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Experimental and theoretical studies on the structure and vibrational properties of nitropyrazoles

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HIGHLIGHTS

• Pyrazoles as models of simple aromatic systems.

• Observed vibrational frequencies with the calculated at the B3LYP/aug-cc-pVDZ was superior to B3LYP/311++G** basis set.

• Calculated geometries of pyrazoles are in excellent agreement with the average experimental geometries.

• Differences in the bond distances and angles are confined to the twist of the nitro group.

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ABSTRACT

We report a theoretical and experimental study on the structure and vibrational properties of pyrazole and its mononitropyrazoles. The infrared (IR) and Raman spectra of pyrazole, N-nitropyrazole, 3-nitropyrazole and 4-nitropyrazole have been recorded in the solid state. To interpret the experimental data, *ab initio* computations of the vibrational frequencies were carried out using the Gaussian 03 program following the full optimizations at the HF/6-311++G(d,p), B3P86/6-311++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVDZ levels. The combined use of experiments and computations allowed a firm assignment of the majority of observed bands for all compounds. The calculated stretching frequencies have been found to be in good agreement with the experimental frequencies. However, the fundamental vibrational frequencies of nitropyrazoles calculated at the B3LYP/aug-cc-pVDZ level are superior compared with those values that are obtained at the HF/311++G(d,p), B3P86/311++G(d,p) and B3LYP/ 311++G(d,p) levels of theory. The differences in the bond distances and bond angles are confined to the twist of the nitro group that present the greatest deviation from planarity in molecules.

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1. Introduction

Pyrazoles have been studied as models of simple aromatic systems, some of which are of biological and pharmaceutical interest [1–4]. These are simplest bi-functional heteroaromatic compounds: they have a hydrogen bond donor atom group (i.e., N—H, pyrrole like nitrogen atom) and hydrogen acceptor group (i.e., N2 atom, pyridine like nitrogen; numeral 2 represents the position of second N-atom in the ring). Nitration of pyrazoles using nitric acid, nitric acid-sulfuric acid, or nitric acid-trifluoroacetic anhydride mixtures leads to substitution in the 4-position [5]. N-nitropyrazoles were rearranged in chlorobenzene, anisole, xylene, mesitylene, *n*-decane, N-methylformamide, propylene glycol, or benzonitrile at moderate temperature (120–190 °C) for 3–7 h into the C-nitropyrazoles [6–8]. C-nitropyrazoles were formed quanti-

tatively and in some instances denitration of N-nitropyrazoles during thermal isomerization was observed. There have been several studies reporting the vibrational analysis of pyrazole derivatives [9–18]. In most of these studies, only the infrared spectra of the normal and deuterated species were presented. In some of the recently reported [16] Raman studies, the spectral data for the gas phase were reported with particular emphasis on the N—H and C—H stretching regions. Durig et al. [17] have investigated the Fourier Transform Raman spectrum of polycrystalline pyrazole with the expectation that these new data well help address some of the questionable assignments.

The influence of substituents on the physico-chemical properties and the structural parameters of azoles is one of the main aspects of physical organic chemistry. Pyrazole, N-nitropyrazole, 3nitropyrazole and 4-nitropyrazole are known for their strong hydrogen bonds in the solid states [1,2]. However, the vibrational spectra of these compounds are not yet fully understood. The aim of this work was the comparison of N-nitropyrazole, 3-nitropyrazole, and 4-nitropyrazole from the viewpoint of vibrational spectroscopy. Furthermore, *ab initio* molecular orbital calculations

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were carried out using the density functional theory (DFT). It is anticipated that DFT level of calculations with 6-311++G(d,p) and aug-cc-pVDZ basis sets are reliable for predicting the vibrational spectra of compounds. Accordingly, we have performed the molecular orbital calculations at the HF/6-311++G(d,p), B3LYP/6-311++G(d,p), B3P86/6-311++G(d,p) and B3LYP/aug-cc-pVDZ level to study the geometric features, electronic structures and vibrational properties of pyrazole, N-nitropyrazole, 3-nitropyrazole, 4nitropyrazole and 5-nitropyrazole.

2. Experimental

All the reagents and solvents were purchased from Sigma-Aldrich and used without further purification. Melting points were recorded by a capillary melting point apparatus and were uncorrected. All experiments were monitored by thin-layer chromatography (silica gel 60F254 Merck). FT-IR spectra were recorded on a Perkin-Elmer FT-IR-1600 spectrophotometer in KBr matrix. The band positions are reported in wave numbers (cm⁻¹). For the measurement of the Raman spectra a Witec alpha 300S (Germany) confocal Raman spectrometer was applied using 2 cm⁻¹ resolution and printed the output to a file in cm⁻¹ steps. ¹H NMR spectra were recorded on a 300-MHz Varian instrument with dimethylsulfoxide (DMSO-d₆) and CDCl₃ solvents. Chemical shift values are reported in δ units (parts per million) relative to tetramethylsilane (TMS) as an internal standard. Gas chromatography-mass spectrometry (GC-MS) was carried out with glass columns packed with 3% OV-17 on Chromosorb W, 100-120 mesh, treated with DMCS in Varian 1400 instrument fitted with flame ionization detector and nitrogen was used as carrier gas.

