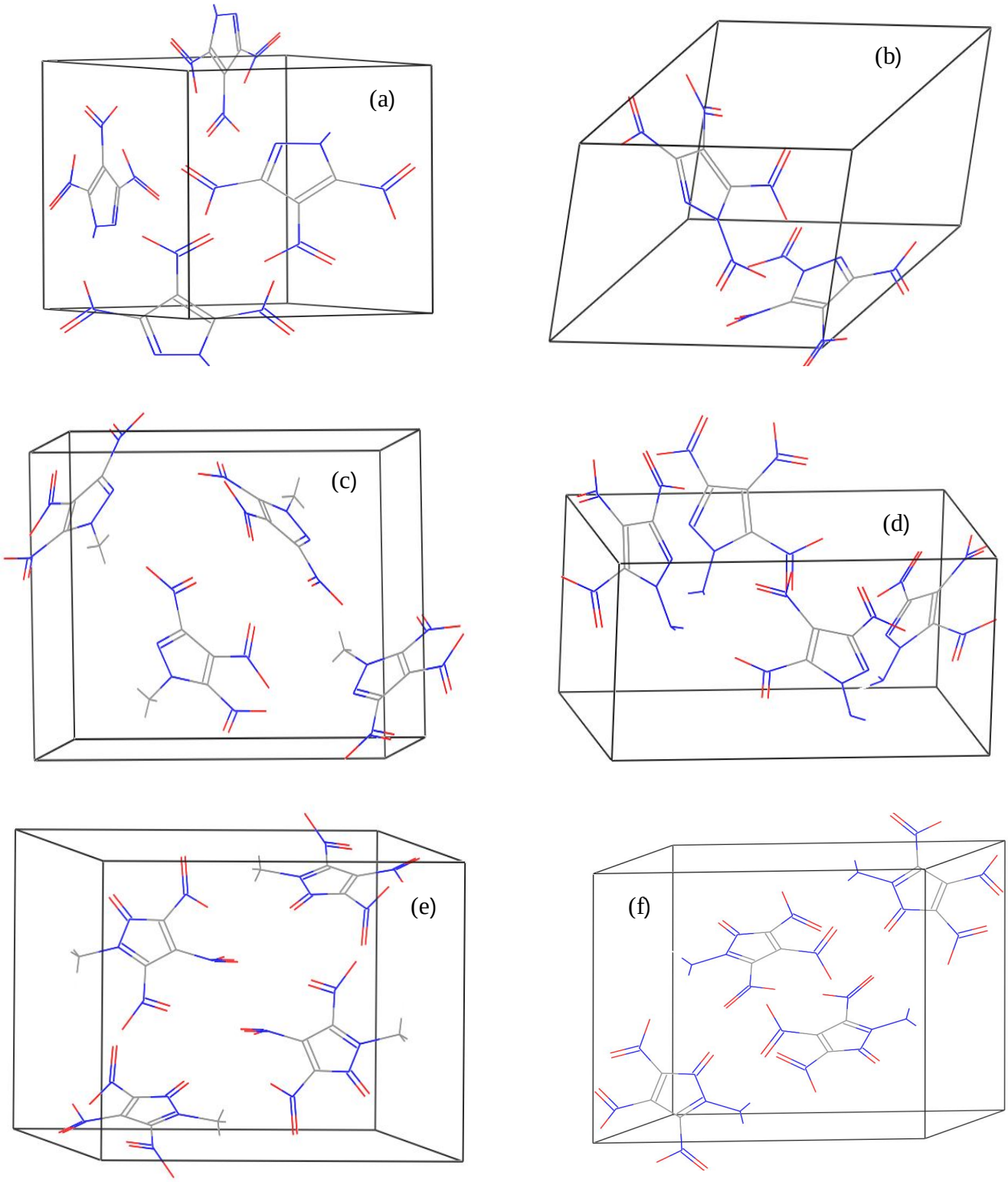

Figure 2.3.2 Crystal characteristics of nitropyrazoles: (a) TNP-1, (b) TNP-5, (c) MTNP-1, (d) ATNP-1, (e) MTNPO-1 and (f) ATNPO-1.

2.3.3 Heat of Explosion

The heat of explosion provides information about the work capacity of the explosive. The liberation of heat under adiabatic conditions is called the heat of explosion. It is an irreversible process and whatever the amount of heat released ultimately lost to surroundings. When an explosive is initiated either to burning or detonation, its energy is released in the form of heat. Explosion is initiated by the stimulus of negligible thermal proportions. Higher the value of heat of explosion for an explosive, more the heat generated when an explosion occurs. We have calculated the heats of explosion (Q) of nitropyrazoles assuming the explosive reactions go to total completion.[13,19] However, in practice the reactions do not go to completion and equilibrium is set up between the reactants and the products. These equilibria are dependent on the oxygen balance of an explosive. The most important equilibria may be presented as

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad H_2O \qquad (22)$$

$$2CO \rightleftharpoons C + CO \quad CO \qquad (23)$$

$$CO + H_2 \rightleftharpoons C + H_2O \quad H_2O \qquad (24)$$

The water-equilibrium equation 24 only becomes important as the oxygen balance decreases and the quantity of carbon monoxide and hydrogen in the products begins increase. The modified Kistiakowsky-Wilson rules[19] give an approximate for the products of decomposition, which is independent of the temperature of explosion. Table 2.3.3 presents the calculated oxygen balance, heats of explosion and performances of nitropyrazoles computed from B3LYP/aug-cc-pVDZ level.

Dinitropyrazole-2-oxides have higher Q values (1.30 to 1.47 kcal/g) compared with dinitropyrazoles (0.95 to 1.10 kcal/g). The Q values for trinitropyrazole-2-oxides are markedly higher (1.56 to 1.67 kcal/g) than for trinitropyrazoles (1.51 to 1.60 kcal/g). However, the Q value is decreased when the labile hydrogen of TNP-1 is substituted by NO_2 group and thus TNP-5 releases low heat. The Q values for aminodinitropyrazole-2-oxides are higher (1.10 to 1.30 kcal/g) than aminodinitropyrazoles (~0.80 kcal/g). The lower Q values of aminodinitropyrazoles are due to the release of free carbon on decomposition. ADNPO-3, ADNPO-8 and ADNPO-12 have shown higher Q values (1.30 kcal/g) among aminodinitropyrazole-2-oxides. Diaminodi-

nitropyrazole-2-oxides have lower Q values (1.06 to 1.18 kcal/g) than aminodinitropyrazole-2-oxides presumably the second NH_2 group drastically decreased the magnitude of heat of explosion. ATNPO-1 (1.71 kcal/g), ATNPO-2 (1.68 kcal/g), ATNPO-3 (1.66 kcal/g) and ATNPO-4 (1.66 kcal/g) have higher Q values whereas ATNP-1 (1.47 kcal/g), ATNP-2 (1.43 kcal/g), ATNP-3 (1.38 kcal/g) and ATNP-4 (1.38 kcal/g) have lower Q values. The Q values are increased with increasing number of NO_2 groups. The heats of explosion reaches maximum for an oxygen balance of zero, since this corresponds to the stoichiometric oxidation of carbon to carbon dioxide and hydrogen to water. Nevertheless, the calculated Q values do not exactly agree with those obtained experimentally because the conditions of loading density, temperature, pressure and so on are not taken into consideration. The total amount of energy liberated depends upon the relative proportions of the reactants to the products. The Q values are related to the number and the relative positions of substituent groups and the strength of N-oxide bond. The detonation energies obtained are for the gas phase compounds and in the reality they should be for the solid phase which would diminish the magnitude of Q values.[13,19]

2.3.4 Detonation Performance

The detonation velocity (D) and detonation pressure (P) are important factors to evaluate the performance of explosives.[13,19,39] For CL-20, ONC, RDX and HMX, the experimental D and P are 9.20, 9.90, 8.75, 8.96 km/ and 42.0, 48.45 34.70, 35.96 GPa respectively.[35,36,39] The calculated D and P of CL-20, ONC, RDX and HMX computed from the B3LYP/aug-cc-pVDZ level are 9.34, 10.06, 8.86, 9.10 km/s and 43.10, 50.0, 34.23, 39.40 GPa respectively.[37,38] The performances of nitropyrazoles are summarized in Table 2.3.3. The calculated performances of dinitropyrazole-2-oxides (D 10.24 to 10.47 km/s and P 52.54 to 55.90 GPa) and trinitropyrazole-2-oxides (D 10.67 to 10.77 km/s and P 58.10 to 59.87 GPa) are superior compared with those of CL-20 and ONC. The higher performance of nitropyrazole-2-oxides is due to their higher densities (2.216 to 2.398 g/cm^3). The performances of aminonitropyrazoles-2-oxides (D 9.38 to 10.85 km/s and P 46.50 to 54.15 GPa) are higher. ADNPO-5 and DADNPO-2 have shown higher performance among aminonitropyrazoles-2-oxides. DADNPO-2 and DADNPO-1 have highest and lowest performance respectively. The performances of ATNPO-1, ATNPO-2, ATNPO-3 and ATNPO-4 are higher (D 10.60 km/s and P 56.60 GPa) compared with dinitro-pyrazole-2-oxides, CL-20 and ONC.

Table 2.3.3 Explosive properties of nitropyrazoles.

HEM	M F	Mw (g mol^{-1})	OB (%)	ρ (g cm^{-3})	Q (kcal g^{-1})	D (km s^{-1})	P (GPa)	$-Q_{NO2}$ (e)	V_{mid}	E_{ES} (J)
NP-1	$C_3H_3N_3O_2$	113	-77.88	1.578	0.94	6.80	18.90	0.280	1.616	7.564
NP-2	$C_3H_3N_3O_2$	113	-77.88	1.542	0.82	6.90	19.18	0.523	1.156	8.342
NP-3	$C_3H_3N_3O_2$	113	-77.88	1.587	0.90	6.54	17.56	0.643	2.108	9.624
NP-4	$C_3H_3N_3O_2$	113	-77.88	1.545	0.87	6.40	16.53	0.541	1.333	9.117
DNP-1	$C_3H_2N_4O_4$	158	-30.38	1.80	0.98	8.34	30.82	0.636	1.603	10.088
DNP-2	$C_3H_2N_4O_4$	158	-30.38	1.82	0.95	8.33	30.98	0.509	1.046	9.460
DNP-3	$C_3H_2N_4O_4$	158	-30.38	1.77	1.00	8.25	29.92	0.566	1.617	10.993
DNP-4	$C_3H_2N_4O_4$	158	-30.38	1.77	1.08	8.34	31.24	0.256	1.731	6.836
DNP-5	$C_3H_2N_4O_4$	158	-30.38	1.77	1.07	8.41	31.07	0.275	1.480	7.031
DNP-6	$C_3H_2N_4O_4$	158	-30.38	1.77	1.05	8.36	31.10	0.130	1.660	5.525
DNPO-1	$C_3H_2N_4O_5$	174	-18.40	2.272	1.34	10.42	54.76	0.596	1.401	10.004
DNPO-2	$C_3H_2N_4O_5$	174	-18.40	2.245	1.30	10.24	52.54	0.491	0.925	9.356
DNPO-3	$C_3H_2N_4O_5$	174	-18.40	2.273	1.37	10.37	53.60	0.571	1.547	10.406
DNPO-4	$C_3H_2N_4O_5$	174	-18.40	2.216	1.47	10.45	54.41	0.218	2.001	6.514
DNPO-5	$C_3H_2N_4O_5$	174	-18.40	2.237	1.44	10.47	54.92	0.306	1.634	7.488
DNPO-6	$C_3H_2N_4O_5$	174	-18.40	2.200	1.46	10.38	53.44	0.003	1.337	4.394
TNP-1	$C_3HN_5O_6$	203	+3.92	2.002	1.51	9.40	41.60	0.531	1.686	10.146
TNP-2	$C_3HN_5O_6$	203	+3.92	1.887	1.60	9.25	39.40	0.047	1.506	5.267
TNP-3	$C_3HN_5O_6$	203	+3.92	1.922	1.62	9.27	39.64	0.176	0.548	6.410
TNP-4	$C_3HN_5O_6$	203	+3.92	1.918	1.60	9.22	39.13	0.222	0.621	6.947
TNP-5	$C_3N_6O_8$	248	+12.87	2.062	1.25	9.24	41.27	0.178	0.561	6.385
TNPO-1	$C_3HN_5O_7$	219	+10.96	2.398	1.56	10.75	59.84	0.533	1.865	10.602
TNPO-2	$C_3HN_5O_7$	219	+10.96	2.351	1.65	10.70	59.87	0.085	1.415	5.848
TNPO-3	$C_3HN_5O_7$	219	+10.96	2.355	1.67	10.77	59.60	0.060	1.279	5.576
TNPO-4	$C_3HN_5O_7$	219	+10.96	2.326	1.66	10.67	58.10	0.273	1.717	7.564
TNPO-5	$C_3N_6O_9$	264	+18.18	2.498	1.15	10.27	55.74	0.081	0.906	11.570

continued…

HEM	M F	Mw (g mol^{-1})	OB (%)	ρ (g cm^{-3})	Q (kcal g^{-1})	D (km s^{-1})	P (GPa)	$-Q_{NO2}$ (e)	V_{mid}	E_{ES} (J)
ADNP-1	$C_3H_3N_5O_4$	173	-32.40	1.808	0.78	7.82	27.23	0.647	1.476	9.705
ADNP-2	$C_3H_3N_5O_4$	173	-32.40	1.787	0.80	7.82	27.17	0.530	0.693	9.165
ADNP-3	$C_3H_3N_5O_4$	173	-32.40	1.816	0.85	8.02	28.74	0.707	1.056	10.953
ADNP-4	$C_3H_3N_5O_4$	173	-32.40	1.807	0.85	8.00	27.42	0.587	1.363	9.784
ADNP-5	$C_3H_3N_5O_4$	173	-32.40	1.798	0.88	7.92	27.56	0.352	1.523	7.247
ADNP-6	$C_3H_3N_5O_4$	173	-32.40	1.797	0.80	7.81	27.04	0.245	1.503	5.972
ADNP-7	$C_3H_3N_5O_4$	173	-32.40	1.806	0.81	8.00	28.57	0.640	1.425	10.031
ADNP-8	$C_3H_3N_5O_4$	173	-32.40	1.769	0.83	7.81	26.78	0.472	1.431	8.510
ADNP-9	$C_3H_3N_5O_4$	173	-32.40	1.766	0.80	7.75	26.37	0.171	1.262	5.626
ADNP-10	$C_3H_3N_5O_4$	173	-32.40	1.797	0.80	7.80	27.02	0564	0.502	9.157
ADNP-11	$C_3H_3N_5O_4$	173	-32.40	1.749	0.88	7.90	27.10	0.355	1.693	6.992
ADNP-12	$C_3H_3N_5O_4$	173	-32.40	1.798	0.83	7.91	27.76	0.317	1.853	6.780
ADNPO-1	$C_3H_3N_5O_5$	189	-21.16	2.176	1.30	10.20	51.33	0.588	1.452	9.422
ADNPO-2	$C_3H_3N_5O_5$	189	-21.16	2.201	1.28	10.24	52.00	0.500	0.958	8.891
ADNPO-3	$C_3H_3N_5O_5$	189	-21.16	2.157	1.30	10.15	50.50	0.586	1.195	9.970
ADNPO-4	$C_3H_3N_5O_5$	189	-21.16	2.200	1.14	9.94	49.00	0.592	1.340	10.078
ADNPO-5	$C_3H_3N_5O_5$	189	-21.16	2.210	1.25	10.21	51.80	0.323	1.095	6.551
ADNPO-6	$C_3H_3N_5O_5$	189	-21.16	2.180	1.28	10.16	50.96	0.010	1.190	3.960
ADNPO-7	$C_3H_3N_5O_5$	189	-21.16	2.240	1.11	10.00	50.05	0.628	1.530	10.005
ADNPO-8	$C_3H_3N_5O_5$	189	-21.16	2.209	1.30	10.31	52.83	0.282	1.320	6.622
ADNPO-9	$C_3H_3N_5O_5$	189	-21.16	2.190	1.26	10.86	51.53	0.046	0.902	3.965
ADNPO-10	$C_3H_3N_5O_5$	189	-21.16	2.230	1.16	10.08	50.75	0.601	1.286	9.355
ADNPO-11	$C_3H_3N_5O_5$	189	-21.16	2.162	1.23	10.00	49.15	0.295	0.802	6.576
ADNPO-12	$C_3H_3N_5O_5$	189	-21.16	2.101	1.30	9.93	47.75	0.241	1.307	6.133
DADNPO-1	$C_3H_5N_6O_5$	204	-34.36	2.150	1.10	9.80	46.85	0.060	0.860	3.942
DADNPO-2	$C_3H_5N_6O_5$	204	-34.36	2.320	1.06	10.31	54.16	0.220	0.934	5.505

continued..

HEM	M F	Mw (g mol^{-1})	OB (%)	ρ (g cm^{-3})	Q (kcal g^{-1})	D (km s^{-1})	P (GPa)	$-Q_{NO2}$ (e)	V_{mid}	E_{ES} (J)
DADNPO-3	$C_3H_5N_6O_5$	204	-34.36	2.094	1.18	9.83	46.72	0.204	1.098	5.722
DADNPO-4	$C_3H_5N_6O_5$	204	-34.36	2.181	1.13	10.00	49.32	0.624	1.106	10.140
DADNPO-5	$C_3H_5N_6O_5$	204	-34.36	2.200	1.11	10.01	49.67	0.654	1.590	10.105
DADNPO-6	$C_3H_5N_6O_5$	204	-34.36	2.152	1.12	9.87	47.70	0.616	1.330	9.370
ATNP-1	$C_3H_2N_6O_6$	218	-7.34	1.934	1.47	9.31	40.13	0.560	1.602	9.906
ATNP-2	$C_3H_2N_6O_6$	218	-7.34	1.918	1.43	9.20	38.80	0.261	1.705	6.706
ATNP-3	$C_3H_2N_6O_6$	218	-7.34	1.905	1.38	9.02	37.15	0.093	1.457	5.150
ATNP-4	$C_3H_2N_6O_6$	218	-7.34	1.900	1.38	9.02	34.15	0.340	1.726	7.281
ATNPO-1	$C_3H_2N_6O_7$	234	+10.26	2.340	1.71	10.98	61.74	0.546	1.826	10.16
ATNPO-2	$C_3H_2N_6O_7$	234	+10.26	2.311	1.68	10.77	58.98	0.081	1.277	5.480
ATNPO-3	$C_3H_2N_6O_7$	234	+10.26	2.273	1.633	10.56	56.33	0.017	0.745	4.831
ATNPO-4	$C_3H_2N_6O_7$	234	+10.26	2.268	1.66	10.60	56.63	0.288	2.296	7.000
MTNP-1	$C_4H_3N_5O_6$	217	-25.80	1.840	1.12	8.68	33.90	0.543	1.513	9.606
MTNP-2	$C_4H_3N_5O_6$	217	-25.80	1.811	1.18	8.70	33.71	0.244	1.833	6.571
MTNP-3	$C_4H_3N_5O_6$	217	-25.80	1.797	1.18	8.66	33.22	0.091	1.636	6.710
MTNP-4	$C_4H_3N_5O_6$	217	-25.80	1.858	1.16	8.83	35.23	0.266	1.606	5.148
MTNPO-1	$C_4H_3N_5O_7$	233	-17.16	2.211	1.37	10.26	52.31	0.537	1.733	10.00
MTNPO-2	$C_4H_3N_5O_7$	233	-17.16	2.200	1.42	10.30	52.26	0.026	1.134	4.630
MTNPO-3	$C_4H_3N_5O_7$	233	-17.16	2.200	1.42	10.24	52.11	0.063	1.353	5.058
MTNPO-4	$C_4H_3N_5O_7$	233	-17.16	2.230	1.38	10.32	52.36	0.190	1.451	6.161

Aminotrinitropyrazoles (ATNP-1, ATNP-2, ATNP-3 and ATNP-4) have shown superior performance (D 9.02 to 9.30 km/s and P 37.0 to 40.13 GPa respectively) compared with HMX and methyltrinitropyrazoles (MTNP-1, MTNP-2, MTNP-3 and MTNP-4). Overall, the higher performances of nitropyrazole-2-oxides are presumably due to their positive heats of formation, better oxygen balance and higher densities. The performance values are related to the number and the relative positions of substituent groups and the strength of trigger bonds.

2.3.5 Impact Sensitivity Correlations

The impact sensitivity ($h_{50\%}$) is usually measured by the height, from where a given weight falling upon the explosive gives 50% probability of initiating detonation. Depluech and Cherville[40,41] related the shock and thermal sensitivities to the molecular electronic structure and the properties of trigger C-NO_2, N-NO_2 and O-NO_2 bonds such as electrostatic potential, length and strength. Xiao[42] suggested that stronger are these trigger bonds, more stable is the molecule. Kamlet and Adolph[43] found the linear relationship between the impact sensitivity and the oxygen balance. Mullay[44] gave statistically significant relationship between the impact sensitivity and molecular electronegativity of nitro compounds. Politzer and coworkers[45,46] related the bond energies, electrostatic potential maxima and the impact sensitivity. They also have related the impact sensitivity to the degree of positive charge buildup over the covalent bonds within the molecular frame work.[47-50] Pospìšil[51] correlated the crystal volume to the impact sensitivity. Zeman[52,53] related the detonation and thermal decomposition, ^{13}C NMR and ^{15}N NMR chemical shifts to the impact sensitivity. Zhang et al[20-22] correlated the electronic structure to the impact sensitivity by NO_2 group charge analysis.

We have predicted the impact sensitivity of nitropyrazoles from the electronic structures by the Mulliken atomic charge analysis of NO_2 group. As for the NO_2 groups in nitro compounds, they are electron-withdrawing. Higher negative charge the nitro group possesses, lower the electron withdrawing ability and therefore the more stable is the compound. In explosives, R-NO_2 bonds (R = C, N, O) are usually weakest and their breaking is often the initial step in the decomposition or detonation of explosive molecule. The nitro group charge ($-Q_{NO_2}$) is calculated by the sum of the net Mulliken atomic charges on the nitrogen and oxygen atoms and of the nitro group.

$$-Q_{NO_2} = Q_N + Q_{O1} + Q_{O2} \tag{25}$$

$$V_{mid} = \frac{Q_C}{0.5\ R} + \frac{Q_N}{0.5\ R} \tag{26}$$

where R is trigger length, Q_C, Q_N and Q_{O1}, Q_{O2} and are the Mulliken charges on carbon, nitrogen and oxygen atoms respectively. The higher is $-Q_{NO_2}$, higher is the impact insensitivity. The

molecular structures of nitropyrazoles with trigger bond encircled; the list of the values beside each structure shows the trigger lengths, nitro group charges and midpoint electrostatic potentials are presented in Figure 2.3.1. The computed nitro group charge ($-Q_{NO2}$), midpoint electrostatic potential (V_{mid}) along with their explosive properties of nitropyrazoles are presented in Table 2.3.3.

