JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 637–645 (1997)

STRUCTURE OF 3-NITROPYRAZOLE IN SOLUTION AND IN THE SOLID STATE

CONCEPCION FOCES-FOCES[1]*, ANTONIO L. LLAMAS-SAIZ[1], MARGARITA MENÉNDEZ[2], NADINE JAGEROVIC[3] AND J. ELGUERO[3]

[1] *Departamento de Cristalografía, Instituto de Química Fímica 'Rocasolano,' CSIC, Serrano 119, E-28006 Madrid, Spain*
[2] *Departamento de Química Física de Macromoléculas Biológicas, Instituto de Química Física 'Rocasolano,' CSIC, Serrano 119, E-28006 Madrid, Spain*
[3] *Instituto de Química Médica, Centro de Química Orgánica 'Manuel Lora Tamayo,' CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain*

The molecular and crystal structure of 3-nitropyrazole was determined by X-ray analysis. The triclinic unit cell contains 12 molecules which form four hydrogen-bonded (N—H···N) trimers. Each trimer comprises of pseudo-ring in a flattened envelope distorted towards a chair conformation. The crystal packing consists of layers formed by centrosymmetric related trimers joined through C–H···O interactions. *Ab initio* calculations were performed on 3(5)-nitro- and 4-nitropyrazole and their corresponding protonated forms up to the MP2/6–31G level of theory. The origin of the difference in aqueous basicities between both nitropyrazoles is discussed.** © 1997 John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 637–645 (1997) No. of Figures: 4 No. of Tables: 5 No. of References: 28

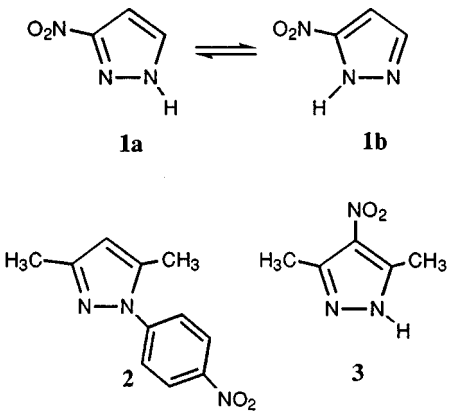
Keywords: 3-nitropyrazole; structure

Received 22 January 1997; revised 5 March 1997; accepted 11 March 1997

INTRODUCTION

There are two main reasons for studying 3(5)-nitropyrazole (**1**), its solid state and acid–base properties. In the solid state, the interest in nitropyrazoles is a consequence of their non-linear optical (NLO) and second harmonic generation (SHG) properties; for instance, 3,5-dimethyl-1-*p*-nitrophenylpyrazole (DMNP) (**2**) is a compound of reference in non-linear optics[1–3] while 3,5-dimethyl-4-nitropyrazole (**3**) crystallizes in the space group $P3_121$ and shows appreciable NLO properties.[4] These observations prompted us to determine the crystal structure of a series of 4-nitropyrazoles related to compound **3**.[5]

Concerning the acid–base properties of pyrazoles, we have published a series of papers both in solution[6,7] and in the gas-phase [by Fourier transfor ion cyclotron resonance (FT-ICR)].[8–11] Two of the conclusions we reached are worth of summarizing: (i) there exists a linear relationship between the acidity in water as measured by the pK_a (proton lost) and the basicity in water as measured by the pK_a (proton gained);[11] and (ii) there exists a linear relationship between the aqueous basicity and the gas-phase basicity (*GB*) as measured by the proton affinities (*PA*).[12]

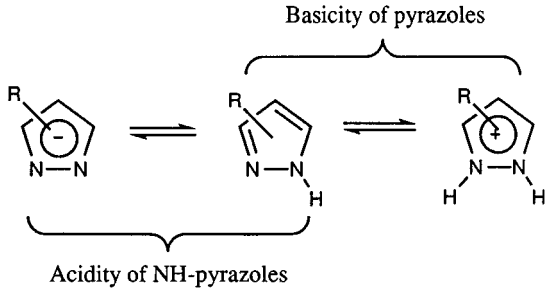


Concerning acid–base properties, previous studies have shown that pyrazoles behave differently to other azoles. For pyrazoles (excluding tautomeric compounds), the following equation was found:[11]

$$\text{p}K_a\ (\text{proton lost}) = 11{\cdot}0 + 0{\cdot}92\ \text{p}K_a\ (\text{proton gained}) \quad n = 9,\ r^2 = 0{\cdot}962 \qquad (1)$$

*Correspondence to: C. Foces-Foces.
Contract grant sponsor: DGICYT; *Contract grant number*: PB93-0125; *Contract grant number*: PB93-0197-CO2; *Contract grant number*: PB93-0284-CO2.