2.1. Synthesis of N-nitropyrazole

Freshly prepared acetyl nitrate (HNO₃, 1.8 mL, d = 1.54 g cm⁻³ and acetic anhydride, 4.2 mL) was added to pyrazole (1.0 g) dissolved in acetic acid (2.8 mL) at 25 °C. After stirring for 30 min the reaction mixture was poured into water. The crude yield after washing with water and drying was 1.4 g (84%). m.p. 91–92 °C. FT-IR (KBr, cm⁻¹): 1617, 1320 (N–NO₂). ¹H NMR (DMSO-*d*₆) δ : 8.65 (d, 1H, 5-H), 7.80 (s, 1H, 3-H), 6.73 (m, 1H, 4-H). EI-MS: m/z 113 (M⁺).

Anal. Calcd for C₃H₃N₃O₂ (113.08): C, 31.83; H, 2.67; N, 37.26. Found: C, 32.88; H, 2.62; N, 37.43.

2.2. Synthesis of 3-nitropyrazole

A solution of 1.0 g of N-nitropyrazole in 10 mL of benzonitrile was heated for 3 h at 180 °C, after cooling the reaction mixture was poured into 30 mL of hexane. 3-nitropyrazole was collected by filtration. The crude yield after washing with hexane and drying was 0.93 g (98%). The solid was recrystallized from water. m.p. 174–175 °C. FT-IR (KBr, cm⁻¹) 3180 (N–H), 1520 and 1351 cm⁻¹ (NO₂). ¹H NMR (DMSO-*d*₆) δ : 7.96 (d, 1, 5(3)-H), 6.96 (d, 1, 4-H). EI-MS: m/z 113 (M⁺⁻). Anal. Calcd for C₃H₃N₃O₂: C, 31.86; H, 2.67; N, 37.16. Found: C, 32.19; H, 2.84; N, 37.18.



Fig. 1. The molecular formula of pyrazoles with the numbering of atoms as used in the text: (a) pyrazole, (b) N-nitropyrazole, (c) 3-nitropyrazole, (d) 4-nitropyrazole and (e) 5-nitropyrazole.

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2.3. Synthesis of 4-nitropyrazole

1-Nitropyrazole (1 g) was slowly added to a round-bottomed flask containing H₂SO₄ (98%, 5 mL) and stirred for 20 h at room temperature. The reaction mixture was slowly transferred to a beaker containing ice with stirring. The solution was extracted with ether. The organic layer was dried with Na₂SO₄ then evaporated to afford 4-nitropyrazole as a colorless solid (0.97 g, 96%). The solid was recrystallized from ether/hexane to get white crystalline compound. m.p. 163–165 °C; FT-IR (KBr, cm⁻¹) 3186 (N–H), 1526 and 1353 cm⁻¹ (NO₂). ¹H NMR (DMSO-*d*₆) δ : 8.26 (d, 1, 5-H), 6.76 (d, 1, 5-H), 6.76 (d, 1, 5-H), 6.76 (d, 1).

Table 1	1
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Geometric parameters of pyrazole.

Parameter ^a	HF/6- 311++G(d,p)	B3P86/6- 311++G(d,p)	B3LYP/6- 11++G(d,p)	B3LYP/ aug-cc- pVDZ	Expt. values from X-ray [28]
N1-N2	1.328	1.338	1.348	1.349	1.344
N2-C3	1.301	1.326	1.329	1.334	1.333
C3–C4	1.415	1.409	1.414	1.417	1.378
C4–C5	1.363	1.377	1.377	1.385	1.382
C5-N1	1.341	1.352	1.358	1.359	1.325
N1-H6	0.992	1.006	1.007	1.009	1.040
C3—H7	1.072	1.078	1.079	1.086	0.92
C4—H8	1.069	1.077	1.077	1.084	0.96
C5—H9	1.071	1.078	1.078	1.085	0.97
N1-N2-C3	105.2	104.3	104.3	104.2	104.8
N2-C3-C4	111.5	111.8	11.80	111.8	111.4
C3-C4-C5	103.9	104.5	104.6	104.5	104.7
C4-C5-N1	106.6	106.1	106.1	106.1	107.1
C5-N1-N2	112.7	113.3	113.1	113.2	111.9
H6-N1-N2-C3	-180.0	-180.0	-180.0	-180.0	-
N1-N2-C3-H7	180.0	180.0	180.0	180.0	-
N2-C3-C4-H8	-180.0	-180.0	-180.0	-180.0	-
C3-C4-C5-H9	180.0	180.0	180.0	180.0	-
C4-C5-N1-H6	180.0	180.0	180.0	180.0	-

^a Bond distances in Å and bond angles in degree.

Table 2

Geometric parameters of N-nitropyrazole.