The calculated $-Q_{NO2}$ values of methyltrinitropyrazoles are varying from 0.543 to 0.200 e whereas the $-Q_{NO2}$ values of aminotrinitropyrazoles are varying from 0.560 to 0.180 e. As per the predicted by Zhang et al[20-22], calculated $-Q_{NO2}$ are found to be higher with respect to RDX (0.105 e), HMX (0.112 e), TNAZ (0.114 e), CL-20 (0.081 e), ONC (0.146 e) and thus appear to be more insensitive. The $-Q_{NO2}$ values of MTNP-1 (0.560 e) and MTNP-3 (0.543 e) are superior to TNT (0.249 e), TATB (0.416 e), FOX-7 (0.365 e), LLM-105 (0.264 e) and NTO (0.264 e). The presence of NH_2 group and N-oxide noticeably decreases the $-Q_{NO2}$ values of model molecules. The C3-NO_2 bond in DNP-1, DNP-2, DNPO-1 and DNPO-2 is the site of impact/or shock initiation with their nitro group charges 0.633, 0.509, 0.596 and 0.491 e respectively. The C5-NO_2 bond in DNP-3 and DNPO-3 is the trigger site with their nitro group charges 0.566 and 0.571 e respectively. TNP-1 is highly insensitive ($-Q_{NO2}$ 0.531 e) while TNP-2 is less insensitive ($-Q_{NO2}$ 0.047 e). Similarly, TNPO-1 is highly insensitive ($-Q_{NO2}$ 0.533 e) compared with TNPO-2 (0.085 e) and TNPO-3 (0.060 e). TNP-5 is more insensitive compared with TNPO-5 with their $-Q_{NO2}$ values 0.178 and 0.080 e respectively. The $-Q_{NO2}$ values of DNP-1 (0.636 e), DNP-2 (0.509 e), DNP-3 (0.560 e), DNPO-1 (0.596 e), DNPO-2 (0.491 e), DNPO-3 (0.571 e), TNP-1 (0.53 e) and TNPO-1 (0.533 e) are far higher with respect to TNT, FOX-7, LLM-105, NTO and DNPP. The $-Q_{NO2}$ values of DNP-4 (0.256 e), DNP-5 (0.275 e), DNPO-4 (0.218 e), DNPO-5 (0.306 e), TNP-3 (0.176 e), TNP-4 (0.222 e), TNP-5 (0.178 e) and TNPO-4 (0.273 e) are fairly higher. DNPO-6 (0.003 e) and TNP-2 (0.047 e) are highly sensitive compared with CL-20. TNPO-2 (0.085 e) and TNPO-5 (0.080 e) have shown similar sensitivity like as CL-20. The N-NO_2 bond is trigger site in DNP-4, DNP-5, DNP-6, TNP-2, TNP-3, TNP-4, TNP-5 and TNPO-5 with their $-Q_{NO2}$ values 0.256, 0.275, 0.130, 0.047, 0.176, 0.222, 0.178 and 0.080 e respectively.

The calculated $-Q_{NO2}$ values for aminonitropyrazole-2-oxides have been varying from 0.500 to 0.830 e. The C3-NO_2 bond in ADNPO-1, ADNPO-2, ADNPO-7, ADNPO-10,

DADNPO-6, DADNPO-5 and ATNPO-1 is the site of shock initiation with their $-Q_{NO_2}$ values 0.588, 0.500, 0.628, 0.601, 0.654, 0.616 and 0.546 e respectively. The C5-NO_2 bond in ADNPO-3, ADNPO-4 and DADNPO-4 is the trigger site with their nitro group charges 0.586, 0.592 and 0.624 e respectively and are far higher with respect to TNT, FOX-7, RDX, HMX, TNAZ, LLM-105, NTO, DNPP, CL-20, ONC. The impact sensitivities of ADNPO-6, ADNPO-9, DADNPO-1, ATNPO-2 and ATNPO-2 are lower compared with CL-20 and ONC. The similar trend has also been observed for the midpoint electrostatic potentials (V_{mid}) of model molecules. ATNPO-1 has the higher V_{mid} value (1.826). ADNPO-11, DADNPO-11 and ATNPO-3 have lower V_{mid} values 0.810, 0.860 and 0.745 respectively. The substitution of hydrogen at 1-position of TNP-1 by NH_2 or CH_3 group shows better impact sensitivity. The impact sensitivity can also be used to show the stability of model compounds and the stability here is attributed to the presence of π-excessive aromatic heterocyclic ring, delocalization of π-electrons and presence of intramolecular N-H···O, C…O and N···O interactions.

2.3.6 Electric Spark Sensitivity Correlations

The electric spark sensitivity is the degree of sensitivity of an explosive to the electric discharge. Zeman[52,53] have related electric spark sensitivity (E_{ES}) to the squares of detonation velocity and reciprocal temperature, the Piloyan activation energy and heats of fusion. Skinner et al[54] gave the relationship between the electric spark sensitivity and the reciprocal temperature. Wang et al[55,56] gave suitable correlations between the electric spark sensitivity and detonation performance of nitramines and nitroarenes. We have calculated the electric spark sensitivity of nitropyrazoles from the lowest unoccupied molecular orbital and nitro group charge.[23]

$$E_{ES}\,(J) = (-1)^{n1} 10.16\, Q_{NO_2} - 1.05_{\,n1\,n2}\, E_{LUMO} - 0.20 \qquad (27)$$

where, n1 is the number of aromatic rings, n2 is the number of substituted groups attached to the aromatic ring like alkyl (-R) or amino (-NH_2) groups, Q_{NO_2} is the minimum Milliken charge of NO_2 group and E_{LUMO} is the lowest unoccupied molecular orbital energy in eV. The electric spark sensitivities along with other explosive properties of the designed compounds are presented in Table 2.3.3. The calculated electric spark sensitivity values of C-nitro compounds are higher (8.342 to 10.602 J) compared with TNT (6.94 J). The spark sensitivities of DNP-4

(6.836 J), DNP-6 (5.525 J), DNPO-4 (6.514 J), DNPO-6 (6.394 J), TNP-2 (5.207 J), TNP-3 (6.41 J), TNP-5 (6.38 J), TNPO-2 (5.85 J) and TNPO-3 (5.57 J) are lower compared with TNT. The calculated electric spark sensitivity values of C-nitropyrazoles are higher (8.890 to 10.16 J). However, the spark sensitivities of ADNPO-5, ADNPO-12, ADNPO-8, ADNPO-6, ADNPO-11, ADNPO-9, DADNPO-6, DADNPO-2, DADNPO-1, ATNP-2, ATNPO-3 and ATNPO-4 are lower (3.94 to 6.55 J). The discrepancies in the electric spark sensitivities among the isomers are caused by the relative positions of NO_2 and CH_3 or NH_2 groups in the pyrazole ring.

2.3.7 Stability Correlations

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies play a prominent role in governing the chemical reactions of the compounds.[13,24] It has been revealed in several studies that the band gap $\Delta E_{(LUMO-HOMO)}$ between the LUMO and HOMO is an important stability index of the molecules.[25,26,57] A large band gap implies high stability and small band gap implies low stability in turn high stability indicates low chemical reactivity and low stability indicates high reactivity i.e., smaller the band gap between HOMO and LUMO, easier the electron transition and lesser the stability of the explosive will be. The compounds having large differences in frontier orbital energies that is if $\varepsilon_{HOMO} - \varepsilon_{LUMO} >> 0$, then very little electron transfer occurs. If the respective orbital energies are quite similar that is if $\varepsilon_{HOMO} - \varepsilon_{LUMO} \approx 0$, strong electron transfer occurs. The frontier molecular orbital energies and their gaps are shown in Table 2.3.1.

The band gap values of dinitropyrazoles are varying from 0.16993 to 0.19414 a.u. DNPO-1 (0.1504 a.u.) and TNPO-1 (0.1300 a.u.) are more stable while DNPO-3 (0.1434 a.u.) and TNPO-3 (0.1114 a.u.) are lesser stable. The substitution of acidic hydrogen of TNP-1 by NO_2 group increased the band gap from 0.17348 to 0.17431 a.u. TNP-5 is more stable than TNPO-5 with the band gap values 0.17431 and 0.13028 a.u. respectively. As for aminonitro pyrazoles, the band gap of ADNPO-6 is the largest (0.1641 a.u.) and ADNPO-5 is the smallest (0.0920 a.u) indicating the former is more stable than the later. DADNPO-3 has higher band gap (0.1303 a.u.) compared with DADNPO-6. ADNPO-5, ADNPO-6 and DADNPO-3 are lesser stable. The most and least stable aminotrinitropyrazole-2-oxides are ATNPO-1 (0.1400 a.u.) and ATNPO-2 (0.0900 a.u.) respectively. Amino derivatives have higher band gap values (>0.1320

a.u.). The energies of the frontier orbitals are decreased by increasing the NO_2 groups from one to three in the pyrazole ring. This is a general trend of electron withdrawing substituent groups lower the LUMO and HOMO energy levels.[13,57] Nevertheless, the discrepancies in the band gap values among the isomers are caused by the relative positions of NO_2 and CH_3 or NH_2 groups in the pyrazole ring. Larger the length of trigger bonds of molecule is, easier is the dissociation or breakdown, thus the molecule becomes lesser stable. The R-NO_2 are the trigger bonds in these molecules and resonance in the pyrazole moiety strengthens these bonds thereby the molecules gets stabilized. Also, higher is the total energy of the molecule, lesser is the stability.

2.4 Conclusions

We have explored the geometry, band gap, heat of explosion, density, detonation properties of nitropyrazoles using density functional theory at the B3LYP/aug-cc-pVDZ level. The non-planarity or co-planarity of a molecule is due to the repulsion between the neighboring nitro groups, which rotate the oxygen atoms away from the molecular plane. The optimized structures were used to determine the densities (ρ) of nitropyrazoles using Materials Studio 4.1 package with CVFF force field and Ewald summation method. The higher densities of nitropyrazole-2-oxides are probably due to the intramolecular hydrogen bonds as well as the layered structures in the crystal lattice. Kamlet-Jacob semi-empirical equations were used to calculate the performance properties. The detonation energies obtained are for the gas phase compounds and in the reality they should be for the solid phase which would diminish the magnitude of Q values. The model compounds satisfy the criteria as the high energy materials (HEMs). It has been found that NO_2, NH_2 group(s) and N-oxide bond increases heat of explosion, density and the detonation properties tremendously. The higher performances of polynitropyrazole-2-oxides are due to their higher densities. The substitution of the labile hydrogen at 1-position of TNP-1 by NH_2 or CH_3 group shows better impact sensitivity or stability. The discrepancies in sensitivity/or stability, heat of detonation, density and detonation properties are presumably due to the relative positions and the orientations of CH_3, NH_2 and NO_2 groups in the pyrazole ring.

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57. Koch, E. -C. *Prop., Explos., Pyrotech.* **2005**, *30*, 5.

Chapter 3

3.1 Introduction

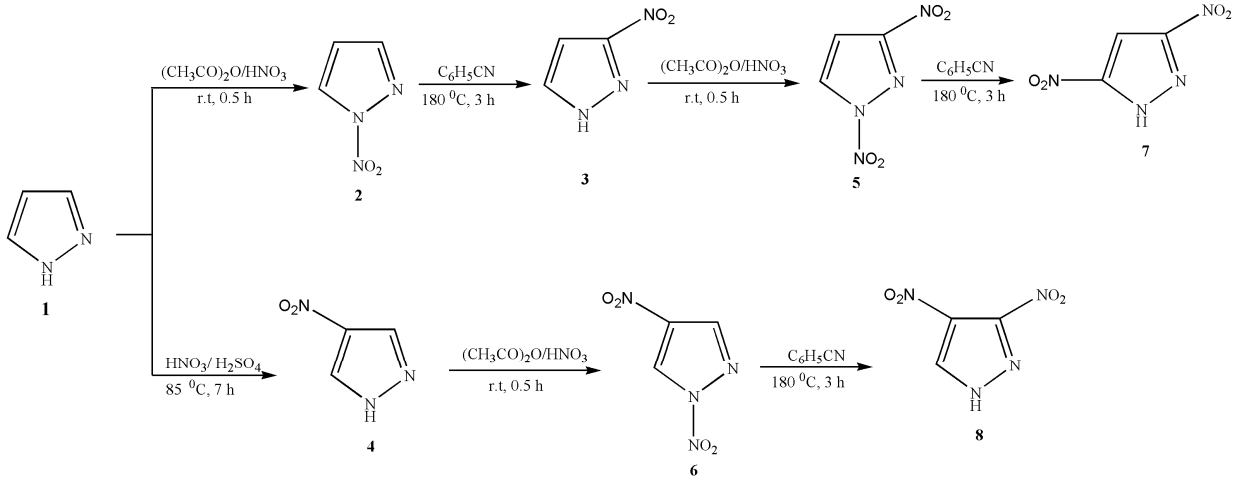
Nitropyrazoles have diverse biological activity, are useful intermediates and are of potential interest as energetic materials and blowing agents.[1-4] Approaches to the synthesis of nitropyrazoles comprise: (i) direct nitration, (ii) ring construction and (iii) functional group transformation. However, published methods usually suffer from low yields, starting material availability, harsh conditions, and/or difficulty to separate isomer formation.[5-10] This prompted us for more general and milder routes. The iodination and nitrodeiodination (ipso nitration) methodologies have been used to prepare nitropyrazoles in higher yields starting from pyrazole. I_2-potassium iodide in sodium hydroxide pyrazole gave an unstable N-iodopyrazole in low yields.[11] Iodination reagents such as ICl-hydrochloric acid,[11] I_2-silver sulfate,[12] I_2-ammonium hydroxide,[11] I_2-iodic acid,[13] I_2-iodobenzene diacetate,[14] iodosuccinamide in acetone,[15] I_2-ceric ammonium nitrate[16,17] and ICl-silver sulfate[18,19] have been used for the iodination of pyrazoles. Kim et al[20] synthesized 4-iodopyrazoles using I_2-hydrogen peroxide, a facile and green iodinating reagent.

It is known that substituting hydrogen at 1-position of pyrazole or C-substituted pyrazoles decreases the melting points.[1] 1-Methylpyrazoles can be synthesized from 1,3-dicarbonyls condensing with the pertinent substituted-hydrazines, or via methylation of pyrazole using an excess of methyl halides,[21] dimethyl sulfate[22] and dimethyl carbonate.[23-25] The methylation of pyrazole using stoichiometric amounts of bases or even under phase transfer conditions, microwave irradiations in the absence or presence of bases have also been known. Dimethyl carbonate (DMC) is a versatile compound that represents an attractive eco-friendly alternative to both methyl halides and dimethyl sulfate for methylation. DMC allows unprecedented toward mono-C- and mono-N-methylation reactions. Methylating pyrazole with DMC prior to electrophilic or nucleophilic substitution has been found to be convenient route. The present chapter describes the iodination of pyrazole and 1-methylpyrazole into 4-iodopyrazole, 3,4-di-iodopyrazole, 3,4,5-triiodopyrazole, 1-methyl-4-iodopyrazole, 1-methyl-3,4-diiodopyrazole and 1-methyl-3,4,5-triiodopyrazole in good yields using I_2-ammonium hydroxide and I_2-iodic acid. Iodopyrazoles were nitrodeiodinated into nitropyrazoles in higher yields using fuming nitric acid and nitric acid-sulfuric acid mixture.

3.2.1 Direct Nitration of Pyrazole and 1-Methylpyrazole

The direct nitration of pyrazole using nitric acid or mixture of nitric acid and sulfuric acid leads to substitution at 4-position.[1] Huttel and Buchele[26] synthesized N-nitropyrazole and its substituted derivatives. They also described the rearrangement of N-nitropyrazoles to the 4-nitro pyrazole derivatives in sulfuric acid solution in cold. Janssen et al[5-7] have synthesized C-nitro pyrazoles by rearrangement of N-nitropyrazoles in anisole, n-decane, mesitylene, nitrobenzene and benzonitrile at moderate temperatures (120-190 °C) for 3-7 h. 3,4-Dinitropyrazoles have been synthesized in quantitative yield from 3-nitropyrazoles using Morgan and Ackerman nitration methodology.[6,27] Katrizky et al[28] improved the yield of 3,4-dinitropyrazole using nitric acid-trifluoroacetic anhydride at room temperature for 12 h. Pyrazole has been used as the starting material to synthesize nitropyrazoles. We have obtained 3-nitropyrazole (**3**) in 98% yield heating 10% solution of N-nitropyrazole (**2**) in benzonitrile at 180 °C for 3 h (Scheme 10). The isomerization obeys first-order kinetics perfectly and no divergent reaction paths were observed when the thermolyses were performed in the presence of phenol, quinoline or toluene, which may act as catalyst or scavenger of intermediates.[5]

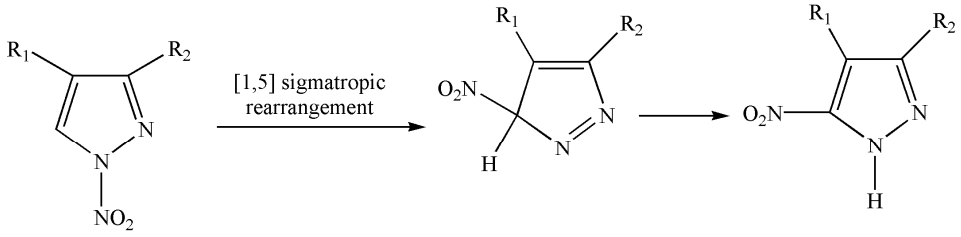
Scheme 10



The formation of small quantities of N-acetyl compounds as by-products on N-nitration have also been observed in some cases. Usually, N-nitropyrazoles could be purified by direct

crystallization or by very mild acid hydrolysis of the N-acetyl derivatives prior to crystallization. For the mechanism of the rearrangement of N-nitropyrazoles, a two-step process has been proposed, involving an unprecedented [1,5]sigmatropic shift of the nitro group and fast rearomatization of the intermediately formed 3H-pyrazole (Scheme 12). Nevertheless, a sigmatropic process adequately accounts for NO_2 migration to 3(5)-position. The thermal rearrangement of N-nitropyrazoles unsubstituted at the 3(5)-position has been proved to be a convenient method for the synthesis of 3(5)-nitropyrazoles.

Scheme 12



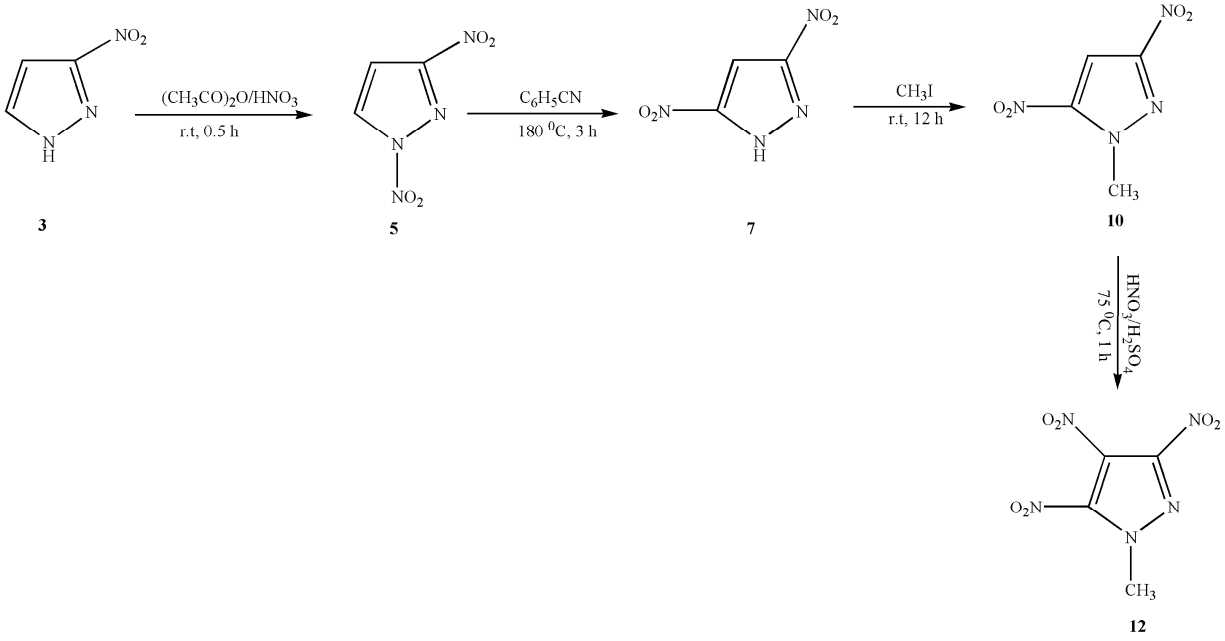
2, **5**, **6** **3**, **7**, **8**

4-Nitropyrazole (**4**) in 82% yield has been prepared using nitric acid-sulfuric acid mixture at 85 °C for 7 h. 1,3-Dinitropyrazole (**5**) and 1,4-dinitropyrazole (**6**) have been obtained in high yields from C-nitropyrazoles (**3** and **4**) with a freshly prepared acetyl nitrate. N-Nitropyrazoles as in general are readily characterized through tlc and IR spectroscopy. In addition to the absence of a N-H absorption band, the NO_2 stretching frequencies for a N-nitro groups are found at lower wave numbers (1295 to 1275 cm^{-1}) for the symmetric stretching vibration and a higher wave number (1625 to 1605 cm^{-1}) for asymmetric vibration. However, the NO_2 stretching frequencies for a C-nitro group are found at lower wave numbers (1385 to 1360 cm^{-1}) for the symmetric stretching vibration and a higher wave number (1565 to 1545 cm^{-}) for asymmetric vibration. For C-nitro groups in nitropyrazoles we found ν_{sym} 1375 to 1330 cm^{-1} and ν_{asym} 1545 to 1590 cm^{-1}.

We have obtained 3,5-dinitropyrazole (**7**) in 88% yield by heating 10% solution of 1,3-di nitropyrazole (**2**) in benzonitrile at 180 °C for 3 h. Thermolysis of 1,4-dinitropyrazole (**6**) gave 3,4-dinitropyrazole (**8**) in low yield (15%) presumably due to the denitration of N-nitropyrazole at higher temperature into 4-nitropyrazole (**4**), which is known to be the stable nitropyrazole. 3,4-Dinitropyrazole (**8**) in 92% yield has been synthesized from 3-nitropyrazole (**3**) under

Morgan and Ackermann nitration conditions.[27] The efforts were failed to obtain 3,4-dinitro-pyrazole (**8**) from 4-nitropyrazole (**4**) under similar conditions rather recovered starting compound in quantitative yield. It is known that substituting the acidic hydrogen of C-nitro pyrazoles (**7**,**8**) by CH_3 group decreases the melting point. Therefore, the first step in the preparation of 1-methyl-3,4-dinitropyrazole (**9**), 1-methyl-3,5-dinitropyrazole (**10**) and 1-methyl-3,4,5-trinitropyrazole (**12**) is to substitute methyl group at the 1-position of pyrazole or polynitropyrazole with methyl iodide, dimethyl sulfate or dimethyl carbonate. Herve et al[29] have synthesized 1-methyl-3,4,5-trinitropyrazole (**12**) from pyrazole via sodium trinitropyrazolate. They have obtained 3,4,5-trinitropyrazole (TNP) by vicarious nucleophilic substitution of 3,5-dinitropyrazole (**7**) followed by reduction of 4-amino-3,5-dinitropyrazole (LLM-116). We have obtained trinitropyrazole (**12**) by further nitration of 1-methyl-3,5-dinitropyrazole (**10**) starting from 3-nitropyrazole (Scheme 13).