Parameter ^a	HF/6- 311++G(d,p)	B3P86/6- 311++G(d,p)	B3LYP/6- 11++G(d,p)	B3LYP/ aug-cc- pVDZ	Expt. values from X-ray [29]
N1-N2	1.336	1.335	1.345	1.348	1.387
N2-C3	1.288	1.318	1.321	1.326	1.315
C3–C4	1.431	1.421	1.425	1.428	1.407
C4–C5	1.347	1.366	1.369	1.374	1.341
C5-N1	1.367	1.368	1.375	1.376	1.364
N1-N6	1.372	1.427	1.437	1.429	1.399
C3—H9	1.071	1.081	1.079	1.086	0.94
C4—H10	1.068	1.078	1.078	1.084	0.93
C5-H11	1.067	1.076	1.075	1.082	0.93
N6-07	1.170	1.196	1.202	1.207	1.204
N6-08	1.187	1.209	1.215	1.222	1.201
08-H11	2.471	2.496	2.519	2.512	-
N1-N2-C3	104.3	103.5	103.5	103.4	102.3
N2-C3-C4	112.1	112.2	112.2	112.2	112.8
C3–C4–C5	104.7	105.5	105.2	105.2	105.7
C4-C5-N1	105.3	104.7	104.8	104.8	105.2
C5-N1-N2	113.4	114.6	114.3	114.4	113.9
07-N6-08	1127.7	129.2	129.0	128.7	120.0
N6-N1-N2-C3	-180.0	180.0	180.0	180.0	-
N1-N2-C3-H9	180.0	-180.0	180.0	-180.0	-
N2-C3-C4-H10	-180.0	-180.0	-180.0	180.0	-
C3-C4-C5-H11	180.0	180.0	180.0	-180.0	-
C4-C5-N1-N6	180.0	-180.0	-180.0	-180.0	-
07-N6-N1-N2	-0.03	0.04	0.23	-0.02	-
08-N6-N1-C5	-0.02	-0.05	-0.14	-0.04	-

^a Bond distances in Å and bond angles in degree.

3-H). EI-MS: m/z 113 (M⁺). Anal. Calcd for C₃H₃N₃O₂: C, 27.54; H, 3.88; N, 32.42. Found: C, 28.31; H, 3.21; N, 31.38.

3. Computational detail

Ab initio molecular orbital calculations were carried out on a desktop Pentium computer using the Gaussian 03 suite [19]. The

Table 3
Geometric parameters of 3-nitropyrazole.

Parameter ^a	HF/6- 311++G(d,p)	B3P86/6- 311++G(d,p)	B3LYP/6- 11++G(d,p)	B3LYP/ aug-cc- pVDZ	Expt. values from X-ray [30]
N1-N2	1.314	1.329	1.337	1.337	1.341
N2-C3	1.296	1.326	1.329	1.332	1.329
C3–C4	1.407	1.407	1.411	1.413	1.369
C4–C5	1.363	1.3765	1.379	1.381	1.367
C5-N1	1.348	1.361	1.365	1.365	1.335
C3—N6	1.445	1.445	1.452	1.455	1.453
N1-H9	0.993	1.011	1.009	1.011	-
C4—H10	1.067	1.008	1.077	1.082	-
C5-H11	1.069	1.089	1.079	1.084	-
N6-07	1.188	1.220	1.226	1.223	1.213
N6-08	1.197	1.228	1.235	1.232	1.220
08—H10	2.722	2.725	2.737	2.747	-
N1-N2-C3	104.01	103.0	103.1	103.2	101.7
N2-C3-C4	113.4	113.6	113.5	113.5	114.8
C3–C4–C5	102.6	103.2	103.3	103.3	102.9
C4-C5-N1	106.7	106.3	106.3	106.3	107.3
C5-N1-N2	113.2	113.9	113.7	113.8	113.3
07-N6-08	125.8	125.7	125.5	125.6	124.2
H9-N1-N2-C3	180.0	180.0	180.0	180.0	-
N1-N2-C3-N6	-180.0	180.0	180.0	180.0	-
N2-C3-C4-H10	180.0	-180.0	-180.0	180.0	-
C3-C4-C5-H11	-180.0	-180.0	180.0	180.0	-
C4-C5-N1-N9	180.0	-180.0	-180.0	-180.0	-
07-N6-C3-N2	0.11	0.06	0.00	0.05	-
08-N6-C3-C4	0.07	0.075	-0.00	0.05	-

^a Bond distances in Å and bond angles in degree.

Table 4			
Geomet	ric parame	eters of 4-niti	opyrazole.
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Parameter ^a	HF/6- 311++G(d,p)	B3P86/6- 311++G(d,p)	B3LYP/6- 11++G(d,p)	B3LYP/ aug-cc- pVDZ	Expt. values from X-ray
				I	[31]
N1-N2	1.339	1.351	1.359	1.358	1.345
N2-C3	1.297	1.323	1.326	1.327	1.312
C3-C4	1.411	1.410	1.415	1.417	1.374
C4–C5	1.367	1.383	1.386	1.388	1.362
C5-N1	1.327	1.342	1.347	1.348	1.317
N1-H9	0.993	1.008	1.009	1.010	-
C3—H10	1.068	1.079	1.079	1.034	-
C5—H11	1.068	1.079	1.079	1.083	-
C4—N6	1.421	1.425	1.431	1.434	1.420
N6-07	1.195	1.227	1.234	1.231	1.217
N6-08	1.198	1.229	1.236	1.233	1.235
07—H10	2.803	2.807	2.817	2.823	-
08–H11	2.766	2.783	2.795	2.801	-
N1-N2-C3	105.6	104.8	104.7	104.8	108.9
N2-C3-C4	109.8	110.3	110.3	110.3	107.8
C3-C4-C5	106.0	106.3	106.4	106.3	106.0
C4-C5-N1	105.0	104.5	104.7	104.7	108.0
C5-N1-N2	113.5	114.1	113.8	113.9	108.8
07-N6-08	125.3	125.2	125.0	125.0	124.2
H9-N1-N2-C3	-180.0	-180.0	180.0	-180.0	-
N1-N2-C3-H10	180.0	-180.0	-180.0	180.0	-
N2-C3-C4-N6	180.0	180.0	180.0	-180.0	-
C3-C4-C5-H11	180.0	-180.0	180.0	-180.0	-
C4-C5-N1-H9	180.0	180.0	-180.0	180.0	-
07-N6-C4-C5	0.01	-0.01	0.04	-0.01	-0.2
08-N6-C4-C3	0.01	-0.01	0.02	-0.01	-

^a Bond distances in Å and bond angles in degree.

basis sets implemented in the program were employed without modification. The geometry of pyrazole and nitropyrazoles were fully optimized without symmetry constraints by the energy gradient methods. All optimized geometries were obtained by using the HF (Hartree-Fock), Becke 3LYP (B3LYP) and Becke 3P86 (B3P86) hybrid density functional with the 6-311++G(d,p) and aug-ccpVDZ basis sets [20-24]. Vibrational frequencies were calculated by using the analytical second derivatives at the HF/6-311++G(d,p), B3P86/6-311++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVDZ levels to confirm the stationary structures and to correct for the zero-point vibrational energy. The normal mode analysis for each structure yielded no imaginary frequencies for the 3*N*-6 vibrational degrees of freedom, where *N* is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process.

4. Results and discussion

4.1. Synthesis aspects

Table 5

The direct nitration of pyrazole using nitric acid or nitric acidsulfuric acid mixture leads to substitution in the 4-position. Hüttel and Büchele [5] synthesized N-nitropyrazole and its substituted derivatives. They also have described the rearrangement of Nnitropyrazoles to the 4-nitropyrazole derivatives in sulfuric acid solution in cold. We have synthesized nitropyrazoles starting from pyrazole (1) as shown in Scheme 1. N-Nitropyrazole (2) was synthesized in good yield (84%) using preformed acetyl nitrate at room

Geometric parameters of 5-nitropyrazole.								
Parameter ^a	HF/6- 311++G(d,p)	B3P86/6- 311++G(d,p)	B3LYP/6- 11++G(d,p)	B3LYP/ aug-cc- pVDZ	Expt. values from X-ray [30] ^b			
N1-N2	1.315	1.328	1.336	1.336	1.341			
N2-C3	1.102	1.338	1.342	1.343	1.329			
C3–C4	1.410	1.404	1.408	1.410	1.369			
C4–C5	1.360	1.380	1.384	1.385	1.367			
C5-N1	1.338	1.352	1.358	1.358	1.335			
N1-H9	0.994	1.010	1.011	1.0119	1.453			
C3-H10	1.069	1.080	1.080	1.085	-			
C4-H10	1.068	1.078	1.078	1.083	-			
C5-N6	1.428	1.425	1.431	1.433	-			
N6-07	1.190	1.224	1.230	1.227	1.213			
N6-08	1.198	1.232	1.238	1.235	1.220			
07H11	2.840	2.874	2.882	2.887	-			
O8H9	2.484	2.477	2.498	2.496	101.7			
N1-N2-C3	106.1	105.0	105.0	105.1	114.8			
N2-C3-C4	111.5	112.0	112.0	111.9	102.9			
C3–C4–C5	102.6	103.1	103.2	103.2	107.3			
C4-C5-N1	108.6	107.9	107.1	107.8	113.3			
C5-N1-N2	11.15	11.9	111.8	112.0	124.2			
07-N6-08	126.1	125.8	125.6	125.6	-			
H9-N1-N2-C3	-180.0	-180.0	-180.0	180.0	-			
N1-N2-C3-H10	180.0	180.0	-180.0	-180.0	-			
N2-C3-C4-H11	180.0	-180.0	-180.0	-180.0	-			
C3-C4-C5-N6	180.0	180.0	180.0	-180.0	-			
C4-C5-N1-H9	180.0	180.0	180.0	-180.0	-			
07-N6-C5-N1	0.01	0.05	0.05	180.0	-			
08-N6-C5-C4	0.00	0.02	0.03	0.01				

^a Bond distances in Å and bond angles in degree.

^b 3-Nitropyrazole and 5-nitropyrazole are annular tautomers and known to exist in solution state.



Fig. 2. 3D molecular electrostatic potential maps of model molecules: (a) pyrazole, (b) N-nitropyrazole, (c) 3-nitropyrazole, (d) 4-nitropyrazole and (e) 5-nitropyrazole.

temperature. Usually, N-nitropyrazole could be purified by direct crystallization or by very mild acid hydrolysis of the N-acetyl derivatives prior to crystallization. We have synthesized 3-nitropy-razole (**3**) in higher yield (98%) heating 10% solution of N-nitropyrazole (**2**) in benzonitrile at 180 °C for 3 h.

For the mechanism of the rearrangement of N-nitropyrazoles, Janssen et al. [6–8] proposed a two-step process involving an unprecedented [1,5]-sigmatropic shift of the nitro group and fast re-aromatization of the intermediately formed 3*H*-pyrazole (**5**). 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 [7]. The thermal rearrangement of N-nitropyrazole unsubstituted at the 3-position has been found to be a convenient method for the synthesis of 3-nitropyrazole (yield, 98%). Hüttel and Büchele method was used to synthesize 4-nitropyrazole (**4**) (yield, 96%) using nitric acid-sulfuric acid mixture.

4.2. Optimized structures

We have optimized the structures at the HF/6-311++G(d,p), B3LYP/6-311++G(d,p), B3P86/6-311++G(d,p) and B3LYP/aug-ccpVDZ levels and the molecular frameworks of pyrazoles with the numbering are presented in Fig. 1. No imaginary vibration frequencies were found confirming that these structures correspond to true energy minima. All the model molecules belonged to C₁ point group. The lowest frequency, total energy, zero-point energy, thermal correction to enthalpy and frontier molecular orbital energies and their gaps of pyrazole, N-nitropyrazole, 3-nitropyrazole, 4nitropyrazole and 5-nitropyrazole are summarized in Table 1S



Fig. 3. 3D Frontier molecular orbital maps of model molecules computed from the B3LYP/aug-cc-pVDZ level.