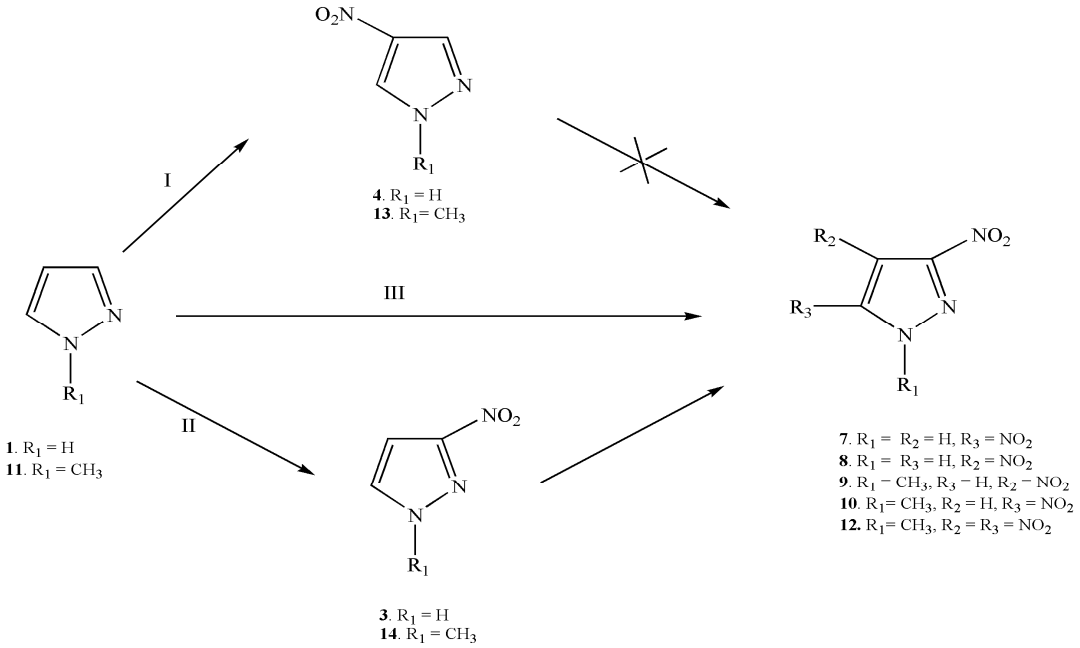
Scheme 13



Grimmet et al[30] obtained a mixture of 1-methyl-3,4-dinitropyrazole (**9**) and 1-methyl-4-nitropyrazole (**13**) later being major compound by the nitration of 1-methylpyrazole (**11**) using 68% nitric acid-sulfuric acid mixture at 85 °C for 18 h (Scheme 14). We have synthesized 1-methylpyrazole (**11**) using DMC according to the literature procedure.[25] The direct nitration of compound (**11**) with fuming nitric acid-oleum at 110 °C gave 1-methyl-3,4,5-trinitropyrazole

(**12**) in low yield (route III). Attempts were failed to nitrate 1-methyl-3,4-dinitropyrazole (**9**) to 1-methyl-3,4,5-trinitropyrazole (**12**) irrespective of nitration mixtures and reaction conditions. 4-Nitropyrazole (**4**), 1,4-dinitropyrazole (**6**), 1-methyl-4-nitropyrazole (**13**) and 1-methyl 3,4-di nitropyrazole (**9**) are known to be highly stable and thus either decomposed, tarry products or starting compounds can recovered in quantitative yields on prolonged nitration or thermolysis.

Scheme 14



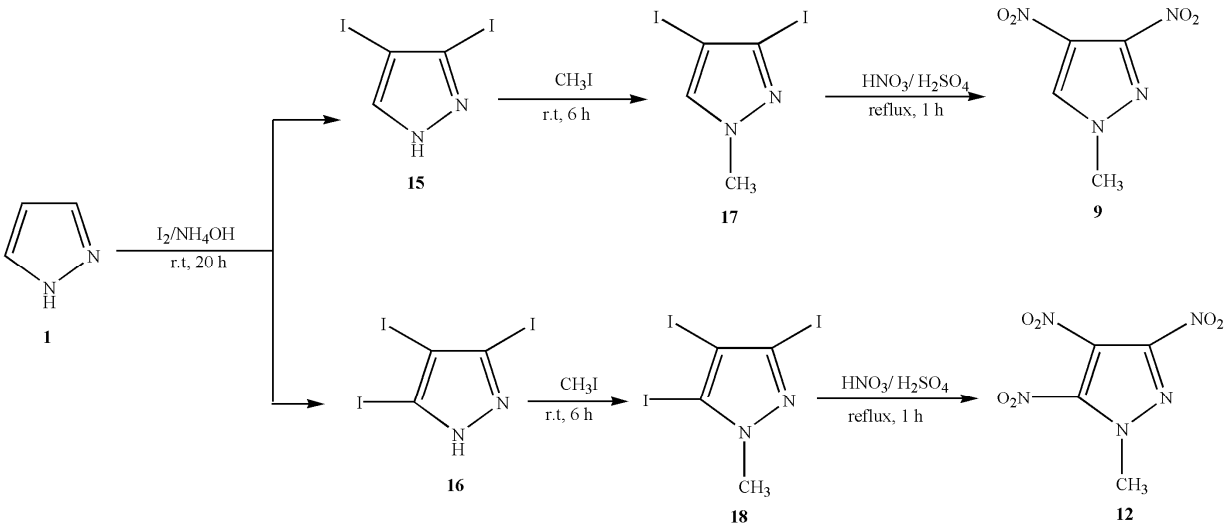
One of the decomposition reactions observed was the denitration of N-nitropyrazoles giving back the N-unsubstituted starting materials.[6] Such denitrations also occurred in case of the thermolysis of 1,3-dinitropyrazoles as observed from the presence of 10-15% of 3-nitropyrazole on work-up of the reaction mixture (route II). No trace of 3,4-dinitropyrazole (**8**) could be detected when 4-nitropyrazole was subjected to the same dinitration conditions of 3-nitro pyrazole (route I). Nevertheless, thermal rearrangement of N-nitropyrazoles offers a convenient method to synthesize 3-nitropyrazoles, which in turn may undergo electrophilic substitution preferably in the 4-position as observed for the nitration reaction.

3.2.2 Nitrodeiodination of Iodopyrazoles

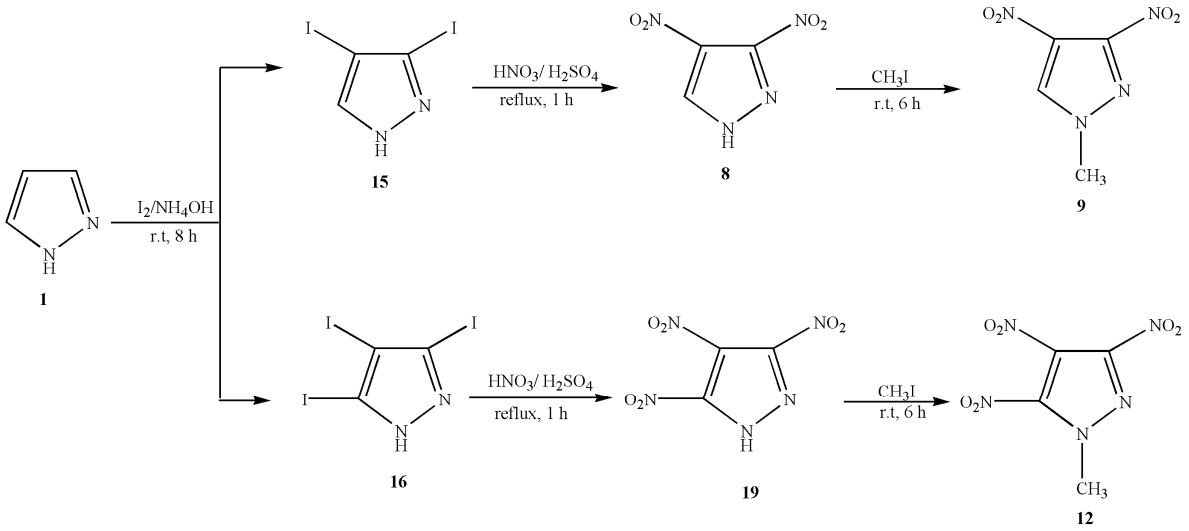
The available methods for the synthesis of C-nitropyrazoles have involved the rearrangement of N-nitropyrazoles at 145-190 °C for 3-10 h in anisole or benzonitrile.[6] N-Nitro

pyrazoles can be easily rearranged to 4-nitropyrazoles in H_2SO_4 solution at 0 °C. 4-Nitropyrazole is not preferred starting or intermediate compounds to synthesize C-polynitropyrazoles.[2] Normally, C-nitropyrazoles are formed quantitatively however, in some instances the denitration of N-nitropyrazoles decreases the overall yield of desired nitro compound. The limitations and drawbacks of conventional methods such as tedious work-up procedures, step-wise nitration, denitration of N-nitropyrazoles, oxidation ability of reagents, thermal rearrangements and safety problems can be avoided using iodopyrazoles.[1,2] Iodination and nitrodeiodination (ipso nitration) methodologies have been used to synthesize polynitropyrazoles in higher yields starting from pyrazole and 1-methylpyrazole. In this section we describe a convenient procedure for the preparation of iodopyrazoles by exhaustive iodination of the pyrazole ring with subsequent nitrolysis. 3,4-Diiodopyrazole (**15**) and 3,4,5-triiodopyrazole (**16**) were synthesized from pyrazole using I_2-25% ammonium hydroxide at room temperature for 20 h. 3,4-Diiodo- and 3,4,5-triiodopyrazoles were methylated with methyl iodide and also with dimethyl sulfate (DMS) in anhydrous DMF under N_2 atmosphere into 3,4-diiodo-1-methylpyrazole (**17**) and 3,4,5-triiodo-1-methylpyrazole (**18**) respectively in higher yields. These iodopyrazoles (**15**,**16**,**17**,**18**) were nitrodeiodinated by refluxing with fuming nitric acid at 100 °C for 1 h or nitric acid-sulfuric acid (30% SO_3) mixture at 85 °C for 1.5 h gave 3,4-dinitropyrazole (**8**) and 3,4,5-trinitropyrazole (**19**) respectively in good yields (Scheme 15 & 16).

Scheme 15

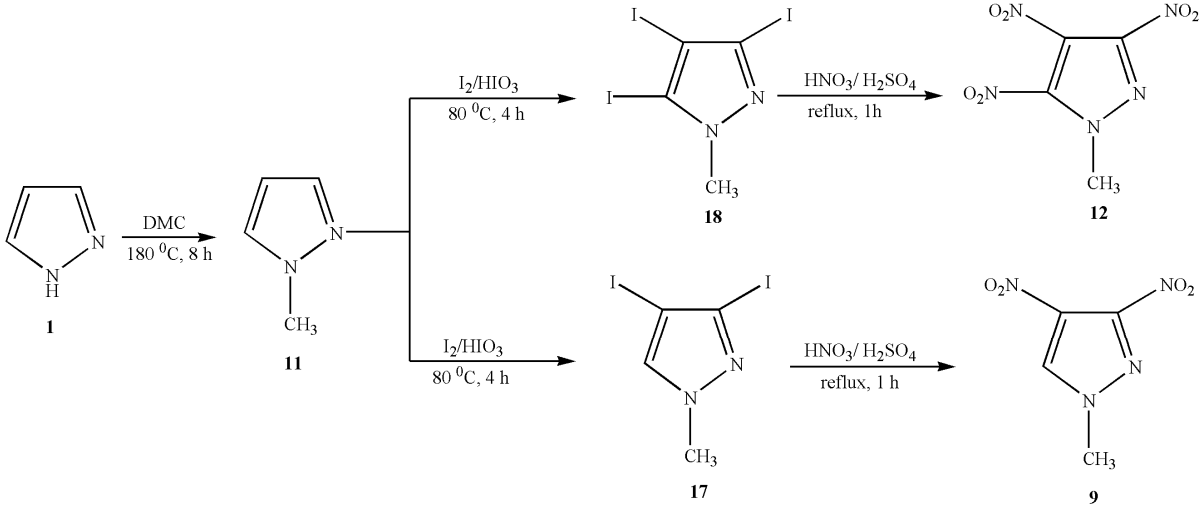


Scheme 16

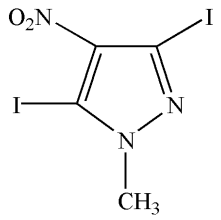


3,4-Dinitropyrazole (**8**) and 3,4,5-trinitropyrazole (**19**) were methylated both with methyl iodide and dimethyl sulfate under alkaline condition into 1-methyl-3,4-dinitropyrazole (**9**) and 1-methyl-3,4,5-trinitropyrazole (**12**) respectively. The oxidative iodination of 1-methylpyrazoles using I_2/HIO_3 is an efficient method to synthesize iodo derivatives containing electron-withdrawing substituents in the pyrazole ring.[13] However, our attempts to iodinate 4-nitro pyrazoles have been unsuccessful. 3,4,5-Triiodo-1-methylpyrazole (**18**) prepared from 1-methyl pyrazole (**11**) using I_2/HIO_3 (oxidative iodination) was refluxed with fuming nitric acid at 100 °C for 1 h or nitric acid-sulfuric acid (30% SO_3) mixture at 85 °C for 1.5 h gave 86% of 1-methyl-3,4,5-trinitropyrazole (**12**) (Scheme 17).

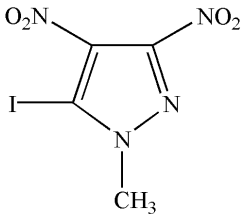
Scheme 17



3,4-Diiodo-1-methylpyrazole synthesized in two steps was refluxed with fuming nitric acid at 100 °C for 40 minutes or the mixture of fuming nitric acid and 98% sulfuric acid at 85 °C for 1 h gave 74% of 1-methyl-3,4-dinitropyrazole. 3,4,5-Triiodo-1-methylpyrazole gave 3,5-diiodo-1-methyl-4-nitropyrazole (**20**) and 5-iodo-1-methyl-3,4-dinitropyrazole (**21**) with nitric acid-sulfuric acid and the nature of nitro derivative being depends upon the concentration of nitric acid and reaction temperature.



20



21

In order to establish the generality of nitrodeiodination and its applicability to the synthesis of polynitropyrazoles we have nitrated 3,4-diiodopyrazole (**15**) 1-methyl-3,4-diiodo-pyrazole (**17**), 3,5-diiodo-1-methyl-4-nitropyrazole (**20**), 5-iodo-1-methyl-3,4-dinitropyrazole (**21**) and 1-methyl-4,5-diiodo-3-nitropyrazole (**22**). It has been demonstrated that even the vicinal iodine atom or nitro group(s) did not prevent ipso substitution. Surprisingly, tlc analysis of the reaction mixture after it had been heated 55-100 °C for 1-1.5 h showed the absence of starting material. The replacement of iodine atom proceeded smoothly in fuming nitric acid of nitric acid-sulfuric mixture at 55-100 °C in yields 75-88%. Methylating pyrazole with dimethyl carbonate (DMC) prior to oxidative iodination and nitrolysis have been found to be conventional route to synthesize 1-methyl-3,4-dinitropyrazole (**12**) and 1-methyl-3,4,5-trinitropyrazole (**12**). Polyiodopyrazoles are preferred starting or intermediate compounds to synthesize 3,4-dinitro pyrazole (**8**) and 3,4,5-trinitropyrazole (**19**) in higher yields.

3.2.3 Explosive Properties of Nitropyrazoles

3,4,5-Trinitropyrazole (**19**) is known to exhibit remarkable and unprecedented properties.[4,29,31] It is neither hygroscopic nor highly acidic in nature. It displays low sensitivity to external stimuli and outstanding thermal and chemical stability of any fully nitrated aromatic compounds. The exceptional stability/or low sensitivity of **19** is due to its low acidity (pKa 2.35).

Increasing the number of nitro groups on pyrazole ring increases the acidity. The presence of NO_2, NH_2 and CH_3 groups at 1-position of **19** have enhanced the chemical stability.[31] Moreover, the dinitro compounds (**8**,**9**) are completely deactivated by vicinal nitro groups thus hinders the substitution at 5-position of pyrazole ring. The explosive properties of dinitropyrazoles (**7**,**8**,**9**,**10**) and trinitropyrazoles (**12**,**19**) are summarized in Table 1.2.1 (Chapter 1). 1-Methyl-3,4,5-trinitro pyrazole (**12**) is under consideration as next generation melt cast explosive with its higher performance and lower sensitivity. It has m p 91.5 ^{0}C, oxygen balance -25.81%, density 1.786 g/cm^3, heat of explosion 1.12 kcal/g, detonation velocity 8.65 km/s, detonation pressure 33.65 GPa and impact sensitivity 78 cm.[29,31]

3.2.4 Thermal Decomposition of 1-Methyl-3,4,5-trinitropyrazole (12)

Thermal decomposition of trinitropyrazole (**12**) has been investigated using TG-DTA technique under nitrogen atmosphere. Several methods are known to calculate the kinetic parameters of solid state reactions based on the Arrhenius equation.[32-36] The model fitting approach needs thermal analysis measurement however it suffers from an inability to determine the reaction model uniquely. On the other hand, the isoconversional principle based model-free methods avoid the problems originated from the ambiguous evaluation of the reaction model. The isoconversional methods yield effective activation energy as a function of the extent of conversion and permit to draw reliable mechanistic conclusions. We have calculated the activation energy of synthesized compound **12** using Friedman's differential method[33] and Flynn-Wall-Ozawa integral method.[34] Thermal analysis measurements were carried out on a TA instruments Q600 SDT instrument. The sample (~1 mg) taken in alumina crucible and the reference were heated from 25 to 300 °C under nitrogen environment (flow rate of 100 cm^3/min) as the purge and protective gas. The reference was an empty alumina crucible. Non-isothermal TGA runs were conducted from 25 to 300 °C at heating rates 2.5, 5, 10 and 20 °C/min. Friedman's differential method and Flynn-Wall-Ozawa integral method were used for the kinetic analysis of the compound. Energy of activation was calculated from the peak values of exothermic decomposition peaks from the DTA thermogram. The rate constant for the solid sate decomposition was assumed to follow the Arrhenius rate law and the first stage exothermic decomposition reaction is used to calculate the kinetic parameters considering as a single step.

The extent of conversion (α) has been computed from the weight loss data using the reported standard method. Δα of 0.01 and a Δα of 0.025 were used to compute the activation energy from the differential and the integral methods respectively. For comparison and plotting, constant α values were shown at an interval of 0.025. The activation energy of **12** has been calculated using Friedman's differential method and Flynn-Wall-Ozawa integral method. The dependence of rate constant (k) of the chemical reaction the temperature (T) and activation energy (E_a) is as shown below.

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{28}$$

Friedman's method applies the logarithm of conversion rate as a function of the reciprocal temperature at different degrees of conversion. Friedman's equation is obtained by simple rearrangement of eq. (28).

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln\left[A_\alpha f(\alpha)\right] - \left(\frac{E_\alpha}{RT_{\alpha,i}}\right) \tag{29}$$

where the subscripts i and α denotes the different heating rates and the conversion values. The value of dα/dt is obtained numerically using Δα = 0.02 and linear interpolation of the experimental data. The plot of ln(dα/dt) versus 1/T at constant α values gives a family of straight lines with slope $-E_\alpha/R$. This is a model-free method can be applied to the data sets obtained at different heating rates β_i and/or different temperatures, Ti. The value for A is obtained by extrapolation of a plot of the intercept against α_i to $\alpha_{i=}0$. Flynn-Wall-Ozawa method is a model-free method which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, β and plotting ln(α) against 1/T and the slopes of such plots give $-E_a/R$. If E_a varies with α, the results should be interpreted in terms of multi-step reaction mechanisms. However, the method is less precise than the Friedman's method. The Arrhenius rate law eq. (28) was integrated and Doyle approximation was applied to obtain eq. (30). The plot of lnβ versus 1/T gives straight line with slope -1.052E/R.

$$\ln \beta = \ln \frac{AE}{R} - \ln G(\alpha) - 5.55305 - 1.052 \frac{E}{RT} \qquad (30)$$

The samples (~1 mg) in alumina crucible were heated from 25 to 300 °C under nitrogen environment at the flow rate 100 cm^3 per minute. Trinitropyrazole (**12**) underwent single stage decomposition evident from TG thermogram Fig. 4.2.4. The compound showed good thermal stability with no weight loss observed up to 150 °C. DTA revealed two signals an endothermic peak corresponding to the melting of the compound at 90.3 °C followed by an exothermic decomposition peak at 248 °C (peak temperature). The compound showed weight loss in the temperature range from 150 to 250 °C The compound showed maximum weight loss at 248 °C indicating the poor oxygen balance (OB% -28.81%) of the material. It is seen from the plot that the rate of decomposition seems to be autocatalytically increasing over temperature. As observed for many energetic materials, the decomposition temperature of compound increased with increase in temperature.[32,36] The peak temperature from the DTA thermograms was utilized for kinetic analysis.

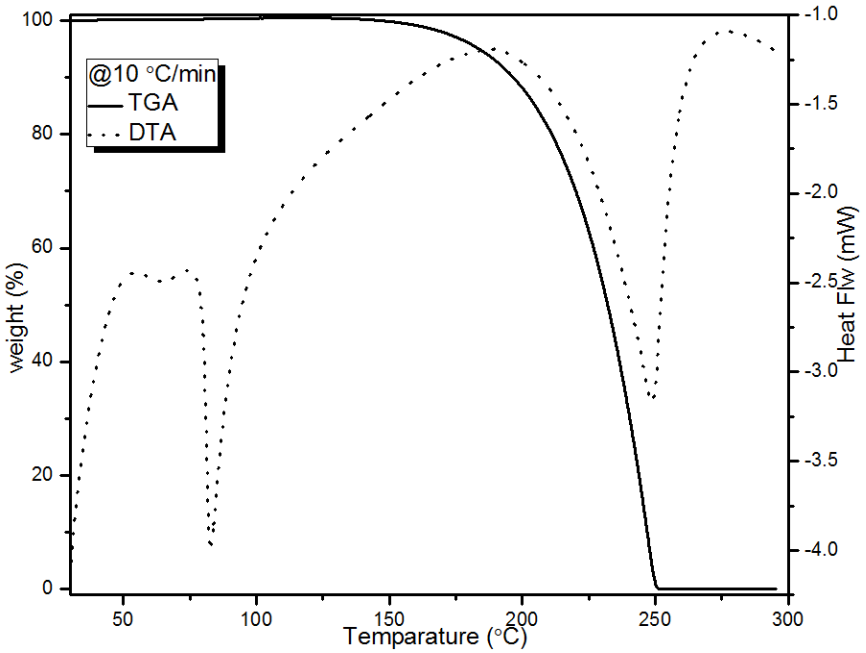


Figure 4.2.4 The effect of temperature on the weight loss of 1-methyl-3,4,5-trinitropyrazole.