Fig. 4. Theoretical IR spectra of pyrazoles computed from the B3LYP/aug-cc-pVDZ level.

(supporting information). The lowest frequencies varying from 64 to 102 cm^{-1} are for the torsions of NO₂ groups [25–27]. The selected bond lengths and angles for the geometrical parameters for pyrazole, N-nitropyrazole, 3-nitropyrazole, 4-nitropyrazole and 5-nitropyrazole at the different theoretical levels are presented in Tables 1-5 respectively. Their pyrazole rings do not deviate significantly from the planarity. It should be noted that our theoretical calculations indicate that NO₂ group is not symmetric and it is slightly tilted away from the imino nitrogen of the azole ring (i.e., the NO bond lengths are slightly different and thus also O-N-O angles). In the present calculations, the HF/6-311++G(d,p), B3LYP/6-311++G(d,p), B3P86/6-311++G(d,p) and B3LYP/aug-cc-pVDZ bond lengths differ from the crystal averages with deviations of 0.027-0.034 Å. Additionally, some ring deformations in the crystalline phase compared to the structure in the gas phase exist. Evidence for the planarity of the molecules arrives from the variation analysis of rotational parameters with vibrational quantum numbers and from inertial defect values. The bond

Table 6

Theoretical and calculated frequencies of pyrazole.

lengths, bond angles, total energies and frontier molecular orbital energies were varying with the position of NO₂ group. Comparing the C3-C4 bond lengths in all compounds irrespective position of NO₂ group have been found to be longer. This might be due to electron withdrawing effect of NO2 group attached to ring C or N atom and thus C3-C4 bond stands for the longest bond distance among the other bonds. Furthermore, the N1–NO₂ bond length in N-nitropyrazole is longer. As seen by comparing the experimental data of pyrazole, N-nitropyrazole, 3-nitropyrazole and 4-nitropyrazole to the theoretical results at the HF/6-311++G(d,p), B3P86/6-311++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-ccpVDZ levels, the optimized bond lengths are in good agreement with experimental values of the crystalline state [28-31]. However, there is a little difference in the N–NO₂ bond length. The calculated N-NO₂ distance (1.427–1.437 Å) computed from the B3P86/6-311++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-ccpVDZ levels is higher than the corresponding experimental distance in the crystalline state (1.399 Å). However, the calculated N–NO₂ length (1.347 Å) computed from the HF/6-311++G(d,p) level is smaller than the experimental value. The crystalline structure of nitropyrazole shows that the N-O oxygen forms a hydrogen bond with the hydrogen of the N-H group of the other nitropyrazole molecule. These results indicate that there is an intermolecular effect (hydrogen bonding) especially shown on the N–O bond length of nitropyrazole in the crystalline state that is longer than the optimized value in the gas phase.

4.3. Molecular electrostatic potentials and Frontier molecular orbital energies

The molecular electrostatic potential is the potential energy of a proton at a particular location near a molecule. Negative electrostatic potential corresponds to an attraction of proton by concentrated electron density in the molecules (colored in shades of red). Positive electrostatic potential corresponds to repulsion of the proton by the atomic nuclei in regions where low electron density exists and the nuclear charge is incompletely shielded (colored in shades of blue). The calculated partial charges represented as spheres (yellow is negative and red is positive) show how the molecule would interact with approaching protons or positive charges (Fig. 2). As a proton approaches a negative region an attractive

Mode nos. (Pyrazole)	Experimental		HF/6-311++G(d,p)	B3P86/6-311++G(d,p)	B3LYP/6-11++G(d,p)	B3LYP/aug-cc-pVDZ	Assignments
	FT-IR	FT-Raman					
1	3159	3684	3915	3684	3664	3660	N—H str
2		3402	3422	3284	3267	3277	N—H str
3		3388	3402	3265	3250	3259	C—H str
4		3284	3388	3251	3236	3244	C—H str
5		1727	1727	1574	1563	1560	C=N str
6	1647		1621	1493	1477	1480	N1-N2
7	1557	1533	1532	1437	1420	1424	Ring def
8		1530	1530	1395	1382	1379	Ring def
9	1470	1477	1395	1287	1279	1274	Ring def
10	1396	1287	1279	1197	1176	1177	Ring def
11	1358	1219	1219	1153	1141	1138	Ring def
12	1136	1196	1133	1059	1053	1047	Ring def
13	1034	1134	1117	1056	1045	1042	Ring def in plane
14			1014	943	941	934	Ring def in plane
15			1014	923	924	917	Ring def in plane
16	937	980	997	893	893	885	Ring def
17		943	980	844	843	836	Ring def
18	840	924	845	752	750	746	Ring def
19	758	750	741	693	686	687	Ring def
20	615	687	682	636	633	635	Ring def out of plane
21		565	565	542	523	545	Ring def out of plane

interaction results in negative potential energy (colored in shades of red). The electron density isosurface is a surface on which the molecule's electron density has a particular value and that encloses a specified fraction of the molecule's electron probability density. The electrostatic potential at different points on the electron density isosurface is shown by coloring the isosurface with contours.

Table 7		
Theoretical and calculated	frequencies	of N-nitropyrazole.

Mode nos. (N-	Experi	mental	HF/6- B3P86/6-	B3LYP/6-	B3LYP/aug-cc-	Assignments	
nitropyrazole)	FT- IR	FT- Raman	311++G(d,p)	311++G(d,p)	11++G(d,p)	pVDZ	
1		3296	3461	3309	3297	3308	C—H str
2		3254	3419	3275	3260	3268	C—H str
3	3125		3397	3254	3240	3248	
4			1864	1743	1692	1691	C=N str
5		1749	1749	1574	1561	1560	NO ₂ str
6	1620	1607	1607	1456	1436	1441	NO ₂ str
7		1555	1555	1425	1406	1407	NO ₂ str
8		1482	1519	1371	1344	1349	NO ₂ str
9	1321	1371	1482	1340	1311	1316	Ring def + NO ₂ str
10		1263	1403	1263	1254	1248	Ring def
11	1290	1178	1334	1194	1178	1181	Ring def
12		1076	1177	1076	1066	1065	Ring def
13	1163	1047	1104	1047	1040	1037	Ring def + NO_2 str
14	1062	1036	1036	974	958	956	Ring def
15		1033	1033	921	921	915	Ring def
16	1028		1008	912	912	903	Ring def
17			995	871	871	863	Ring def + NO ₂ bend
18	937		941	845	834	822	Ring def out of plane + NO ₂
							bend
19		865	866	768	765	763	Ring def in plane
20			845	744	733	746	Ring def out of plane
21	777	648	696	648	644	647	Ring puckering
22	630		644	586	575	580	N–NO ₂ bending
23	563	593	594	574	567	572	Ring def + NO_2 bend
24	455	438	523	444	433	438	$N-NO_2$ str.
25		303	303	264	261	262	Ring def + NO_2 bend
26		137	138	144	138	160	NO ₂ bend
27		78	89	80	78	86	NO ₂ ben

Table 8

Theoretical and calculated frequencies of 3-nitropyrazole.

Mode nos. (3-	Experi	imental	HF/6-	B3P86/6-	B3LYP/6-	B3LYP/aug-cc-	Assignments
nitropyrazole)	FT- IR	FT- Raman	311++G(d,p)	311++G(d,p)	11++G(d,p)	pVDZ	
1		3444	3915	3682	3658	3639	N—H str
2		3308	3478	3326	3312	3301	C—H str
3	3157	3268	3444	3294	3279	3267	N—H str
4		1841	1841	1668	1621	1614	C=N str
5	1556	1742	1742	1581	1566	1558	NO ₂ str
6	1514		1670	1514	1493	1488	NO ₂ str
7	1483	1472	1627	1472	1451	1448	NO ₂ str
8	1423	1417	1571	1445	1417	1410	NO ₂ str
9	1383	1427	1559	1427	1402	1398	–N–H def + ring def + NO ₂ str
10	1352	1396	1396	1293	1277	1273	Ring def + —N—H def in plane
11	1250		1340	1255	1232	1226	Ring def + —N—H def in plane
12	1210	1188	1188	1111	1098	1092	—N—H def in plane + ring def
13	1090	1160	1160	1068	1068	1056	Ring def + —N—H def in plane + NO ₂ str
14	1050		1083	1000	993	989	Ring def + —N—H def in plane
15	990		1022	943	941	939	—N—H def in plane + ring def
16	927	883	1011	883	881	872	Ring def in plane
17	823	830	932	838	829	832	Ring def + NO_2 bend
18	787	786	895	792	786	793	Ring def out of plane + NO ₂ bend
19	756		860	765	761	760	Ring def in plane
20		748	747	691	684	687	Ring def out of plane
21	611	690	690	630	626	630	Ring def out of plane
22			640	593	577	593	-N-H def + ring def + NO ₂ bend
23			588	543	538	537	Ring def + NO_2 bend + $-N-H$ def
24	439	438	482	444	438	437	Ring def + NO_2 bend
25			262	237	238	23	Ring def + NO_2 bend
26		248	248	220	220	220	NO ₂ bend
27		66	66	67	65	65	NO ₂ bend

The more red/blue differences, the more polar the molecule. If the surface is largely white or lighter color shades, the molecule is mostly non-polar.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies play a crucial role in governing the chemical reactions. In several studies it is revealed

Table 9

Theoretical and calculated frequencies of 4-nitropyrazole.