DTA analysis was carried out at five different heating rates so as to obtain five peak values to generate the kinetic parameters using Friedman's differential method and Flynn-Wall-

Ozawa integral method. The activation energy required for the thermal decomposition according to Flynn-Wall-Ozawa method and Friedman method are 240.5 kJ mol^{-1} and 241.8 kJ mol^{-1} respectively. Figure 4.2.5 show the plot α against T and the slope values have been used for the kinetic computations.

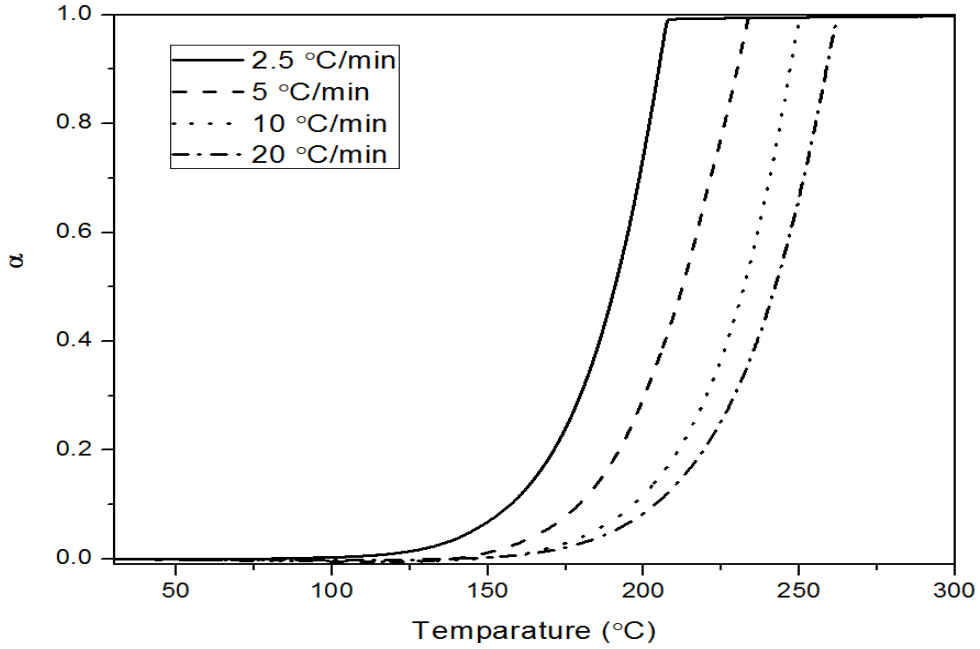


Figure 4.2.5 The effect of temperature on the extent of conversion (α) of 1-methyl-3,4,5-trinitropyrazole.

A linear relationship of activation energy with the conversion rate indicates the possibility of single reaction mechanism or the unification of multiple-reaction mechanisms. However, the compound **12** showed non-linear relation indicating the involvement of multi-step decomposition pathway. The stability of **12** has been proved by the E_α versus α relation experimentally. Though the trends are appearing to be similar in relation to activation energy with an extent of conversion nevertheless, the numerical values of activation energy obtained using differential and integral isoconversional methods showed a difference. These differences could be due to the approximation of the temperature integral that were used in the derivations of the relations of non-linear isoconversional methods. The compound showed good thermal stability with high insensitivity. The possible decomposition paths of 1-methyl-3,4,5-trinitropyrazole (**12**) is shown in Figure 4.2.6. Azoles are known to undergo ring decomposition rather than at the side chain.[1]

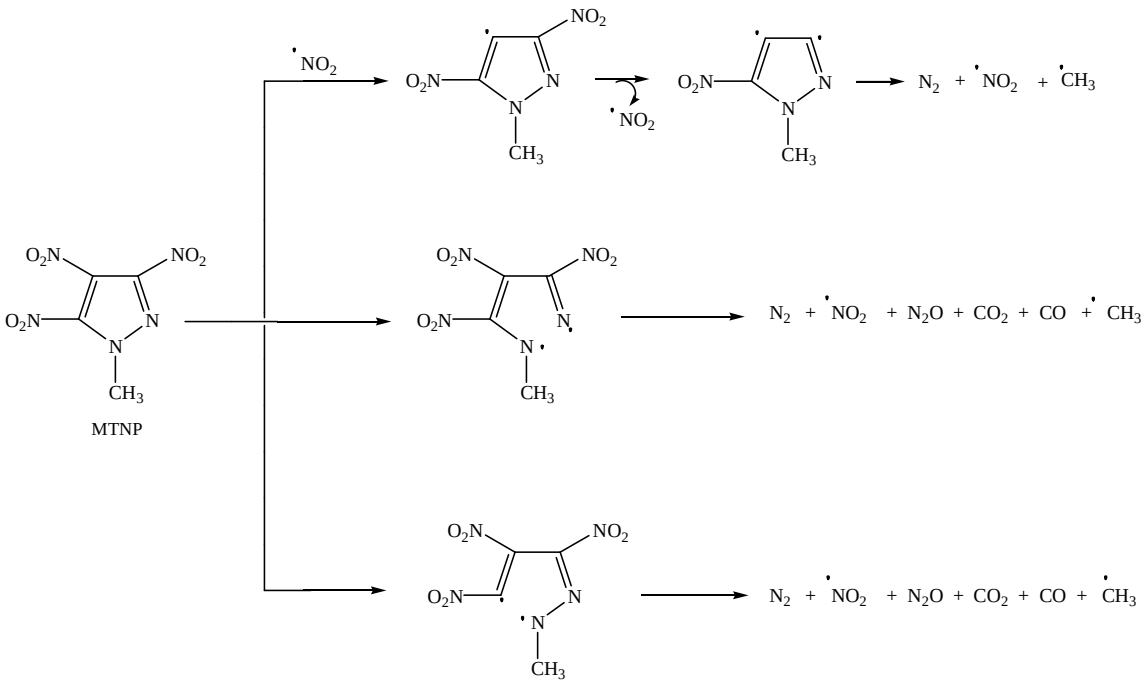


Figure 4.2.6 The possible decomposition paths of 1-methyl-3,4,5-trinitropyrazole.

The kinetic parameters of the compound were derived using isoconversional methods. Furthermore due to the promising properties such as lower melting points, higher heats of formation, higher densities and performance, **12** may find use as melt cast explosive in near future.[37]

3.3 Conclusions

The possible routes to prepare nitropyrazoles in good yields have been investigated. 3,5-Dinitropyrazole (**7**), 3,4-dinitropyrazole (**8**), 1-methyl-3,4-dinitropyrazole (**9**), 1-methyl-3,5-dinitropyrazole (**10**), 1-methyl-3,4,5-trinitropyrazole (**12**) and 3,4,5-trinitropyrazole (**19**) were synthesized using conventional nitration and nitrolysis methodologies starting from pyrazole and 1-methylpyrazole. The conventional nitration methodologies suffer from low yields, starting material availability, harsh conditions and/or difficulty to separate isomer formation. Pyrazole was methylated with dimethyl carbonate (DMC) prior to oxidative iodination (I_2-HIO_3) to synthesize 1-methyliodopyrazoles. 1-Methyliodopyrazoles and 1-methylnitropyrazoles were also prepared from iodopyrazoles using methyl iodide and dimethyl sulfate under alkaline conditions. Exceptionally higher yields of nitropyrazoles were obtained by the nitrodeiodination of iodopyrazoles using fuming nitric acid or mixtures of nitric acid and sulfuric acid. The replacement of iodine atom proceeded smoothly in fuming nitric acid or nitric acid-sulfuric mixture. Thermal decomposition of 1-methyl-3,4-5-trinitropyrazole (**12**) using isoconversional methods have also been investigated to know the activation energy and decomposition path. Due to the promising explosive properties such as lower melting points, higher heats of explosion, higher densities and better performance, the nitropyrazoles **8** and **12** may find use as melt cast explosives in near future.

3.4 Experimental Section

All the reagents were purchased from Merck, Fluka, Aldrich, Sigma and Acros Chemical Co. and used without further purification. Melting points were recorded by a capillary melting point apparatus and were uncorrected. All experiments were monitored by TLC aluminium sheets (silica gel 60 F254 Merck and Camag TLC lamp (254/366 nm)). The FT-IR spectra were recorded on Perkin Elmer FT-IR-1600 spectrophotometer in KBr matrix. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300 MHz Varian instrument with $CDCl_3$, D_2O, and DMSO-d_6 solvents. The chemical shift values are reported in δ units (parts per million) relative to TMS as an internal standard. Electron impact mass spectra (EIMS) were measured on a double focusing JEOL-DS mass spectrometer at 70 eV by using the direct insertion technique. Elemental analysis was carried out on CE Instrument (Model CHN-1110). Thermo gravimetric analysis (TGA) measurements were carried out on a TA instruments Q600 SDT instrument.

N-nitropyrazoles and C-nitropyrazoles were synthesized as described by Janssen et al.[6]

Caution: All polynitropyrazoles considered as dangerous and proper precaution should be taken in handling and storage of these materials. Iodination of pyrazole using I_2-25% NH_4OH is highly exothermic and the reaction should be carried with care.

Preparation of 3,4-dinitropyrazole (8)

3,4-Diiodopyrazole (2.00 g, 6.25 mmol) was refluxed with nitric acid (ρ 1.54 g cm^{-3}, 20 mL) at 100 °C for 30 minutes during which time a creamy colored precipitate deposited. The cooled reaction mixture was poured onto ice, neutralized by saturated sodium bicarbonate and the mixture reacidified to pH 0.5 by the addition of concentrated hydrochloric acid. The solution was repeatedly extracted with ether, dried over sodium sulfate and the solvent evaporated to obtain crude product. Crystallization from benzene gave white crystals.

Yield	0.92 g (93%)
mp	86-88 ºC
IR (KBr)	(cm^{-1}) 1545, 1504, 1370 and 1326 (C-NO_2), 2901.1 (C-H), 3135 (N-H)
^{1}H NMR	(δ ppm, $CDCl_3$) 10.77 (br s, 1H, NH, D_2O exchangeable), 8.29 (s, 5-H)
^{13}C NMR	(δ ppm, $CDCl_3$) 122.6 (C-4), 142.8 (C-3), 348.3 (C-5)

MS (EI)	m/z 158
Analysis	Calculated for $C_3HN_4O_4$: C, 22.80%; H, 1.28%; N, 35.44%
	Found: C, 22.78%; H, 1.26%; N, 35.54%

Preparation of 1-methyl-3,4-dinitropyrazole (8)

3,4-Diiodo-1-methylpyrazole (2.50 g, 7.48 mmol) was added in small portions to nitric acid (ρ 1.54 g cm^{-3}, 25 mL) and refluxed for 1 h. The solution was poured onto ice water neutralized with sodium bicarbonate and repeatedly extracted with ether and dried over sodium sulfate. Removal of the solvent gave a light yellow oil and crystallized from benzene-hexane as white crystalline compound.

Yield	0.95 g (74%)
mp	20-22 ºC
IR (KBr)	(cm^{-1}) 1550, 1534, 1520, 1370, 1340 (C-NO_2), 2998 (CH_3)
^{1}H NMR	(δ ppm, $CDCl_3$) 4.06 (s, 3H), 8.32 (s, 5H)
^{13}C NMR	(δ ppm, $CDCl_3$) 126.3 (t, C4), 147.4 (t, C3), 132.6 (t, C5)
MS (EI)	m/z 172
Analysis	Calculated for $C_4H_4N_4O_4$: C, 27.94%; H, 2.32%; N, 32.56%
	Found: C, 27.90%; H, 2.31%; N, 32.52%

Preparation of 1-methyl-3,4,5-trinitropyrazole (12)

From 1-methylpyrazole (11):

1-Methylpyrazole (100 mg, 1.22 mmol) was added to nitric acid (ρ 1.54 g cm^{-3}, 3 mL) and then 30% oleum (3 mL) was added under constant stirring. The resultant reaction mixture was refluxed for 2 h. the reaction mixture was cooled to room temperature and then poured onto ice and then product was extracted with ether (3x25 mL). The combine organic phase was washed with water and dried over sodium sulfate. Evaporation of the solvent gave a light yellow solid.

Yield	65 mg (12%)
mp	90-92 ºC

From 1-methyl-3,5-dinitropyrazole (10):

1-Methyl-3,5-dinitropyrazole (0.40 g, 2.33 mmol) was added to nitric acid (ρ 1.54 g cm^{-3}, 4 mL) and then 30% oleum (2 mL) was added under constant stirring. The resultant reaction mixture was refluxed for 2 h. the reaction mixture was cooled to room temperature and then poured onto ice and then product was extracted with ether (3x25 mL). The combine organic phase was washed with water and dried over sodium sulfate. Evaporation of the solvent gave a light yellow solid.

Yield	0.42 g (42%)
mp	90-92 ºC

From 3,4,5-Triiodo-1-methylpyrazole (18):

3,4,5-Triiodo-1-methylpyrazole (2 g, 4.48 mmol) was added in small portions to nitric acid (ρ 1.54 g cm^{-3}, 30 mL) and the reaction mixture was refluxed for 1.5 h. The solution was poured onto ice water neutralized with sodium bicarbonate and repeatedly extracted with ether and dried over sodium sulfate. Removal of the solvent gave a light yellow solid. Crystallized from benzene-hexane gave a light yellow solid.

Yield	0.82 g (87%)
mp	90-92 ºC
IR (KBr)	(cm^{-1}) 1555.5, 1529.1, 1452.5, 1381.9, 1325.8 (C-NO_2), 2998 (CH_3)
^{1}H NMR	(δ ppm, $CDCl_3$) 4.10 (s, 3H)
^{13}C NMR	(δ ppm, $CDCl_3$) 43.2 (t, CH_3), 123.3 (t, C4), 137.4 (t, C3), 148.6 (t, C5)
MS (EI)	m/z 217
Analysis	Calculated for $C_4H_3N_5O_6$: C. 22.12%, H. 1.38%, N. 32.26%
	Found: C. 22.0%, H. 1.2%

Preparation of 3,4-diiodopyrazole (15) and 3,4,5-triiodopyrazole (16)

An aqueous solution (100 mL) of iodine (2.8 g, 11 mmol) and potassium iodide (5.8 g) was added slowly to a stirred solution of pyrazole (3.4 g, 5 mmol) in ammonium hydroxide (25%, 200 mL) at room temperature and left to stirring continued for 20 h. The solution was decolorized with sodium bisulfate, filtered off and dried to get white crude compound (**15**). Crystallized from aqueous ethanol (1:1 ratio) gave white creamy compound.

Yield	5.72 g (35%)
mp	161-163 ºC
IR (KBr)	(cm^{-1}) 607.3 (C-I), 1637.5 (N-N), 3124.6 (N-H)
^{1}H NMR	(δ ppm, $CDCl_3$)10.72 (s, 3H), 154.3 (t, C5)
^{13}C NMR	(δ ppm, $CDCl_3$) 126 (t, C4), 144.2 (t, C3), 153.1 (t, C5)
MS (EI)	m/z 320
Analysis	Calculated for $C_3H_2N_2I_2$: C, 11.26%; H, 0.63%; N, 79.34%; I, 79.35%
	Found: C, 11.24%; H, 0.63%; N, 79.36%; I, 79.33%.

The ammonical filtrate was acidified with 25% acetic acid to give a white creamy precipitate which was filtered, washed with water and air dried to get creamy compound (**16**). The resulting material was then crystallized from benzene gave white compound.

Yield	9.85 g (43%)
mp	222-224 ºC
IR (KBr)	(cm^{-1}) 604.7 (C-I), 1634.5 (N-N), 3110 (N-H)
^{1}H NMR	(δ ppm, $CDCl_3$) 10.72 (s, 3H, D_2O exchangeable)
^{13}C NMR	(δ ppm, $CDCl_3$) 124.3 (t, C4), 142.6 (t, C3), 151.7 (t, C5)
MS (EI)	m/z 446
Analysis	Calculated for $C_3HN_2I_3$: C, 8.08%; H, 0.23%; N, 6.29%; I, 85.41%
	Found: C, 8.07%; H, 0.23%; N, 79.42%; I, 85.43%

Preparation of 3,4-diiodo-1-methylpyrazole (17)

Potassium carbonate (0.3 g, 2.2 mmol) was added to the stirred solution of 3,4-diiodo pyrazole (0.5 g. 1.12 mmol) in dimethyl formamide (10 mL). The reaction mixture was kept under stirring for 1 h and then methyl iodide (0.6 g, 1.10 mmol) was added slowly under nitrogen atmosphere. Stirring was continued for 6 h at room temperature. The reaction mixture was poured onto water, filtered and repeatedly washed with water and dried to get white creamy compound.

Yield	0.46 g (88%)
mp	65-68 ºC
IR (KBr)	(cm^{-1}) 604.7 (C-I), 1634.5 (N-N), 2998 (CH_3)
^{1}H NMR	(δ ppm, $CDCl_3$) 3.94 (s, 3H), 7.56 (s, 5H)

^{13}C NMR	(δ ppm, $CDCl_3$) 43.14 (t, CH_3), 122.2 (t, C4), 135.8 (t, C3), 143.1 (t, C5)
MS (EI)	m/z 334
Analysis	Calculated for $C_4H_4N_2I_2$: C, 14.39%; H, 1.22%; N, 8.42%; I, 76.01%
	Found: C, 14.36%; H, 1.26%; N, 8.48%; I, 76.10%

Preparation of 3,4,5-triiodo-1-methylpyrazole (18)

From 3,4,5-triiodopyrazole (16):

Potassium carbonate (0.3 g, 2.2 mmol) was added to the stirred solution of 3,4,5-triiodopyrazole (0.5 g. 1.12 mol) in dimethyl formamide (10 mL). The reaction mixture was kept under stirring for 1 h and then methyl iodide (0.6 g, 1.10 mmol) was added very slowly under nitrogen atmosphere. The stirring was continued for 6 h at room temperature. The reaction mixture was poured into water, filtered and repeatedly washed with water and dried to get white crude.

Yield	0.49 g (95.01 %)
mp	154-156 ºC

From 1-methylpyrazole (11):

1-Methylpyrazole (2.05 g, 2.5 mmol), iodine (0.76 g, 2 mmol), and iodic acid (0.26 g, 1 mmol) in a mixture of acetic acid (10 mL), 30% sulfuric acid (1 mL), and carbon tetrachloride (1.25 mL) were heated at 85-90 ºC for 3 h, after which the mixture was diluted with ice water (38 mL). The precipitate was filtered and washed with a saturated solution of sodium sulfite and with water. Crystallized from ethanol-water solution (1:1) gave white crystalline compound.

Yield	10.08 g (88%)
mp	154-156 ºC
IR (KBr)	(cm^{-1}) 642.3 (C-I), 1634.5 (N-N), 2932.9 (CH_3)
^{1}H NMR	(δ ppm, $CDCl_3$) 4.05 (s, 3H)
^{13}C NMR	(δ ppm, $CDCl_3$) 43.8 (t, CH_3), 127.6 (t, C4), 146.2 (t, C3), 154.3 (t, C5).
MS (EI)	m/z 460
Analysis	Calculated for $C_3HN_2I_3$: C, 10.45%; H, 0.66%; N, 6.12%; I, 82.82%
	Found: C, 10.42%; H, 0.63%; N, 6.08%; I, 82.78%.

Preparation of 3,4,5-trinitropyrazole (19)

From 3,4,5-triodopyrazole (16):

3,4,5-Triodopyrazole (2.00 g, 4.48 mmol) was refluxed with nitric acid (ρ 1.54 g cm^{-3}, 30 mL) at 100 °C for 40 minutes during which time a creamy colored precipitate deposited. The cooled reaction mixture was poured onto ice, neutralized by saturated sodium bicarbonate and the mixture reacidified to pH 0.5 by the addition of concentrated hydrochloric acid. The solution was extracted repeatedly with ether, dried over sodium sulfate and the solvent evaporated to obtain crude. Crystallization from benzene gave as white crystals.

Yield	0.76 g (86%)
mp	188-190 ºC
IR (KBr)	(cm^{-1}) 1552.3, 1522, 1446.4, 1411.4, 1373.5, 1347.6, 1286.2 (C-NO_2), 3147.6 (N-H)
^{1}H NMR	(δ ppm, $CDCl_3$) 12.3 (s, 1H, NH, D_2O exchangeable)
^{13}C NMR	(δ ppm, $CDCl_3$) 122.3 (C-4), 143.2 (C-3), 348.9 (C-5)
MS (EI)	m/z 203
Analysis	Calculated for $C_3HN_5O_6$: C, 17.74%; H, 0.51%; N, 34.52%
	Found: C, 17.76%; H, 0.48%; N, 34.48%

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4.1 Introduction

Pyrazoles are nitrated with nitric acid-sulfuric acid, nitric acid-acetic anhydride, nitric acid-trifluoroacetic anhydride or nitromethane-nitronium tetrafluoroborate.[1-3] C-Polynitro pyrazoles have been synthesized from C-polyiodopyrazoles using fuming nitric acid.[4] 1-Methyl-3-nitropyrazole, 1-methyl-4-nitropyrazole, 1-methyl-3,4-dinitropyrazole and 1-methyl-3,4,5-tri nitropyrazole have also been synthesized refluxing 1-methylpyrazole in nitric acid-sulfuric acid mixture.[4,5] Hüttel and Büchele[6] described the rearrangement of N-nitropyrazoles to 4-nitro pyrazoles in sulfuric acid solution in cold. However, N-nitropyrazoles in anisole or benzonitrile at 120-190 ^{0}C for 3-7 h are rearranged to C-nitropyrazoles in higher yields.[7] The conventional methodologies usually suffer from low yields, starting material availability, harsh conditions, and/or difficulty to separate isomer formation prompted us to search for the alternative methodologies.