Mode nos. (4- nitropyrazole)	Experimental		HF/6-	B3P86/6-	B3LYP/6-	B3LYP/aug-cc-	Assignments
	FT- IR	FT- Raman	311++G(d,p)	311++G(d,p)	11++G(d,p)	pVDZ	
1	3178	3665	3920	3688	3666	3645	N—H str
2	3132	3314	3464	3314	3300	3288	C—H str
3	2999	3304	3457	3305	3291	3276	N—H str
4			1808	1645	1601	1594	C=N str
5	1734		1750	1598	1578	1572	NO ₂ str
6			1659	1514	1496.	1494	NO ₂ str
7			1641	1477	1452	1446	NO ₂ str
8	1579	1577	1578	1466	1437	1434	NO ₂ str
9	1504	1530	1531	1399	1378	1372	-N-H def + ring def + NO ₂ str
10	1410	1452	1436	1321	1307	1302	Ring def + —N—H def in plane
11	1358	1307	1313	1218	1207	1197	Ring def + — N—H def in plane
12	1286	1256	1256	1170	1158	1148	—N—H def in plane + ring def
13	1190	1139	1140	1058	1041	1037	Ring def + —N—H def in plane + NO ₂ str
14	1159		1088	1009	1004	1000	Ring def + —N—H def in plane
15	1028	1028	1028	941	937	936	—N—H def in plane + ring def
16	995	1009	1017	898	898	898	Ring def in plane
17	937	1004	1004	844	844	846	Ring def + NO_2 bend
18	895		923	831	822	825	Ring def out of plane + NO ₂ bend
19	852	862	862	763	754	771	Ring def in plane
20			744	690	683	689	Ring def out of plane
21		690	677	621	615	625	Ring def out of plane
22		615	624	583	570	584	Ring def + NO_2 bend
23	592	595	596	547	543	541	Ring def + NO_2 bend
24	434		480	442	438	437	Ring def + NO_2 bend
25			237	215	217	217	Ring def + NO ₂ bend
26		228	228	210	211	210	NO ₂ bend
27		87	98	88	88	87	NO ₂ bend

Table 10

Theoretical and calculated frequencies of 5-nitropyrazole.

Mode nos. (5-	Experimental		HF/6-	B3P86/6-	B3LYP/6-	B3LYP/aug-cc-	Assignments ^a
nitropyrazole)	FT-	FT-	311++G(d,p)	311++G(d,p)	11++G(d,p)	pVDZ	
	IR	Raman					
1		3444	3909	3671	3653	3634	N—H str
2		3308	3467	3318	3303	3292	C—H str
3	3157	3268	3436	3287	3272	3256	N—H str
4		1841	1829	1651	1604	1597	C=N str
5	1556	1742	1760	1593	1574	1568	NO ₂ str
6	1514		1648	1513	1492	1490	NO ₂ str
7	1483	1472	1639	1465	1447	1440	NO ₂ str
8	1423	1417	1566	1431	1398	1396	NO ₂ str
9	1383	1427	1494	1364	1347	1339	Ring def + – N–H def + NO ₂ str
10	1352	1396	1404	1291	1283	1276	—N—H def in plane + ring def
11	1250		1335	1260	1239	1233	—N—H def in plane + ring def
12	1210	1188	1246	1153	1137	1130	Ring def + —N—H def in plane
13	1090	1160	1120	1053	1052	1039	—N—H def in plane + ring def + NO ₂
							str
14	1050		1119	1034	1027	1024	Ring def + —N—H def in plane
15	990		1021	930	929	928	—N—H def in plane + ring def
16	927	883	1008	908	907	898	Ring def in plane
17	823	830	932	830	826	824	Ring def + NO ₂ bend
18	787	786	925	827	821	818	Ring def out of plane + NO ₂ bend
19	756		856	761	752	769	Ring def in plane
20		748	751	699	692	695	Ring def out of plane
21	611	690	673	618	615	620	Ring def out of plane
22			637	591	578	595	Ring def + $-N-H$ def + NO_2 bend
23			588	543	538	538	Ring def + NO_2 bend + $-N-H$ def
24	439	438	483	446	441	440	Ring def + NO ₂ bend
25			248	222	224	223	Ring def + NO ₂ bend
26		248	230	203	202	204	NO ₂ bend
27		66	101	102	100	101	NO ₂ bend

^a 3-Nitropyrazole and 5-nitropyrazole are annular tautomers and known to exist in solution state.

that the band gap between the frontier molecular orbital energies is an important stability index of the molecules [32–39]. 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. In other words, smaller the band gap between HOMO and LUMO easier is the electron transition and thus lowers the stability. The molecule with large band gap that is if $\varepsilon_{\rm HOMO} - \varepsilon_{\rm LUMO} \gg 0$, then very little electron transfer occurs. If the respective orbital energies are quite similar that is if $\varepsilon_{\rm HOMO} - \varepsilon_{\rm LUMO} = 0$, strong electron transfer occurs. The frontier molecular orbitals



Fig. 5. Experimental IR spectra of model compounds: (a) pyrazole, (b) N-nitropyrazole, (c) 3-nitropyrazole and (d) 4-nitropyrazole.

computed from the B3LYP/aug-cc-pVDZ level are shown in Fig. 3. The frontier molecular orbital energies have been decreased by substituting hydrogen for NO₂ group. In other words, the electron withdrawing groups lowers the LUMO and HOMO energy levels while electron donating groups increases the LUMO and HOMO energy levels. Furthermore, the band gap is highly correlative with the Hess-Schaad resonance energy per π -electron, a measure of thermodynamic stability due to the cyclic conjugation [35]. This correlation indicates that thermodynamically stable compounds are also kinetically stable. Thus, for a molecule to be isolated, it must be not only thermodynamically but also kinetically stable. The order of the stability based on the total energy, frontier molecular orbital energies and their gap is as follows: 4-nitropyrazole > 3-nitropyrazole > 1-nitropyrazole > 5-nitropyrazole.