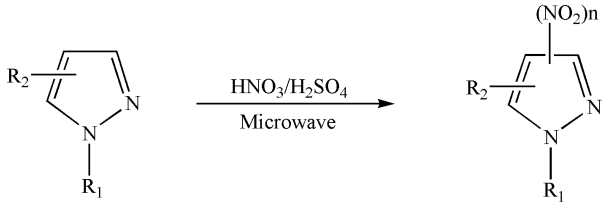
Microwave irradiations have been applied by chemists to get different results.[8-12] The nitration of several arenes can be performed with great success under microwave heating. Further, the supported metal nitrates such as $Bi(NO_3)_3/SiO_2$ or clay,[13,14] $AgNO_3/BF_3$,[15] $Cu(NO_3)_2$/clay,[16] $Ce(NH_4)_2(NO_3)_6/H_2SO_4/ SiO_2$,[17] $Fe(NO_3)_3$/clay[18] and other metal nitrates/clay activated by acetic anhydride[19] have also been used for the nitration of arenes. The limitations and drawbacks of conventional methods such as tedious work-up, strongly acidic media, oxidation ability of reagents, thermal rearrangements and safety problems can be avoided using the impregnated metal nitrates. The nitration of arenes using silica, silica-sulfuric acid or montmorillonite impregnated with bismuth nitrate can be achieved in a few minutes.[13,14,20-24] The supported bismuth nitrate is more active, easier to handle, readily separable from the products by simple filtration, recyclable and require milder reaction conditions and long-lived catalyst for the nitration of arenes. Though the synthesis of nitropyrazoles using various nitration mixtures are known however, to our knowledge synthesis of these compounds with silica, silica-sulfuric acid or montmorillonite impregnated with bismuth nitrate has not yet been reported. We describe in this chapter such alternative methodologies for the nitration of pyrazoles using microwave heating, silica-bismuth nitrate (Method A), silica-sulfuric acid-bismuth nitrate (Method B) and montmorillonite K10-bismuth nitrate (Method C) at room temperature.

4.2 Results and Discussion

4.2.1 Microwave Assisted Synthesis of Nitropyrazoles

The nitration of several aromatic compounds can be performed with great success under microwave irradiation.[8-12] The synthesis of iodopyrazoles[26-35] and nitropyrazoles[4-7] using conventional routes have been reported elsewhere. We describe in this section the synthesis of such compounds in good yields under microwave heating of 400 W (Scheme 18). 4-Nitro pyrazole (**4**) in 86% yield has been prepared from pyrazole (**1**) using nitric acid-sulfuric acid mixture at 85 °C for 10 minutes. Heating 10% of N-nitropyrazole (**2**) in benzonitrile at 180 °C for 5 minutes gave 3-nitropyrazole (**3**) in 99% yield. 3,4-Dinitropyrazole (**8**) in 94% yield has been synthesized from 3-nitropyrazole (**3**) under Morgan and Ackermann nitration conditions.[36] Thermolysis of 1,3-dinitropyrazole (**5**) and 1,4-dinitropyrazole (**6**) in benzonitrile at 180 °C for 5 minutes gave 3,5-dinitropyrazole (**7**) and 3,4-dinitropyrazole (**8**) respectively in higher yields. However, the efforts were failed to obtain 3,4-dinitropyrazoles (**8**,**9**) from 4-nitropyrazoles (**4**,**13**) rather recovered starting compound in quantitative yield. The nitration of pyrazoles and the yields of corresponding nitropyrazoles are shown in Table 4.2.1.

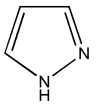
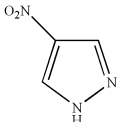
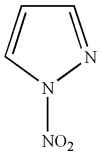
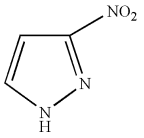
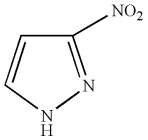
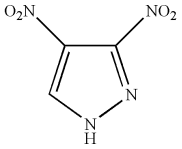
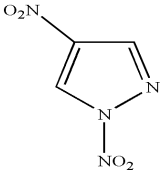
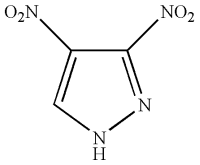
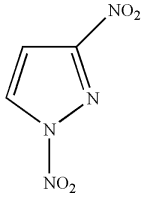
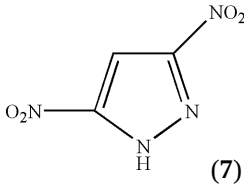
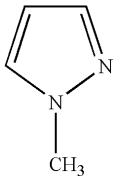
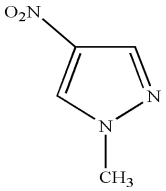
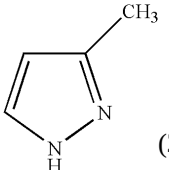
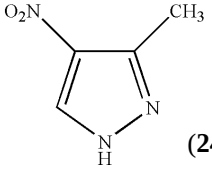
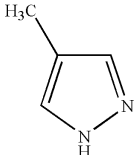
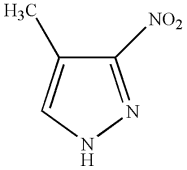
Scheme 18



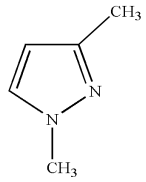
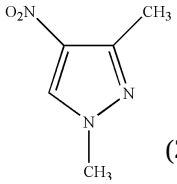
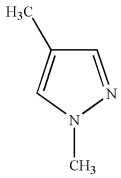
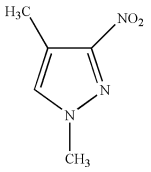
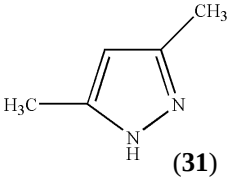
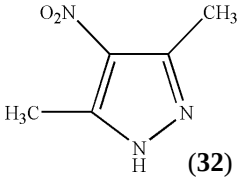
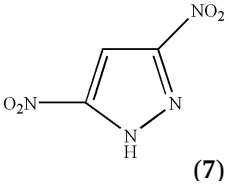
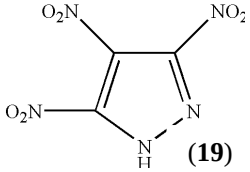
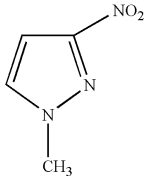
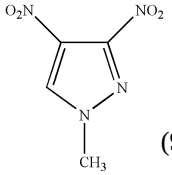
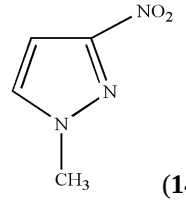
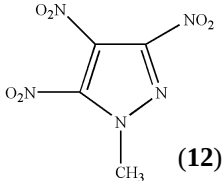
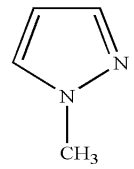
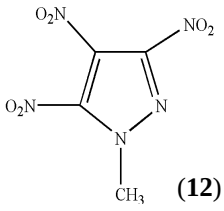
R_1 = H, CH_3, phenyl, p-nitrophenyl, NO_2
R_2 = H, CH_3
n = 1, 2, 3

The first step in the synthesis of 1-methyl-3,4-dinitropyrazole (**9**), 1-methyl-3,5-dinitro pyrazole (**10**) and 1-methyl-3,4,5-trinitropyrazole (**12**) is to substitute the methyl group at position-1 with iodomethane, dimethyl sulfate or dimethyl carbonate.[4,5] Methylation of pyrazole takes place without catalyst suggesting that the lone pair of electrons of nitrogen would be basic enough to react directly with dimethyl carbonate (DMC). It is known that DMC possess two active centers (alkyl and carbonyl carbons) whose reactivity is tuned with temperature. When the reaction temperature is > 120 ^{0}C, methylation reaction occurs through BAL_2 mechanism.[37]

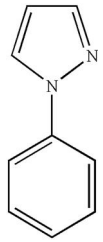
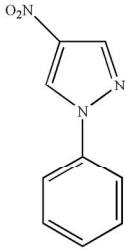
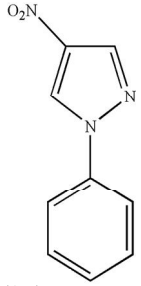
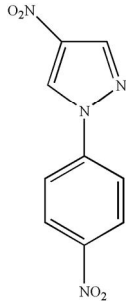
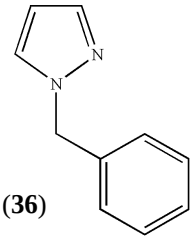
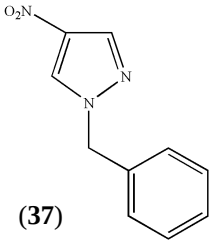
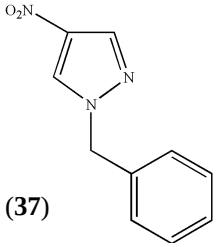
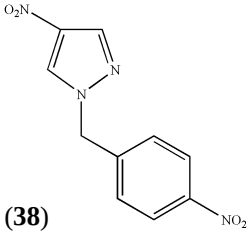
Table 4.2.1 Microwave assisted nitration of pyrazoles.

Entry	Substrate	Product	Time (minutes)	Yield (%)	m p (^{0}C)	
					Found	Literature
1	 (**1**)	 (**4**)	20	86	164-165	162-164[6]
2	 (**2**)	 (**3**)	5	99	172-173	173-174[7]
3	 (**3**)	 (**8**)	10	94	87-88	88-89[7]
4	 (**6**)	 (**8**)	5	92	87-88	88-89[7]
5	 (**5**)	 (**7**)	5	98	173-174	173-174[7]
6	 (**11**)	 (**13**)	20	85	91-92	91-92[5]
7	 (**23**)	 (**24**)	10	87	135-136	134-136[7]
8	 (**25**)	 (**26**)	15	84	187-188	186-187[7]

continued..

Entry	Substrate	Product	Time (minutes)	Yield (%)	m p (^{0}C)	
					Found	Literature
9	 (**27**)	 (**28**)	10	76	159-161	160-162[6]
10	 (**29**)	 (**30**)	10	81	96-97	97-98[38,39]
11	 (**31**)	 (**32**)	10	98	160-161	161-162[36]
12	 (**7**)	 (**19**)	10	92	189-190	188-190[4,25]
13	 (**14**)	 (**9**)	15	95	20-21	21-22[5]
14	 (**14**)	 (**12**)	20	92	90-91	91-93[4,25]
15	 (**11**)	 (**12**)	30	42	90-91	91-93[4,25]

continued..

Entry	Substrate	Product	Time (minutes)	Yield (%)	m p (^{0}C)	
					Found	Literature
16	 (**33**)	 (**34**)	20	87	126-127	125-126[40]
17	 (**34**)	 (**35**)	20	83	163-164	162-163[40]
18	 (**36**)	 (**37**)	20	84	92-93	91-92[41]
19	 (**37**)	 (**38**)	20	78	90-91	90-91[38]

Pyrazole (**1**) has been methylated with DMC and obtained 1-methylpyrazole (**11**) in 98% yield at 180 ^{0}C for 20 minutes. Methylation is favored with increase of temperature from 100 to 210 ^{0}C. The direct nitration of 1-methylpyrazole (**11**) with nitric acid-oleum at 110 °C for 30 minutes gave 1-methyl-3,4,5-trinitropyrazole (**12**) in 42% yield (entry 15). Pyrazole has been iodinated into 3,4-diiodopyrazole (**15**) and 3,4,5-triiodopyrazole (**16**) using I_2-NH_4OH at room

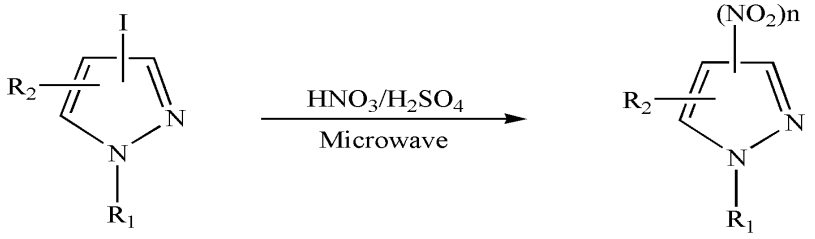
temperature as per literature procedure.[26] The higher yields of 3,4-diiodo-1-methylpyrazole (**17**) and 3,4,5-triiodo-1-methylpyrazole (**18**) were obtained by methylating 3,4-diiodopyrazole (**15**) and 3,4,5-triiodo pyrazole (**16**) with iodomethane and dimethyl sulfate. The oxidative iodination of 1-methylpyrazoles using I_2/HIO_3 has been found to be an efficient method to synthesize iodo derivatives containing electron-withdrawing groups in the pyrozole ring.[27,28] Our attempts to iodinate 4-nitropyrazoles have been unsuccessful. 3,4,5-Triiodo-1-methylpyrazole (**18**) was obtained in 97% yield from 1-methylpyrazole (**11**) using I_2/HIO_3 (oxidative iodination) at 85 ^{0}C per 10 minutes. Polyiodopyrazoles (**15**,**16**,**17**,**18**) were nitrodeiodinated by refluxing with fuming nitric acid at 100 °C for 10 minutes or nitric acid-sulfuric acid (30% SO_3) mixture at 85 °C for 15 minutes gave polynitropyrazoles (**8**,**9**,**12**,**19**) in good yields. 3,4-Dinitropyrazole (**8**) and 3,4,5-tri nitropyrazole (**19**) were methylated both with methyl iodide and dimethyl sulfate into 1-methyl-3,4-dinitropyrazole (**9**) and 1-methyl-3,4,5-trinitropyrazole (**12**) respectively.

3,4,5-Triiodo-1-methylpyrazole (**18**) gave 3,5-diiodo-1-methyl-4-nitropyrazole (**20**) and 5-iodo-1-methyl-3,4-dinitropyrazole (**21**) with 68% nitric acid-sulfuric acid. The nature of ipso nitration depends upon the concentration of nitric acid and reaction temperature. In order to establish the generality of nitrodeiodination and its applicability to the synthesis of polynitropyrazoles we also have nitrated 3,4-diiodopyrazole (**15**) 1-methyl-3,4-diiodopyrazole (**17**), 3,5-diiodo-1-methyl-4-nitropyrazole (**20**), 5-iodo-1-methyl-3,4-dinitropyrazole (**21**) and 1-methyl-4,5-diiodo-3-nitropyrazole (**22**). It has been demonstrated that even the vicinal iodine atom or nitro group(s) did not prevent ipso substitution. Surprisingly, tlc analysis of the reaction mixture after it had been heated 55-100 °C for 5 to 10 minutes showed the absence of starting material. Methylating pyrazole with dimethyl carbonate (DMC) prior to oxidative iodination have been found to be conventional route to synthesize 1-methyl-3,4,5-trinitropyrazole (**12**) in higher yields. Polyiodopyrazoles are preferred to synthesize 3,4-dinitropyrazole (**8**) and 3,4,5-tri nitropyrazole (**19**) in good yields to avoid rearrangement of N-nitropyrazoles at ambient temperatures. The replacement of iodine atom proceeded smoothly in fuming nitric acid or nitric acid-sulfuric mixture at 55-100 °C in yields 71-98%.

4.2.2 Silica-Sulfuric Acid Catalyzed Nitrodeiodination of Iodopyrazoles

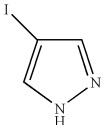
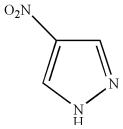
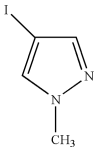
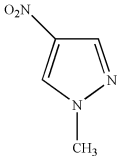
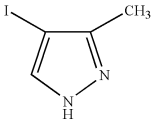
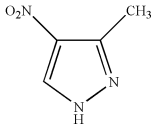
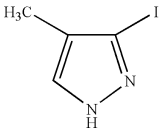
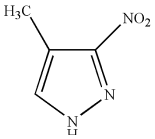
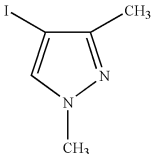
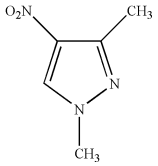
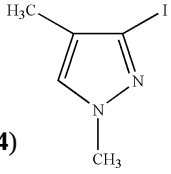
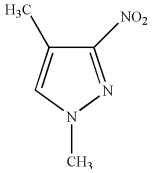
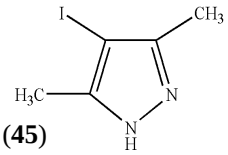
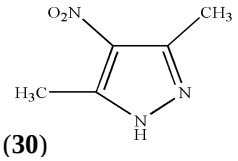
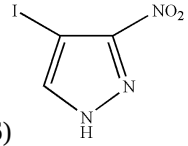
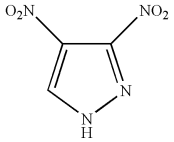
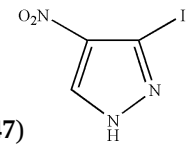
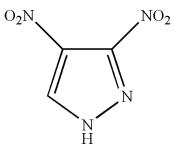
Silica-sulfuric acid is easier to handle because it holds the acidity internally, readily separable from the products by simple filtration, recyclable and require the milder reaction conditions.[24,42-44] To overcome the limitations and drawbacks of the conventional nitration methodologies such as tedious work-up, strongly acidic media, oxidation ability of the reagents, denitration, thermal rearrangements and safety problems, we have used silica-sulfuric acid catalyst for the nitrodeiodination of iodopyrazoles. C-Nitropyrazoles have been synthesized from iodopyrazoles with nitric acid over silica-sulfuric acid catalyst at room temperature. Silica-sulfuric acid has been activated prior to use at 120 ^{0}C for 4 h. The starting materials with nitric acid and silica-sulfuric acid in THF have been stirred at room temperature and evaporation of the solvent under rotavapor comprises the reaction conditions for successful, regiospecific nitration with a series of iodopyrazoles. To ascertain the optimum conditions, several reactions were carried out on 4-iodopyrazole (**39**) and 4-iodo-1-methypyrazole (**40**) as the model substrates by varying the amount of catalyst in THF at room temperature. The general synthetic scheme for the nitrodeiodination of iodopyrazoles is shown in Scheme 19. It has been found that there was no promising change in the yields of **4** and **13** when the reactions prolonged, or increased the catalyst. The replacement of iodine atom proceeded smoothly in fuming nitric acid over silica-sulfuric acid at room temperature. The iodopyrazoles and the yields of corresponding nitro compounds are summarized in Table 4.2.2.

Scheme 19

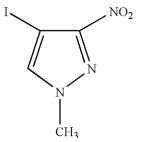
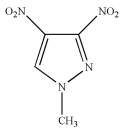
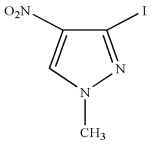
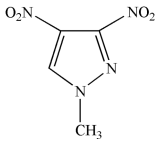
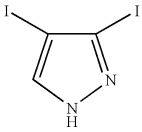
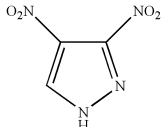
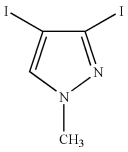
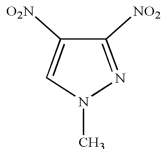
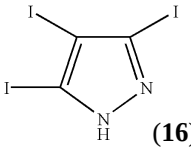
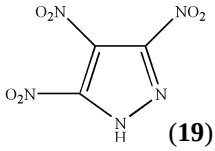
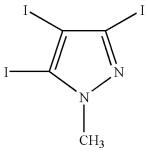
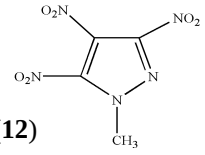
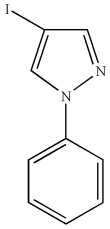
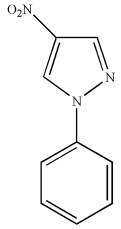
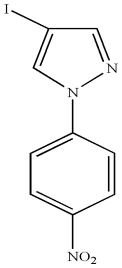
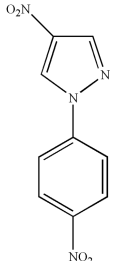


R_1 = H, CH_3, phenyl, p-nitrophenyl, NO_2
R_2 = H, CH_3
n = 1, 2, 3

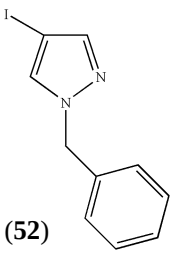
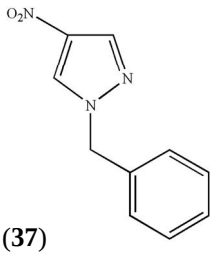
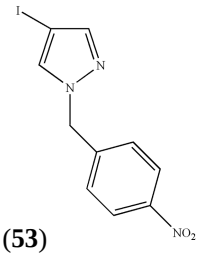
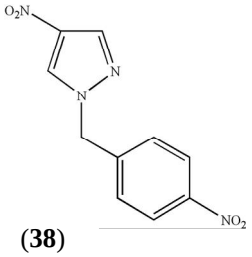
Table 4.2.2 Silica sulfuric acid catalyzed nitrodeiodination of iodopyrazoles.

Entry	Substrate	Product	Time (h)	Yield (%)	m p (^{0}C)	
					Found	Literature
1	 (**39**)	 (**4**)	2.5	92	164-165	162-164[6]
2	 (**40**)	 (**13**)	2.5	86	91-92	91-92[5]
3	 (**41**)	 (**24**)	2.0	92	135-136	134-136[7]
4	 (**42**)	 (**26**)	2.5	87	187-188	186-187[7]
5	 (**43**)	 (**28**)	2.0	92	159-161	160-162[6]
6	 (**44**)	 (**29**)	2.0	87	96-97	97-98[38,39]
7	 (**45**)	 (**30**)	2.0	98	160-161	161-162[36]
8	 (**46**)	 (**8**)	2.5	85	87-88	88-89[7]
9	 (**47**)	 (**8**)	2.5	82	87-88	88-89[7]

continued…

Entry	Substrate	Product	Time (h)	Yield (%)	m p (^{0}C)	
					Found	Literature
10	 (**48**)	(**9**) 	3.0	78	20-21	21-22[5]
11	 (**49**)	(**9**) 	3.0	75	87-88	88-89[7]
12	 (**15**)	(**8**) 	2.5	96	87-88	88-89[7]
13	 (**17**)	(**9**) 	2.5	86	20-21	21-22[5]
14	 (**16**)	 (**19**)	3.0	92	189-190	188-190[4,25]
15	 (**18**)	 (**12**)	3.5	86	90-91	91-93[4,25]
16	 (**50**)	 (**34**)	2.5	88	126-127	125-126[40]
17	 (**51**)	 (**35**)	2.5	81	163-164	162-163[40]

continued…

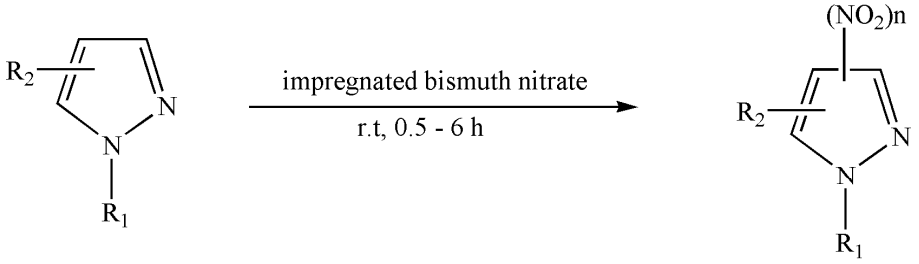
Entry	Substrate	Product	Time (h)	Yield (%)	m p (^{0}C)	
					Found	Literature
18	 (**52**)	 (**37**)	2.5	87	92-93	91-92[41]
19	 (**53**)	 (**38**)	2.5	92	90-91	90-91[38]

Diiodopyrazoles (**15**,**17**) and triiodopyrazoles (**16**,**18**) were nitrated to dinitropyrazoles (**8**,**9**) and trinitropyrazoles (**12**,**19**) respectively in good yields (entries 12-15). The crude obtained after the nitration of 3,4,5-triiodo-1-methylpyrazole (**18**) using 68% nitric acid-sulfuric acid have been found to contain 3,5-diiodo-4-nitropyrazole (**20**) and 5-iodo-3,4-nitropyrazole (**21**). The nitration of **18** with nitric acid for 10 minutes gave higher yield (86%) of trinitropyrazole (**12**). The nitrolysis of 1-phenyl-4-iodopyrazole (**50**), 1-(p-nitrophenyl)-4-iodopyrazole (**51**), 1-benzyl-4-iodopyrazole (**28**) and 1-(p-nitrobenzyl)-4-iodopyrazole gave 1-phenyl-4-nitro- pyrazole (**34**), 1-(p-nitrophenyl)-4-nitropyrazole (**35**), 1-benzyl-4-nitropyrazole (**37**) and 1-(p-nitrobenzyl)-4-nitropyrazole (**38**) respectively (entries 16-18). The determination of the position of nitro group was based on both the difference in the reactivity towards electron withdrawing groups of the 3- or 4-position of the ring and the comparison of the spectral data of the compounds. Finally, we have tested the silica-sulfuric acid catalyst recycling. After filtration, washing with methanol and heating at 120 ºC for 12 h, the silica-sulfuric acid was reused for atleast three times and showed good to high yields. It has been found that the solid catalyst works efficiently up to third cycle thereafter it loses its activity.

4.2.3 Nitration of Pyrazoles by Impregnated Bismuth Nitrate

Bismuth nitrate is an inexpensive, easy-to-handle and commercially available solid metal nitrate used for the nitration.[13,14] The supported bismuth nitrate is the most active and long-lived catalyst for the nitration of arenes. Also, it is easier to handle, readily separable from the products by simple filtration, recyclable and require the milder reaction conditions. The nitration of different pyrazoles using silica-bismuth nitrate (Method A) silica-sulfuric acid-bismuth nitrate (Method B) and montmorillonite-bismuth nitrate (Method C) have been carried out at room temperature. Mixing the starting materials with silica-bismuth nitrate, silica-sulfuric acid-bismuth nitrate or montmorillonite-bismuth nitrate in THF and evaporation of the solvent under vacuum comprise the reaction conditions for successful, regiospecific nitration with a series of pyrazoles. To ascertain the optimum conditions, several reactions were carried out on pyrazole (**1**) and 1-methypyrazole (**11**) as the model substrates by varying the amounts of silica-bismuth nitrate in THF at room temperature. Pyrazoles with electron donating groups readily underwent nitration in excellent yields (> 92%). The deactivated substrates and underwent nitration in good yields (> 80%). The general scheme for the nitration of pyrazoles is shown (Scheme 20). The substrates with electron donating and electron withdrawing groups and their corresponding nitro compounds using supported bismuth nitrate (Method A&B) are summarized in Table 4.2.3.

Scheme 20



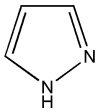
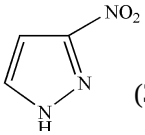
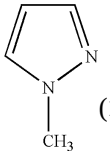
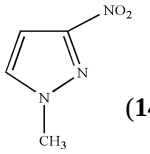
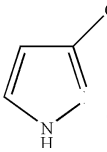
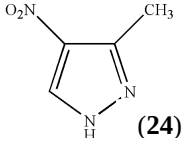
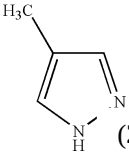
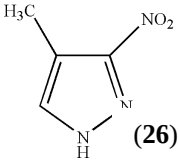
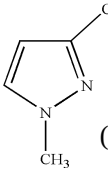
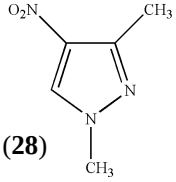
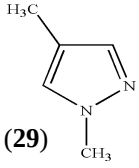
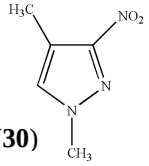
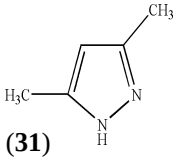
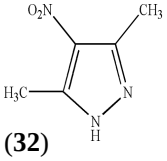
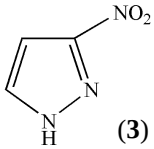
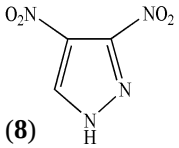
R_1 = H, CH_3, phenyl, p-nitrophenyl, NO_2
R_2 = H, CH_3
n = 1, 2, 3

Pyrazole and methylpyrazoles have been nitrated in excellent yields with silica-bismuth nitrate and silica-sulfuric acid-bismuth nitrate. An exceptionally higher yield of 3,5-dimethyl-4-nitropyrazole (**32**) was obtained in less time. 1,3-Dimethylpyrazole (**27**) and 1,4-dimethyl pyrazole (**29**) were also nitrated to corresponding nitropyrazoles (**28** and **30**) in higher yields. The reaction was very selective and no side-chain substitution products were observed. The

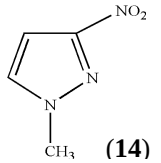
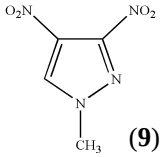
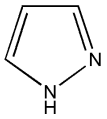
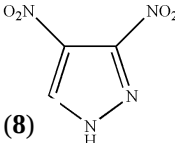
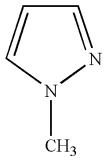
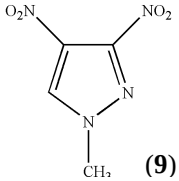
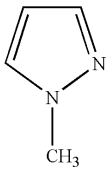
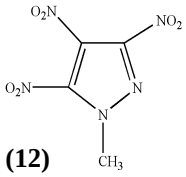
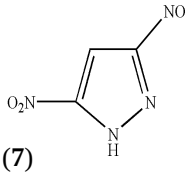
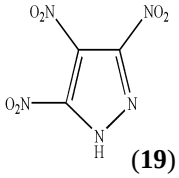
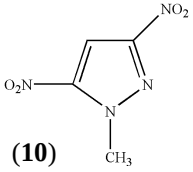
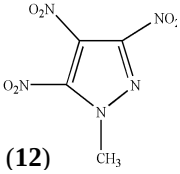
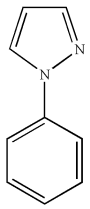
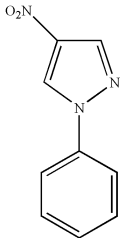
reaction rates of methyl pyrazoles were increased with increasing number of methyl groups. The crude obtained after nitration of **1** contains less than 10% 4-nitropyrazole (**4**), a stable C-nitro pyrazole. Similarly, 1-methyl-4-nitropyrazole (**13**) has been observed to be a major side product in the synthesis of 1-methyl-3-nitropyrazole (**14**) and 1-methyl-3,4-dinitropyrazole (**9**). The prolonged nitration of **1**, **11** or mononitro compounds (**3**,**14**) gave higher yields of polynitro-pyrazoles (**8**, **9**, **12**) using acid-bismuth nitrate in two or three folds via direct nitration .

1-Methylpyrazole (**11**) on nitration gave 76% (Method A) and 88 % (Method B) yields of trinitrocompound (**12**). However, we have detected no nitration of **7** and **9** even after 48 h rather recovered the quantitative amount of starting compounds. 3,5-Dinitropyrazole (**7**) and 1-methyl-3,5-dinitropyrazole (**10**) have not been formed as the by-products in the synthesis of **8** and **9**. Our attempts to obtain 1-methyl-3,4-dinitropyrazole (**9**) from 1-methyl-4-nitropyrazole (**13**) were unsuccessful even the nitration was carried out at 120 ^{0}C for 6 h. The synthesis of 1-methyl-3,4-dinitropyrazole (**9**) from 1-methyl-3-nitropyrazole (**14**) shows that it cannot be from 1-methyl-3,5-dinitropyrazole. Furthermore, 1-phenylpyrazoles and 1-benzylpyrazoles have also been nitrated to examine the position of substitution in the substrate (entries 16-18). It has been known that the use of mixed acid leads to nitration of the conjugate acid of the base, whilst nitric acid-acetic anhydride nitrates the free base, the change in the reacting form of the substrate leading to the change of orientation. The orientation of mononitration of 1-phenylpyrazole depends on the reagent used: mixed acid gives 1-(p-nitrophenyl)pyrazole, whilst nitric acid-acetic anhydride gives 4-nitro-1-phenylpyrazole. The para substituted products (**35** and **39**) have been obtained from 1-(p-nitrophenyl)-4-nitropyrazole (**34**) and 1-(p-nitrobenzyl)-4-nitropyrazole (**38**) respectively.

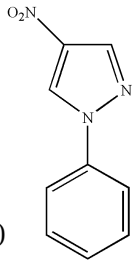
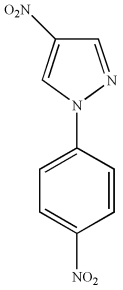
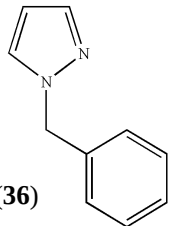
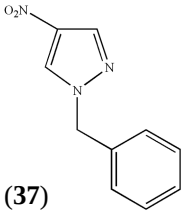
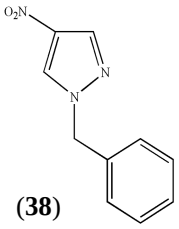
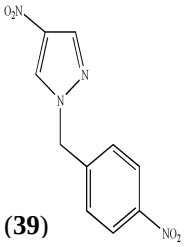
Table 4.2.3 Nitration of pyrazoles using impregnated bismuth nitrate.

Entry	Substrate	Product	Method A		Method B		m p (^{0}C)	
			Time (h)	Yield (%)	Time (h)	Yield (%)	Found	Literature
1	 (**1**)	 (**3**)	6	78	6	83	172-173	173-174[7]
2	 (**11**)	 (**14**)	6	95	6	98	91-92	91-92[5]
3	 (**23**)	 (**24**)	6	91	6	96	135-136	134-136[7]
4	 (**25**)	 (**26**)	6	94	6	96	187-188	186-187[7]
5	 (**27**)	 (**28**)	3	86	3	95	159-161	160-162[6]
6	 (**29**)	 (**30**)	3	92	3	97	96-97	97-98[38,39]
7	 (**31**)	 (**32**)	3	95	3	98	160-161	161-162[36]
8	 (**3**)	 (**8**)	4	92	4	95	87-88	88-89[7]

continued…

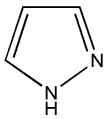
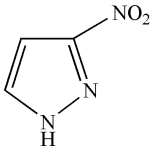
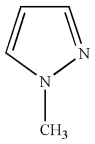
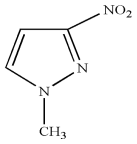
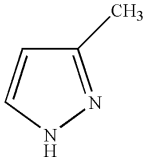
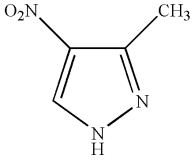
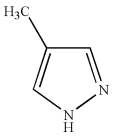
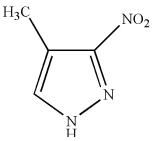
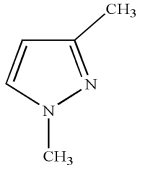
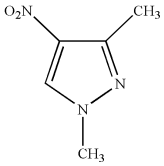
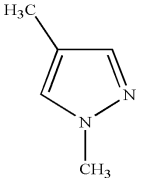
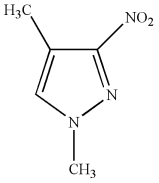
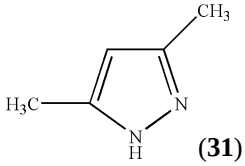
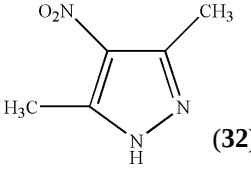
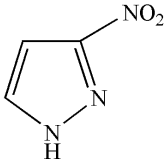
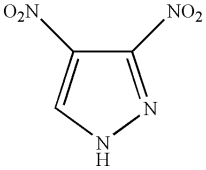
Entry	Substrate	Product	Method A		Method B		m p (^{0}C)	
			Time (h)	Yield (%)	Time (h)	Yield (%)	Found	Literature
9	 (**14**)	 (**9**)	4	91	4	94	20-21	21-22[5]
10	 (**1**)	 (**8**)	12	44	12	47	87-88	88-89[7]
11	 (**11**)	 (**9**)	6	88	6	92	20-21	21-22[5]
12	 (**11**)	 (**12**)	10	76	10	88	90-91	91-93[4,25]
13	 (**7**)	 (**19**)	3	93	3	98	189-190	188-190[4,25]
14	 (**10**)	 (**12**)	4	91	4	96	90-91	91-93[4,25]
16	 (**33**)	 (**34**)	4	83	4	87	126-127	125-126[40]

continued…

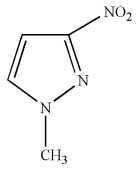
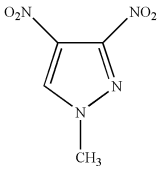
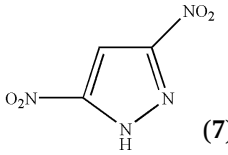
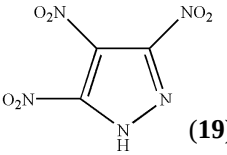
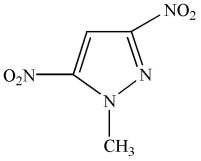
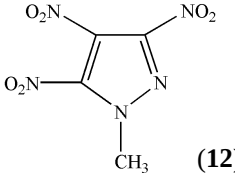
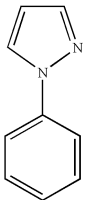
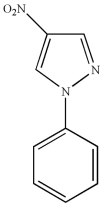
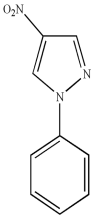
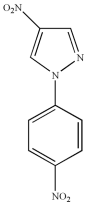
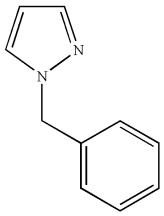
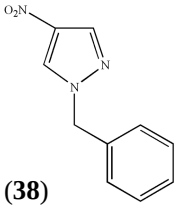
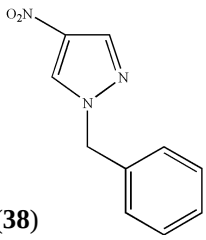
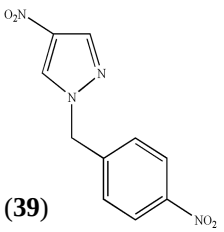
Entry	Substrate	Product	Method A		Method B		m p (^{0}C)	
			Time (h)	Yield (%)	Time (h)	Yield (%)	Found	Literature
17	 (**34**)	 (**35**)	3	88	3	93	163-164	162-163[40]
18	 (**36**)	 (**37**)	4	85	4	87	92-93	91-92[41]
19	 (**38**)	 (**39**)	3	94	3	97	90-91	90-91[38]

We also have carried out the nitration of pyrazoles using nismuth nitrate impregnated with montmorillonite K10. Mixing the substrates with bismuth nitrate and montmorillonite with (THF) and evaporation of the solvent under rotavapor comprise the reaction conditions for successful, regiospecific nitration with a series of pyrazoles (Scheme 20). To ascertain optimum conditions, several reactions have been carried out on 1-methypyrazole (**11**) as a model substrate varying the amounts of montmorillonite and bismuth nitrate in THF at room temperature. The substrates with electron donating and electron withdrawing groups and their corresponding nitro compounds are summarized in Table 4.2.4. The crude obtained after nitration of pyrazole (**1**) and 1-methylpyrazole (**11**) contains <12% yield of stable 4-nitropyrazole (**4**) and 1-methyl-4-nitro pyrazole (**13**) respectively. The prolonged nitration of pyrazole (**1**) or the nitration of 3-nitro pyrazole (**3**) gave 3,4-dinitropyrazole (**8**) in 87 and 92% yields respectively.

Table 4.2.4 Nitration of pyrazoles using montmorillonite impregnated with bismuth nitrate.

Entry	Substrate	Product	Time (h)	Yield (%)	m p (^{0}C)	
					Found	Literature
1	 (**1**)	 (**4**)	2.5	87	172-173	173-174[7]
2	 (**11**)	 (**14**)	2.5	84	91-92	91-92[5]
3	 (**23**)	 (**24**)	3.5	92	135-136	134-136[7]
4	 (**25**)	 (**26**)	3.5	84	187-188	186-187[7]
5	 (**27**)	 (**28**)	0.5	97	159-161	160-162[6]
6	 (**29**)	 (**30**)	0.5	92	96-97	97-98[38,39]
7	 (**31**)	 (**32**)	0.5	97	160-161	161-162[36]
8	 (**3**)	 (**8**)	1.0	92	87-88	88-89[7]

continued…

Entry	Substrate	Product	Time (h)	Yield (%)	m.p (^{0}C)	
					Found	Literature
9	 (**14**)	 (**9**)	1.5	96	20-21	21-22[5]
10	 (**7**)	 (**19**)	2.0	95	189-190	188-190[4,25]
11	 (**10**)	 (**12**)	2.5	93	91.3-92	91-92[6]
12	 (**33**)	 (**34**)	4	96	126-127	125-126[40]
13	 (**35**)	 (**36**)	1.0	93	163-164	162-163[40]
14	 (**37**)	 (**38**)	2.5	87	92-93	91-92[41]
15	 (**38**)	 (**39**)	1.0	92	90-91	90-91[38]

1-Methyl-4-nitropyrazole (**13**) has been found be the major side product irrespective of nitration mixture. The dinitration of 1-methylpyrazole (**11**) or nitration of 1-methyl-3-nitro pyrazole (**14**) gave 1-methyl-3,4-dinitropyrazole (**9**) in 83% and 96% yields respectively. Our attempts to obtain 1-methyl-3,4-dinitropyrazole (**9**) from 1-methyl-4-nitropyrazole (**13**) have been unsuccessful even the reaction carried at 100 ^{0}C for 4 h rather a quantitative amount of starting compound was recovered. The synthesis of **9** from 1-methyl-3-nitropyrazole (**14**) shows that it cannot be from 1-methyl-4-nitropyrazole (**13**). Moreover, 3,5-dinitropyrazole (**7**) and 1-methyl-3,5-dinitropyrazole (**10**) have not been traced in the synthesis of **8** and **9**. The mono-(**3**, **4**) and dinitro compounds (**9**) are formed presumably from pyrazole (**1**) and 1-methyl-3-nitro pyrazole (**14**) respectively. 3-Methylpyrazole (**23**), 4-methylpyrazole (**25**), 1,3-Dimethylpyrazole (**27**), 1,4-dimethylpyrazole (**29**) and 3,5-dimethylpyrazole (**31**) were also nitrated to **24**, **26**, **28**, **30** and **32** respectively. The orientation of mononitration of 1-phenylpyrazole and 1-benzyl pyrazole depends on the nature of reagent is used. The nitration mixture acid gave 1-(*p*-nitro phenyl)pyrazole, while nitric acid-acetic anhydride gave 4-nitro-1-phenylpyrazole. The mixed acid leads to the nitration of conjugate acid of the base, whilst nitric acid-acetic anhydride nitrates the free base. It has been suggested that there is very little difference (about 1 log unit) in reactivity to electrophile between C3, C4 and C5 in the free-base form.[1] 1-Phenylpyrazole and 1-benzylpyrazole gave 4-substituted compounds with nitronium tetrafluoro borate in sulfolane. Therefore, substitution on phenyl or benzyl ring at *p*-position has been observed rather on pyrazole ring of 4-nitro-1-phenylpyrazole (**34**).

Finally, the recycling of impregnated bismuth nitrate was done by evaporating the solvent after completion of the reaction and the recovered solid was dried. It has been found that the impregnated bismuth nitrate works efficiently up to third cycle thereafter it loses its activity. Exceptionally higher yields nitropyrazoles were synthesized. Nevertheless, the impregnated bismuth nitrate catalyzed reactions have been found to be superior in terms of yields of the products and time of the reaction. The relatively non-toxic nature, ease of handling, easy availability and low cost make the present procedure is attractive for the nitration of a wide variety of diazoles in the drug and pharmaceuticals industries.

4.3 Conclusions

We have shown facile, rapid and convenient methodologies for the nitration of pyrazoles. Iodopyrazoles have been found to be desirable precursors to synthesize nitropyrazoles using nitric acid over silica sulfuric acid in higher yields. We have also carried out the nitration of pyrazoles with silica-bismuth nitrate, silica-sulfuric acid-bismuth nitrate and montmorillonite K10-bismuth nitrate. The higher yields of nitropyrazoles were obtained however, 4-nitro pyrazoles were found to be highly resistant to further nitration. The relatively non-toxic nature, ease of handling, easy availability and low cost make the present procedure is attractive for the nitration of a wide variety of diazoles in the drug and pharmaceuticals industries.

4.4 Experimental Section

Melting points were recorded by a capillary melting point apparatus and were uncorrected. All the reagents were purchased from Merck, Fluka, Aldrich, Sigma and Acros Chemical Co. and used without further purification. The microwave irradiation reactions have been carried out in scientific RAGA'S microwave oven at maximum power level of 400 W. All experiments were monitored by TLC aluminium sheets (silica gel 60 F254 Merck and Camag TLC lamp (254/366 nm)). The FT-IR spectra were recorded on Perkin Elmer FT-IR-1600 spectrophotometer in KBr matrix. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300 MHz Varian instrument with $CDCl_3$, D_2O, and DMSO-d_6 solvents. The chemical shift values are reported in δ units (parts per million) relative to TMS as an internal standard. Electron impact mass spectra (EIMS) were measured on a double focusing JEOL-DS mass spectrometer at 70 eV by using the direct insertion technique. Elemental analysis was carried out on CE Instrument (Model CHN-1110).

Caution: All polynitropyrazoles considered as dangerous and proper precaution should be taken in handling and storage of these materials.

Microwave assisted synthesis of nitropyrazoles

Nitropyrazoles have been prepared according to the literature procedure under microwave irradiation of 400 W for required time.[4-7, 25,36-41]

General procedure for the nitrodeiodination of monoiodopyrazoles

Silica-sulfuric acid (250 mg) taken into two necked round bottom flask, iodopyrazole (1 mmol) in THF (10 mL) was added. Nitric acid (ρ 1.54 gcm^{-3}, 10 mL) was added dropwise and the mixtures were stirred for required time at room temperature. The catalyst was recovered by filtration and the filtrate was extracted with dichloromethane. The solvent was removed under reduced pressure to get nitropyrazole.

General procedure for the nitrodeiodination of diiodopyrazoles

Silica-sulfuric acid (500 mg) taken into two necked round bottom flask, diiodopyrazole (1 mmol) in THF (10 mL) was added. Nitric acid (ρ 1.54 gcm^{-3}, 20 mL) was added dropwise and the mixtures were stirred for required time at room temperature. The catalyst was recovered by

filtration and the filtrate was extracted with dichloromethane. The solvent was removed under reduced pressure to get dinitropyrazole.