4.4. Assignment of IR and Raman bands

N-Nitropyrazoles are readily characterized by IR spectroscopy. In addition to the absence of a N-H absorption band, the NO₂ stretching frequencies for a N-nitro groups are found at lower wave numbers (1295–1275 cm⁻¹) for the symmetric stretching vibration and a higher wave numbers (1625–1605 cm⁻¹) for asymmetric vibration [1,2,6,7]. However, the NO₂ stretching frequencies for a C-nitro group are found at lower wave numbers (1385 cm⁻¹– 1360 cm⁻¹) for the symmetric stretching vibration and a higher wave numbers (1565 cm⁻¹–1545 cm⁻¹) for asymmetric vibration. For C-nitro groups in nitropyrazoles we found symmetric vibrations in the 1375 cm^{-1} – 1330 cm^{-1} wave numbers region and asymmetric vibrations in the 1545 cm^{-1} – 1590 cm^{-1} wave numbers region. The band at 1700 cm⁻¹ may be ascribed to the C=N stretching vibration. This higher value is possibly due to the substitution of the NO₂ group on the C=N. The bands at 1550, 1360 and 790 cm⁻¹ can be assigned to the asymmetric and symmetric stretching and bending vibration of the NO₂ group respectively. Most of the remaining bands can be assigned to various amide group vibrations. Thus the bands appearing at 1470 cm^{-1} 1280 cm^{-1} , 740 cm $^{-1}$ and 610 cm $^{-1}$ wave numbers can be ascribed to the vibrations of secondary amino (-N-H) group of the pyrazole ring [40,41].

The predicted IR spectra of pyrazoles computed from the HF/6-311++G(d,p), B3P86/6-311++G(d,p) and B3LYP/6-311++G(d,p) are provided in supporting information. The predicted IR spectra of pyrazoles computed from the B3LYP/aug-cc-pVDZ level is shown in Fig. 4. The assignments of bands of pyrazole, N-nitropyrazole, 3nitropyrazole, 4-nitropyrazole and 5-nitropyrazole are summarized



Fig. 6. Theoretical Raman spectra of model compounds computed from the HF/6-311++G(d,p) level.



Fig. 7. Experimental Raman spectra of model compounds: (a) pyrazole, (b) Nnitropyrazole, (c) 3-nitropyrazole and (d) 4-nitropyrazole.

in Tables 6-10 respectively. The experimental IR spectra of title compounds are shown in Fig. 5. Theoretical Raman spectra of compounds computed from the HF/6-311++G(d,p) level along with the experimental spectra are presented in Fig. 6 and 7 respectively. Assignment of vibrations with only experimental data was very difficult because vibrational motions couple in various patterns. All assignments were determined by comparison of experiment with the calculated wave numbers and vibrational motions at each mode. There are some differences of wave numbers between the calculated and experimental data. This is because the calculated spectrum corresponds to the gas phase where experimental data are taken with solid phase however the spectral patterns are similar. In the previous section, assignments for NO₂ vibrations were discussed and their experimental wave numbers of NO₂ vibrations can be compared to the calculated values. There are good agreements on modes 5, 6, 7, 8 and 9, which are assigned as the NO₂ stretching modes; the observed values 1541 cm^{-1} and 1546 cm^{-1} are at the shoulder compared to ${\sim}1534~\text{cm}^{-1}$ and ${\sim}1562~\text{cm}^{-1}$ computed from the HF/6-311++G(d,p), B3P86/6-311++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVDZ levels. This difference is due to the fact that the measurement takes place in the solid state while the calculation is for the gas phase (i.e., isolated molecule). For instance, in the gas phase, modes 5, 6, 7, 8, and 9 show up to 1573 cm^{-1} . On the other hand, there is a poor agreement for the NO₂ asymmetric vibrations obtained from the HF/ 6-311++G(d,p), B3P86/6-311++G(d,p), B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVDZ levels of theory. For mode 4, the experimental band 1734 cm^{-1} ascribed to the ring C=N stretching is smaller than the calculated values. Expectedly, it was found that there is a difference in the wave numbers of the crystalline and gas phases which can be linked with the results mentioned in the previous discussion regarding bond length and angles. When the N-O bond forms a hydrogen bonding to the N–H group of the other molecule, the optimized C or N–NO₂ distance is higher than the corresponding distance in the crystalline state. There is no contradiction to the result that the wave numbers of NO₂ stretching in the crystalline state may be a smaller value compared to the gas phase (i.e., the optimized value). Nevertheless, our studies suggest that B3LYP/aug-cc-pVDZ level of calculations provided the best agreement amongst the four methods investigated. We feel that B3LYP/aug-cc-pVDZ is an advanced level calculation and, therefore, provided better agreement compared to other methods.

5. Conclusions

The structural properties of pyrazole, N-nitropyrazole, 3-nitropyrazole, 4-nitropyrazole and 5-nitropyrazole have been studied using the HF, DFT-B3LYP and DFT-B3P86 exchange correlations methods. The calculated bond lengths and angles of pyrazoles have been found to be in excellent agreement with the average experimental values. The Fourier transform infrared (solid phase) and Fourier transform Raman spectra of pyrazole, N-nitropyrazole, 3nitropyrazole and 4-nitropyrazole were recorded. The vibrational frequencies of nitropyrazoles in the ground state have been calculated by using HF, B3LYP and B3P86 with 6-311++G(d,p) and augcc-pVDZ as basis sets. The calculated stretching frequencies have been found to be in good agreement with the experimental frequencies. However, the fundamental vibrational frequencies of nitropyrazoles calculated at the B3LYP/aug-cc-pVDZ level are superior compared with those values that are obtained at the HF/ 311++G(d,p), B3P86/311++G(d,p) and B3LYP/311++G(d,p) levels of theory. The differences in the bond distances and bond angles are confined to the twist of the nitro group that present the greatest deviation from planarity in molecules.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013. 03.038.

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