General procedure for the nitrodeiodination of triiodopyrazoles

Silica-sulfuric acid (500 mg) taken into two necked round bottom flask, triiodopyrazole (1 mmol) in THF (10 mL) was added. Nitric acid (ρ 1.54 gcm^{-3}, 30 mL) was added dropwise and the mixtures were stirred for required time at room temperature. The catalyst was recovered by filtration and the filtrate was extracted with dichloromethane. The solvent was removed under reduced pressure to get trinitropyrazole.

Silica-sulfuric acid

Silica-gel (60.0 g) was soaked with 98% sulfuric acid (75 mL), repeatedly washed with water and filtered to get a white solid. Then it was dried at 120-130 ^{0}C for 24 h to get silica-sulfuric acid (76.0 g) solid. The silica-sulfuric acid solid was re-activated prior to use by heating in the oven at 120 ^{0}C for 6 h.

Silica-bismuth nitrate

Bismuth nitrate (10 mmol) was added to acetone (188 mL) in 500 mL evaporating flask. The mixture was stirred vigorously for 15 minutes. Silica (15 g) was added in small amounts and stirring was continued for another 15 minutes. The solvent was removed using rotary evaporator on a water bath keeping the temperature 30-35 ^{0}C and the obtained solid was crushed to get floury powder.

Silica-sulfuric acid-bismuth nitrate

Silica-sulfuric acid (0.8 g, 0.24 mol) and bismuth nitrate (0.16 g, 0.036 mol) taken in a mortar was grinded to get homogeneous floury powder.

General procedure for the synthesis of nitropyrazoles

Method A

The mixture of silica-bismuth nitrate (1.5 g) and pyrazole (17 mmol) in THF (10 mL) was stirred for required time. The reaction was monitored by TLC with ethyl acetate and hexane (3:2) as solvent. Silica-sulfuric acid was filtered off and the solvent was removed to get nitro compounds. The pure compounds were obtained from column chromatography.

Method B

The mixture of silica-sulfuric acid-bismuth nitrate (0.96 mg) and pyrazole (17 mmol) in THF (10 mL) was stirred for required time. The reaction was monitored by TLC with ethyl acetate and *n*-hexane (3:2) as solvent. Silica-sulfuric acid-bismuth nitrate was filtered off and the solvent was removed to get nitro compounds. The pure compounds were obtained from column chromatography.

Method C

Pyrazole (1 mmol) and montmorillonite-K10 (500 mg) were added to the suspension of bismuth nitrate (1 mmol) in THF (10 mL) stirred for required time. The solvent was evaporated under reduced pressure. The mixture was then was repeatedly washed with dichloromethane and crude product was obtained after concentration. The pure product was obtained after column chromatography using hexane and ethyl acetate (6:4) as solvent system.

4.5 References

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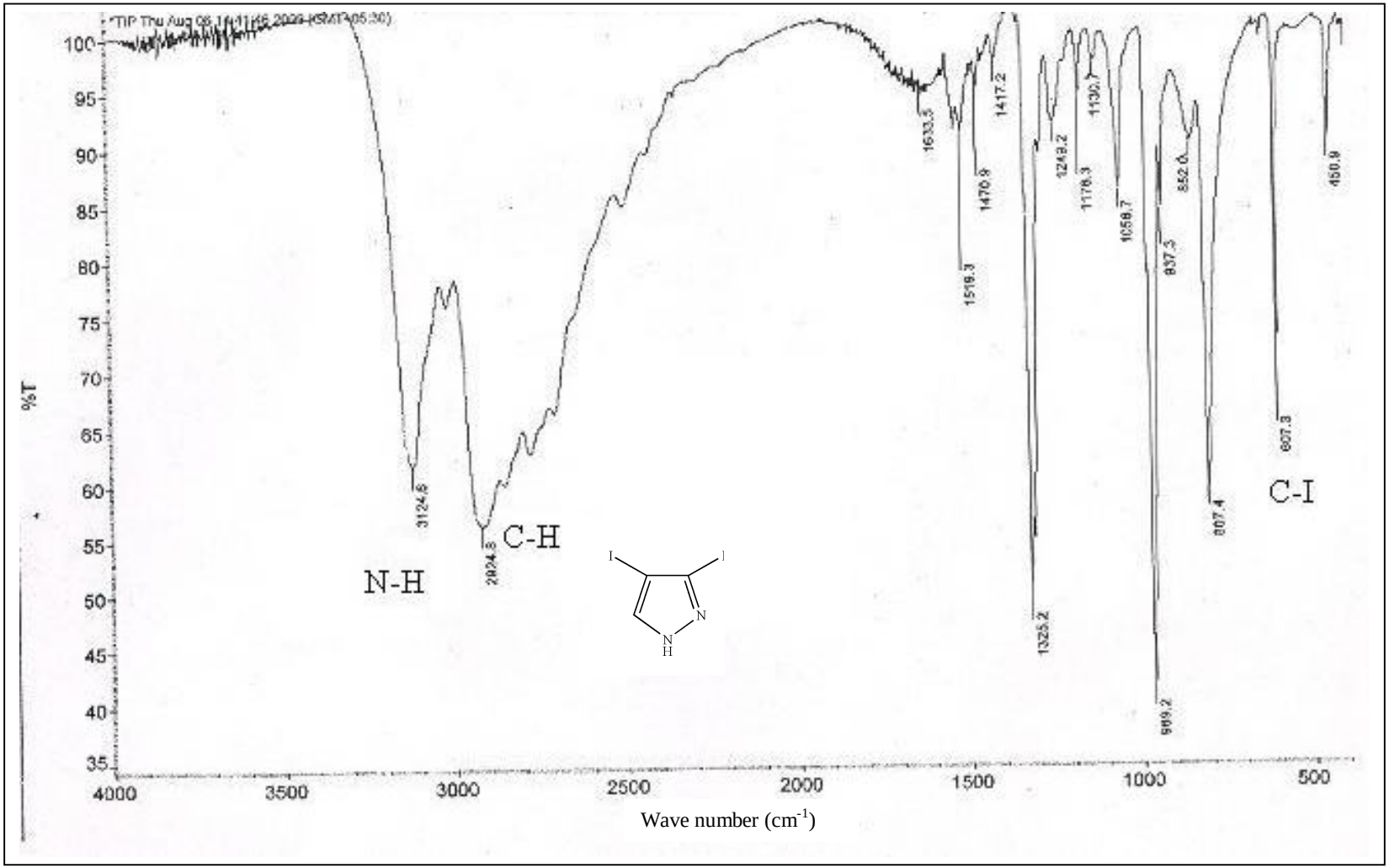
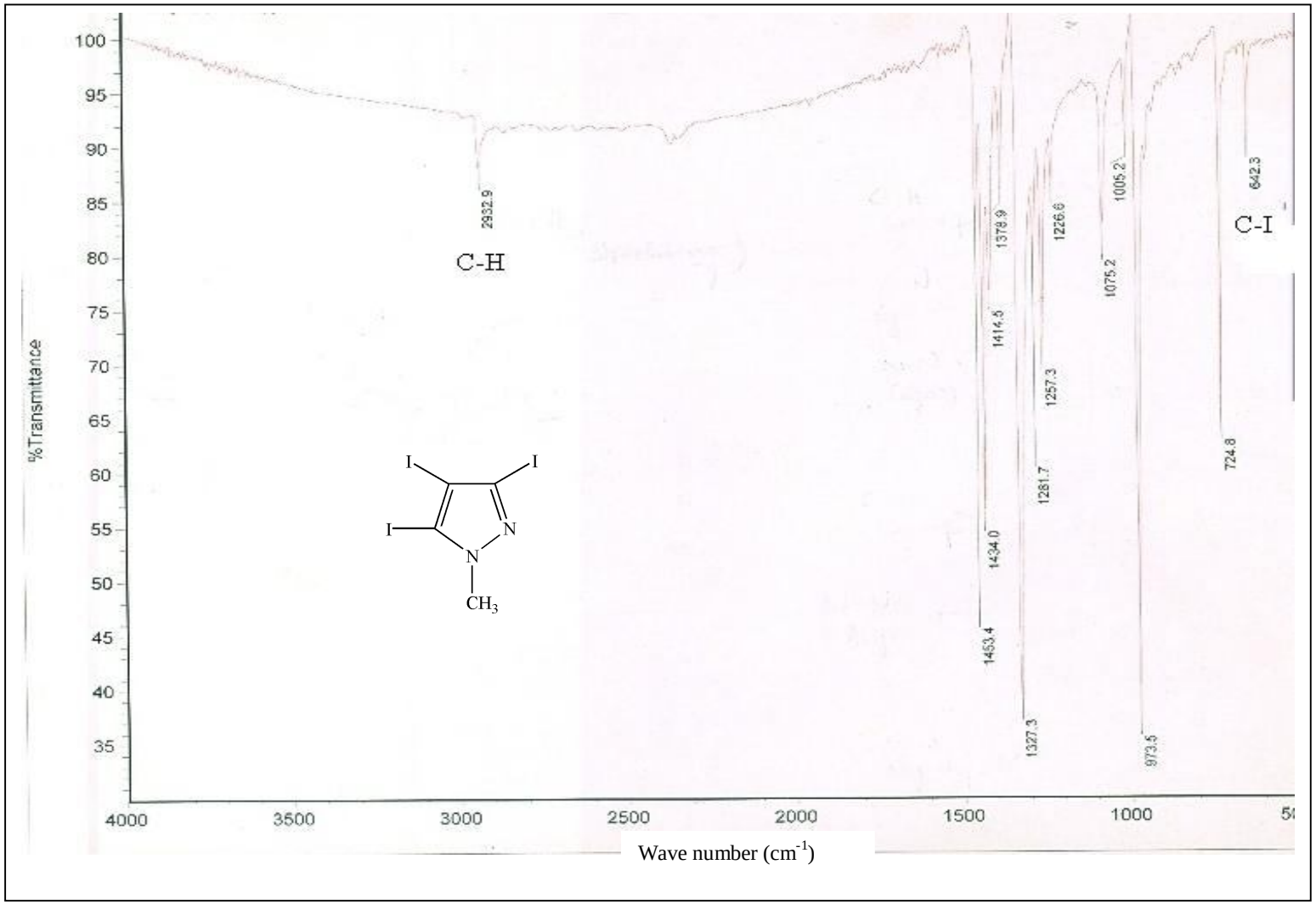
Appendix 1 (Representative Spectra)

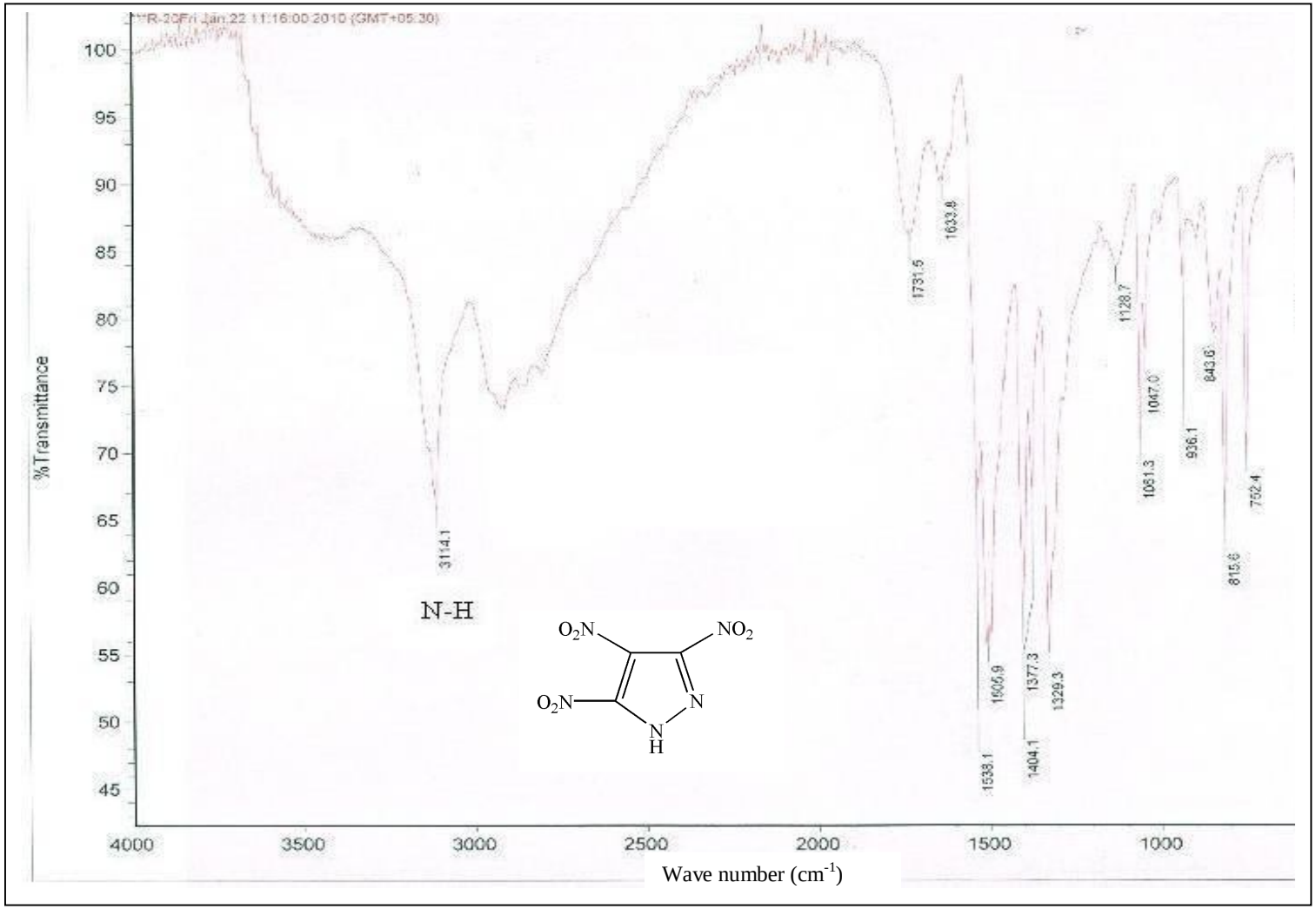
IR spectrum of 3,4-diiodopyrazole (**15**)



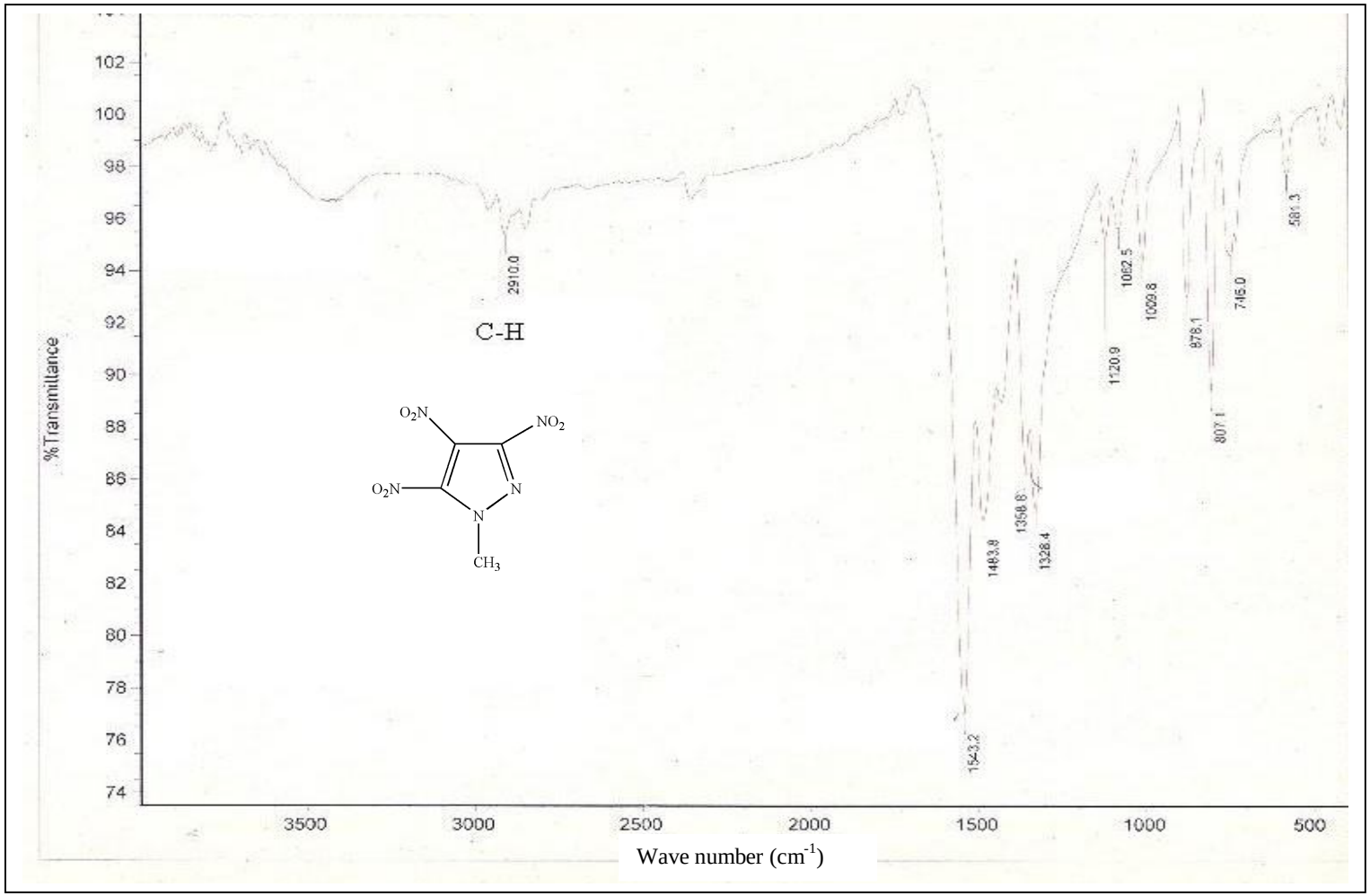
IR spectrum of 1-methyl-3,4,5-triiodopyrazole (**18**)



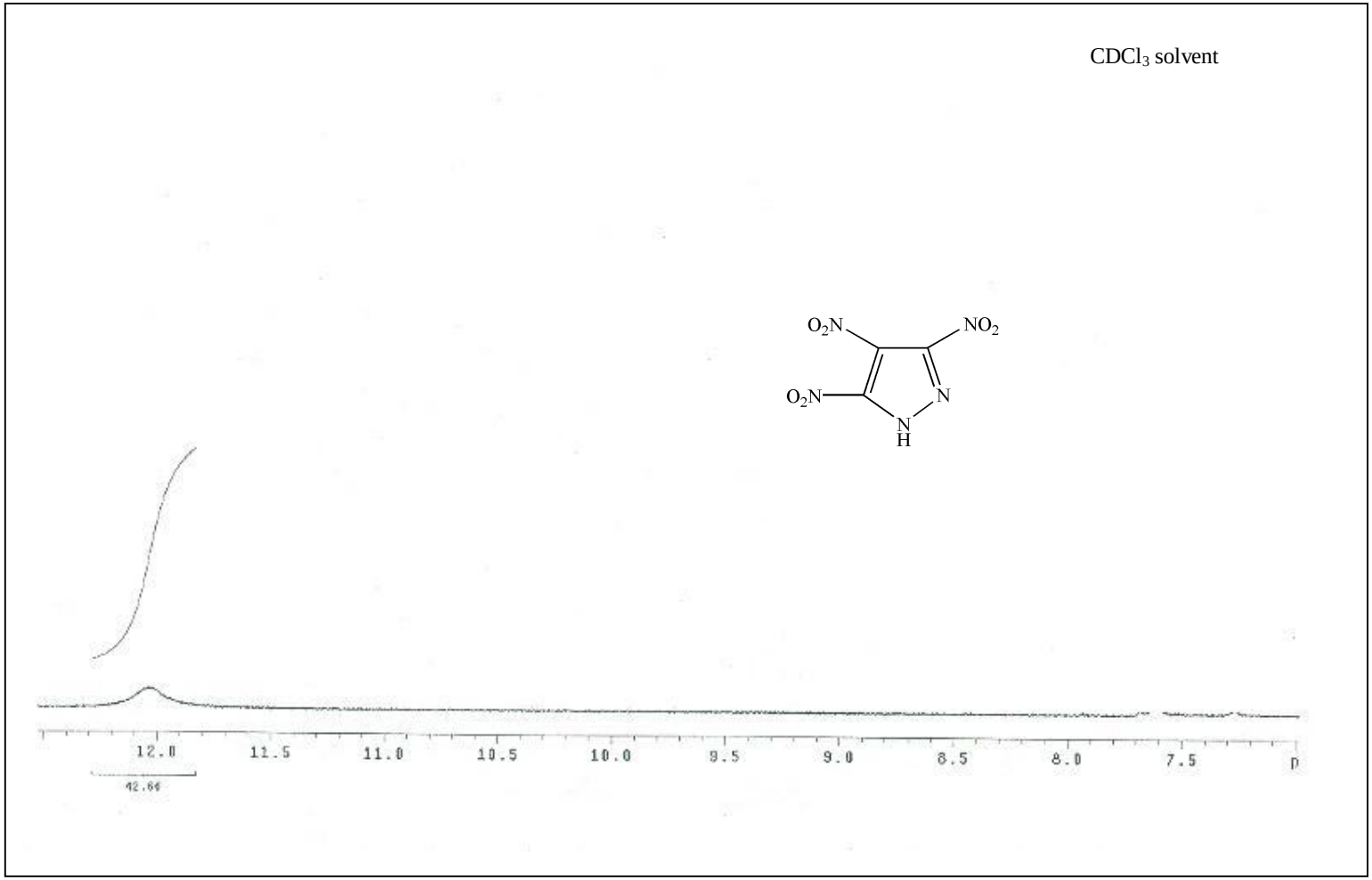
IR spectrum of 3,4,5-trinitropyrazole (**19**)



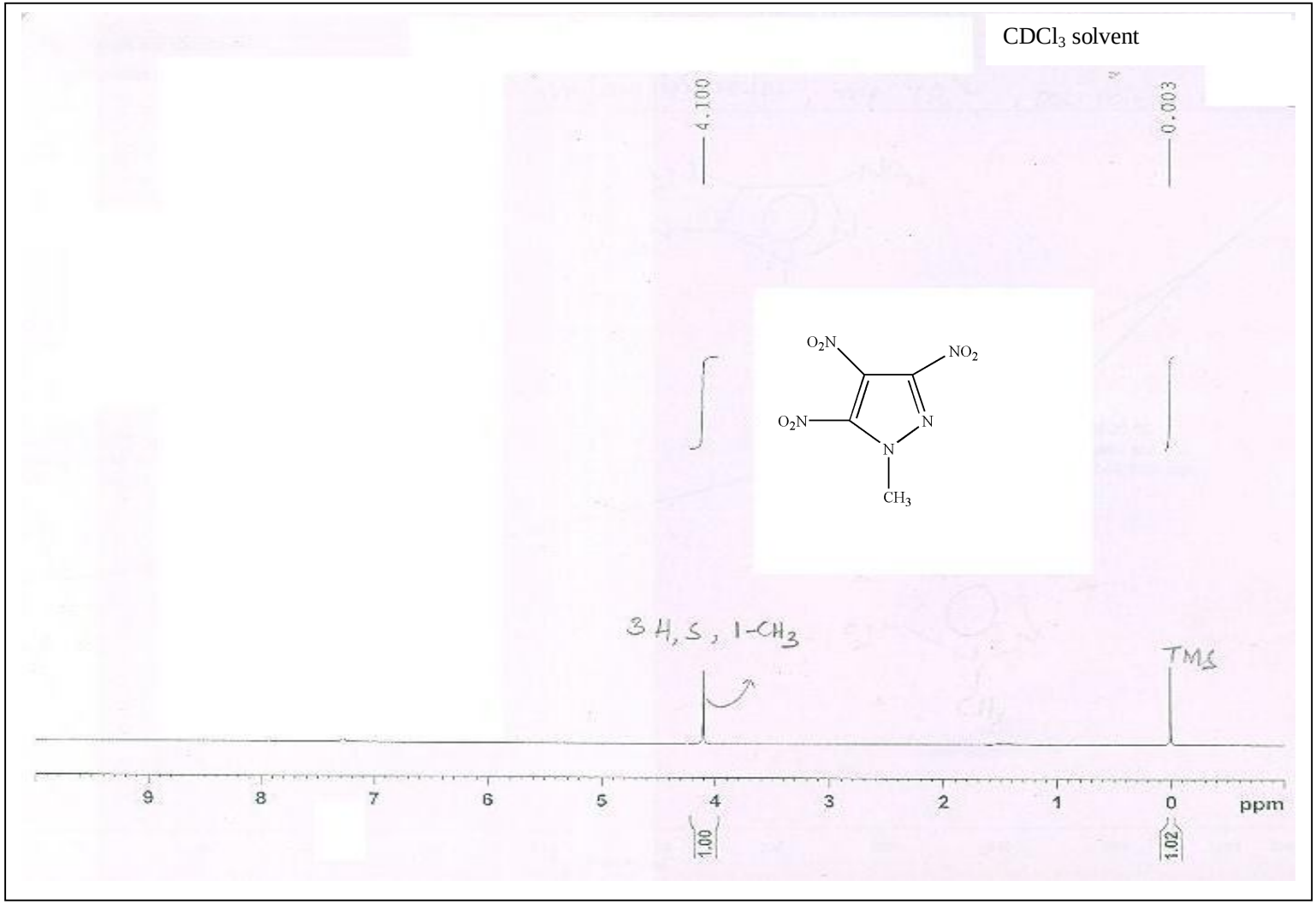
IR spectrum of 1-methyl-3,4,5-trinitropyrazole (**12**)



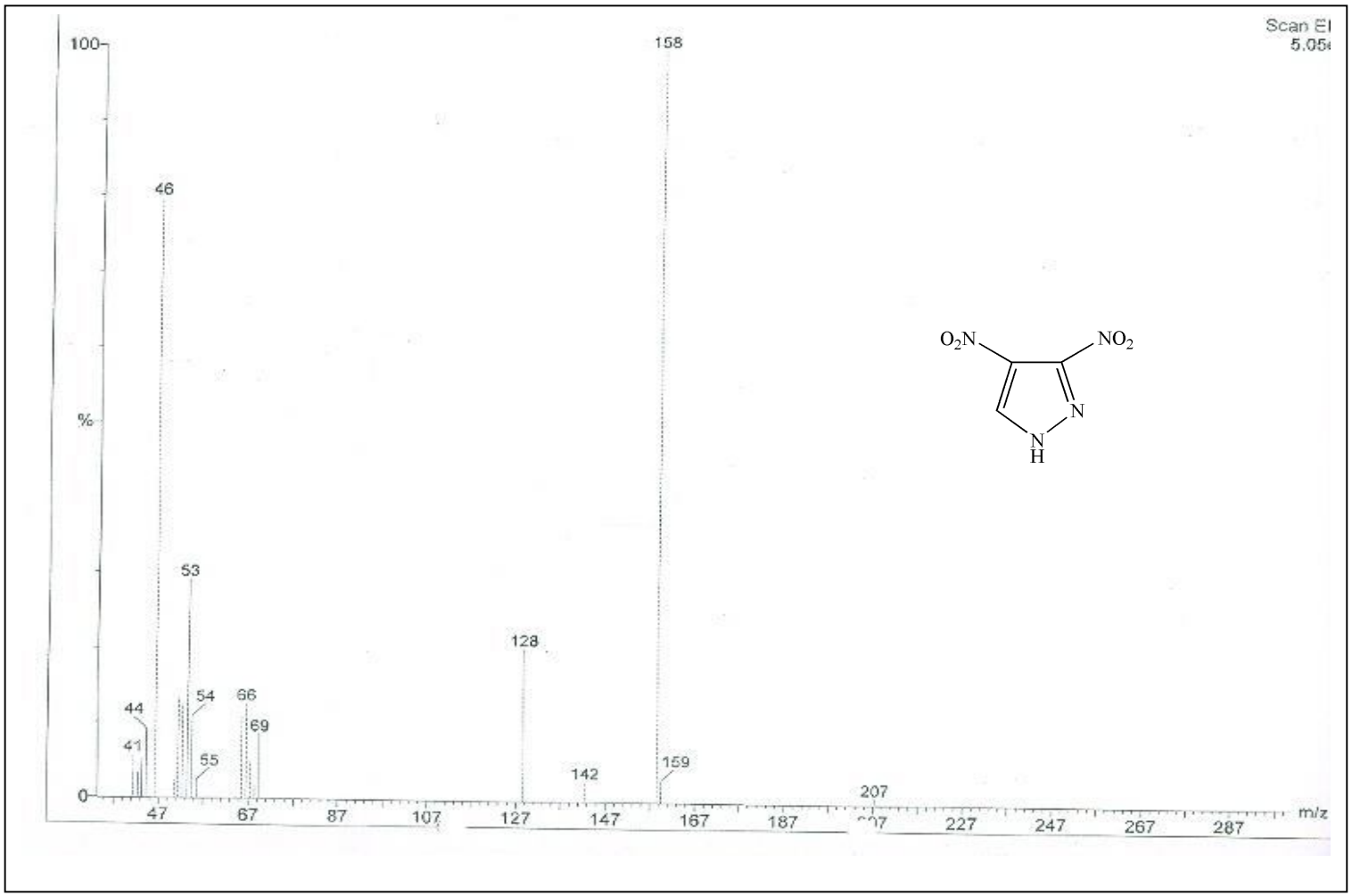
^{1}H NMR spectrum of 3,4,5-trinitropyrazole (**19**)



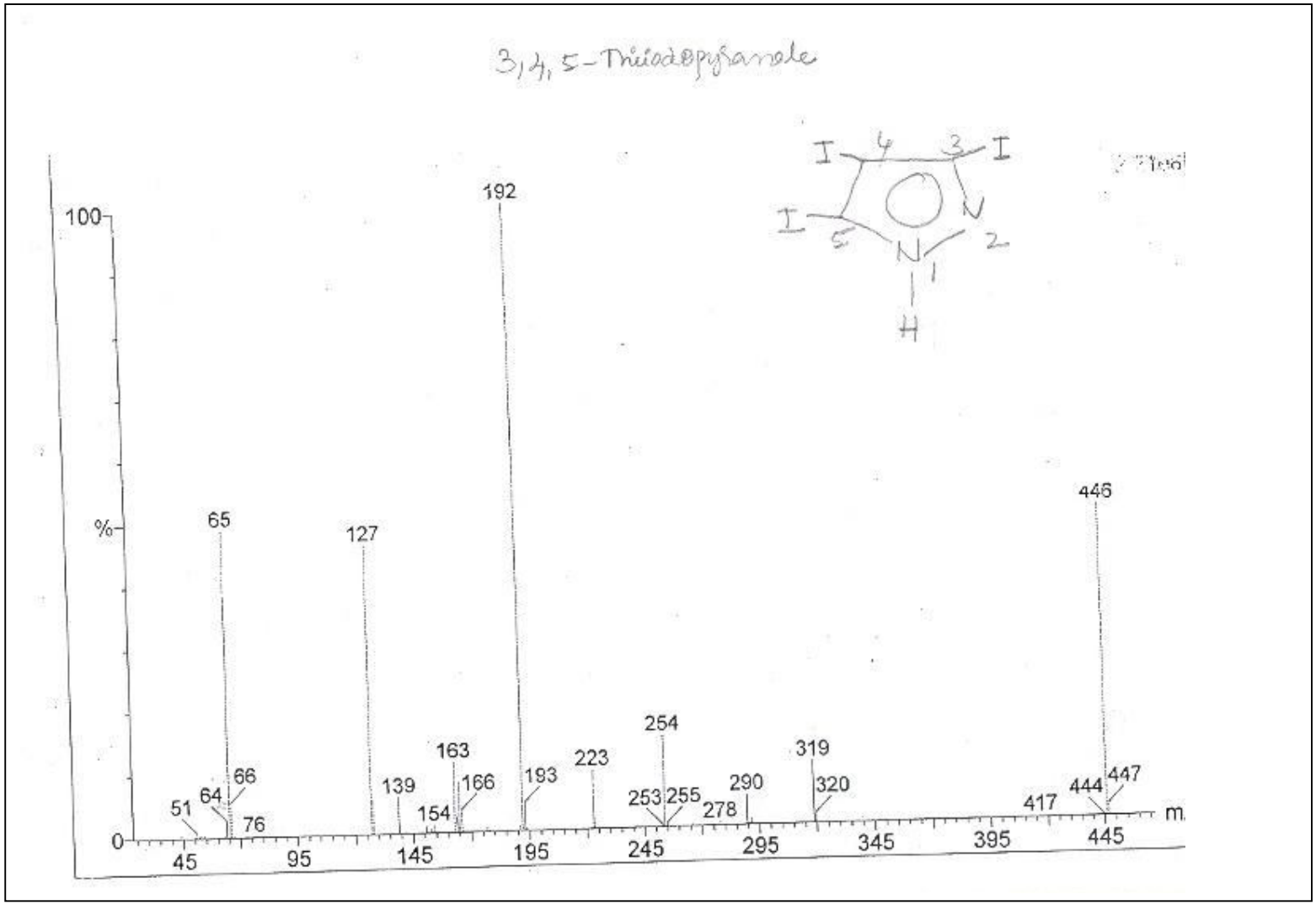
^{1}H NMR spectrum of 1-Methyl-3,4,5-trinitropyrazole (**12**)



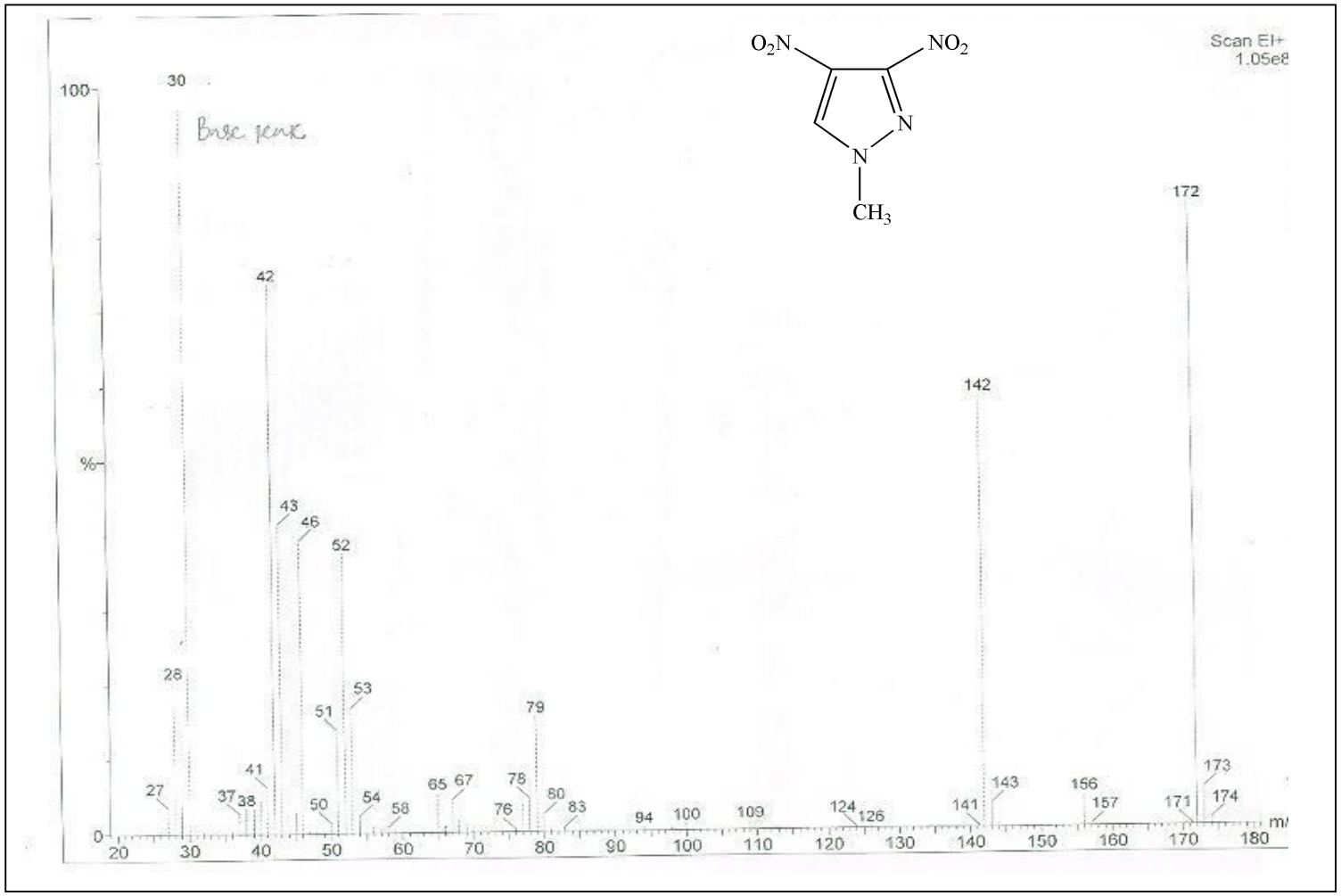
Mass spectrum of 3,4-dinitropyrazole (**8**)



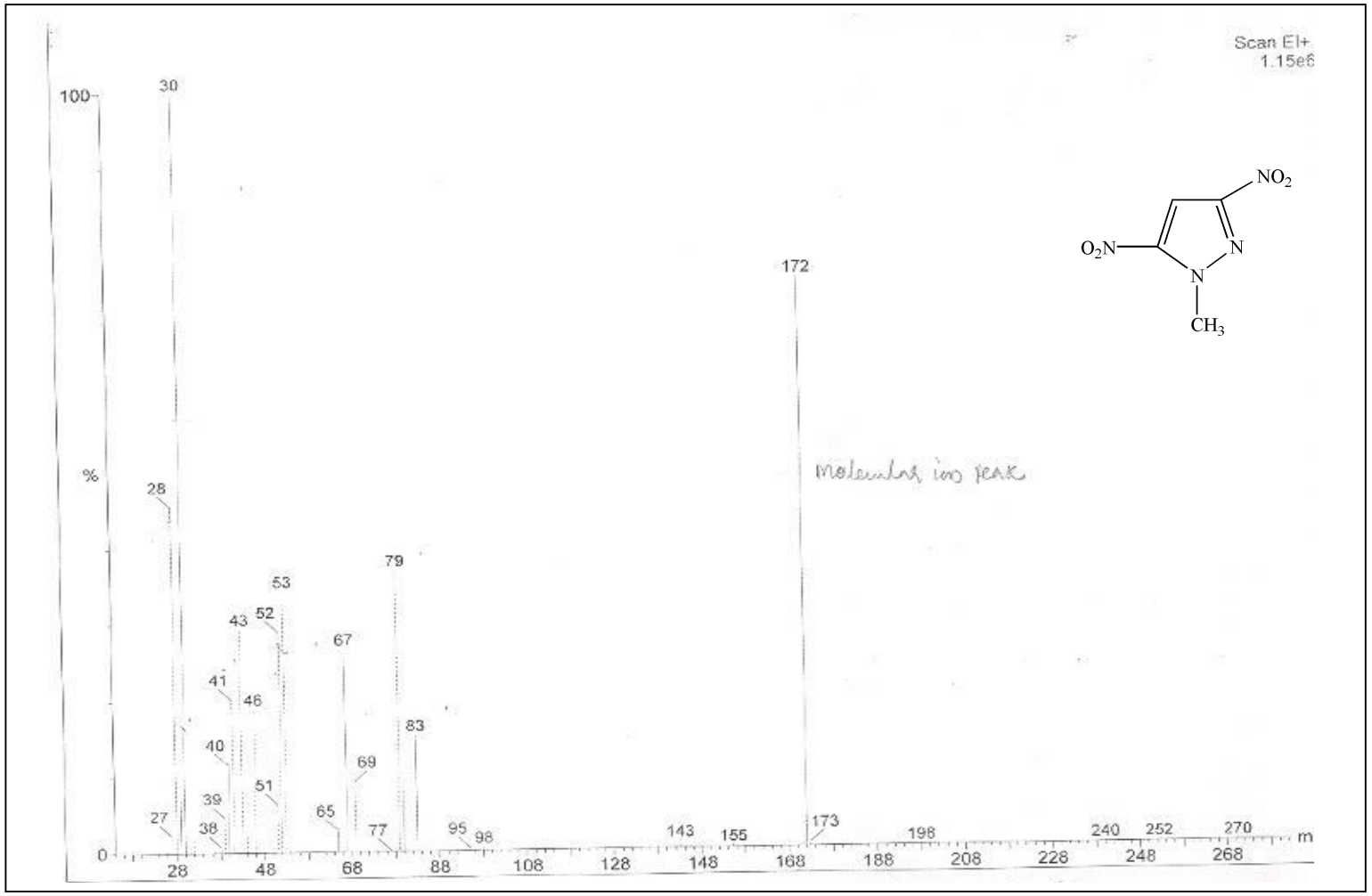
Mass spectrum of 3,4,5-triiodopyrazole (**16**)



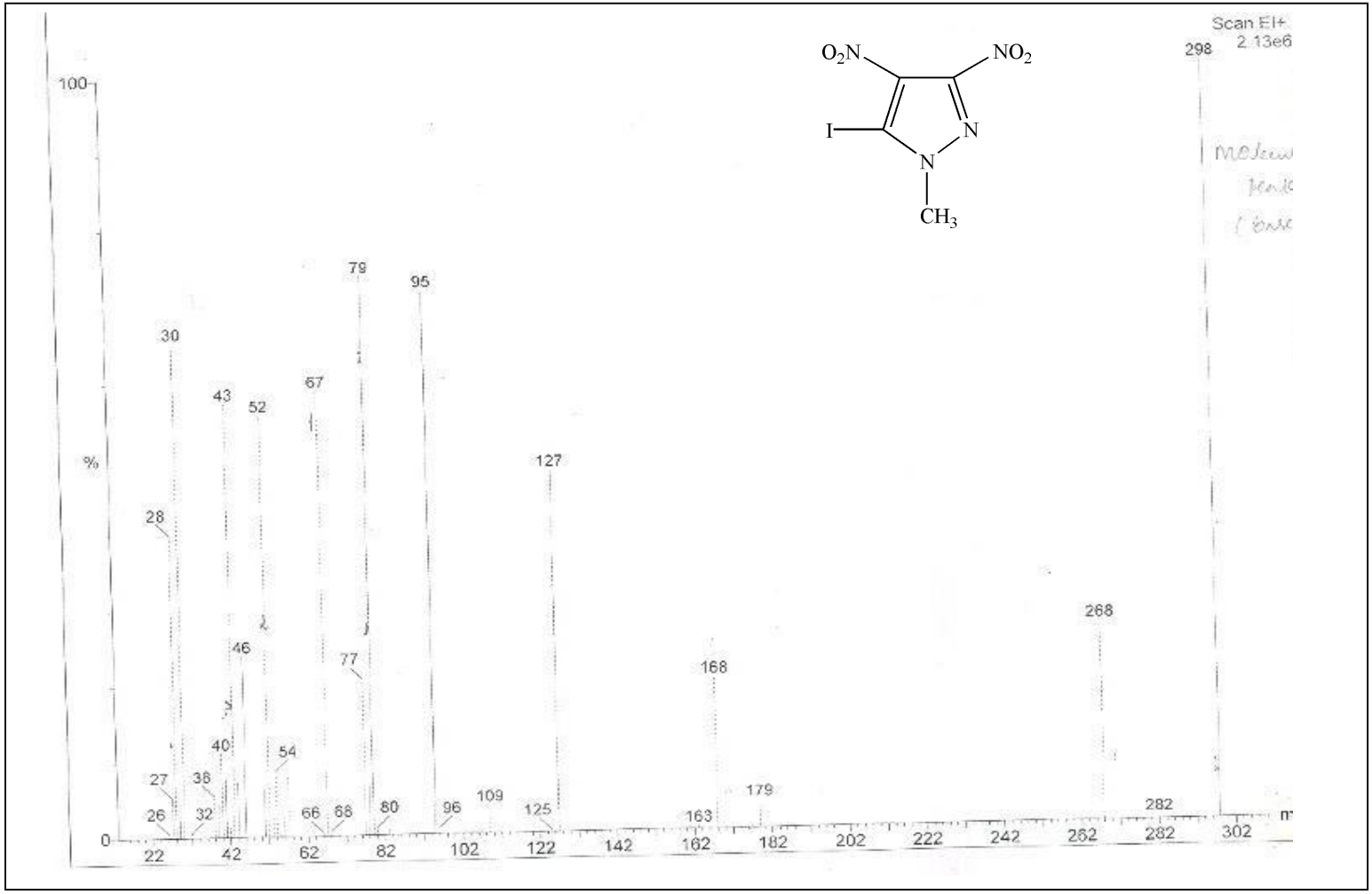
Mass spectrum of 1-methyl-3,4-dinitropyrazole (**9**)



Mass spectrum of 1-methyl-3,5-dinitropyrazole (**10**)



Mass spectrum of 5-iodo-1-methyl-3,4-dinitropyrazole (**21**)



List of Publications

1. **P. Ravi**, Girish M. Gore, V. Venkatesan, Surya P. Tewari, Arun K. Sikder, Theoretical studies on the structure and detonation properties of amino-, methyl and nitro substituted 3,4,5-trinitropyrazoles, *J. Hazard. Mater.* **2010**, *183*, 859-865.
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7. **P. Ravi**, Girish M. Gore, Surya P. Tewari, Arun K. Sikder, A review of melt cast explosives, *Prop., Explos., Pyrotech.*, **2011** (in press).
8. **P. Ravi**, Girish M. Gore, Surya P. Tewari, Arun K. Sikder, Thermal decomposition of melt cast explosive: Isoconversional analysis of 1-methyl-3,4,5-trinitropyrazole (MTNP) *Thermochimica Acta* **2011** (communicated).