 CCC 0894–3230/97/080637–09 $17.50



Since 3(5)-substituted pyrazoles have tautomeric equilibrium constants almost equal to 1,[12] all the data can be treated simultaneously:

pK_a (proton lost) = (11·5 ± 0.1) + (0·95 ± 0·05)pK_a (proton gained)

$$n = 14,\ r^2 = 0{\cdot}965 \qquad (2)$$

In these equations, the point corresponding to 3(5)-nitropyrazole (**1**) was not used [pK_a (proton lost) = 9·81,[13] pK_a (proton gained) = − 4·66[14]]. If this point is introduced, the regression becomes worse:

pK_a (proton lost) = (12·0 ± 0·2) + (0·76 ± 0·07)pK_a (proton gained)

$$n = 15,\ r^2 = 0{\cdot}904 \qquad (3)$$

An examination of the plot containing the 15 points (Figure 1) calls attention to the problem with nitropyrazoles. If, instead of removing the 3-nitropyrazole point equation (2)], the three 4-nitropyrazoles are excluded, the equation becomes equation (4) [the lines corresponding to equations (2), (3) and (4) are represented in Fig. 1]:

pK_a (proton lost) = (12.5 ± 0.1) + (0.62 ± 0.04)pK_a (proton gained)

$$n = 12,\ r^2 = 0.959 \qquad (4)$$

It is difficult to decide which equation, (2) or (4), is more representative; in any case, data on both kinds of pyrazoles are mutually inconsistent; for instance, 4-nitropyrazole (**4**) has an acidity [pK_a (proton lost) = 9·64, ΔpK_a (proton lost) = − 0·17][11] similar to that of 3-nitropyrazole but it is a much stronger base, pK_a (proton gained) = − 2·00 [ΔpK_a (proton gained) = 2·66].[11]

We will now try another relationship, which was previously discussed in point (ii), between pK_a (proton gained) and *PA* (Figure 2):

pK_a (proton gained) = (− 1·1 ± 0·5) + (0·26 ± 0·03)*PA* (kcal-

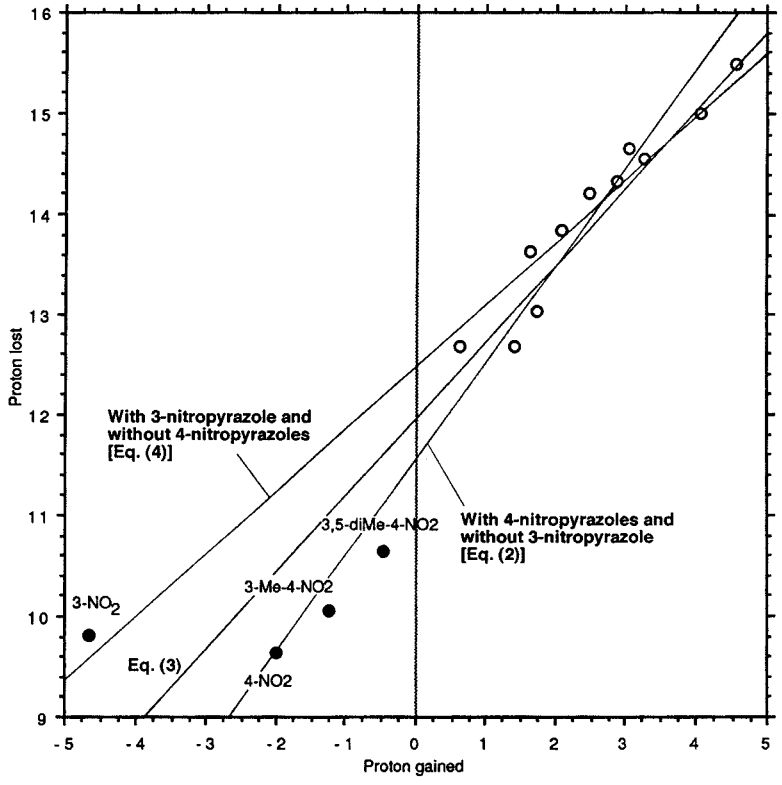


Figure 1. Plot of pK_a(acid) *vs* pK_a(basic)

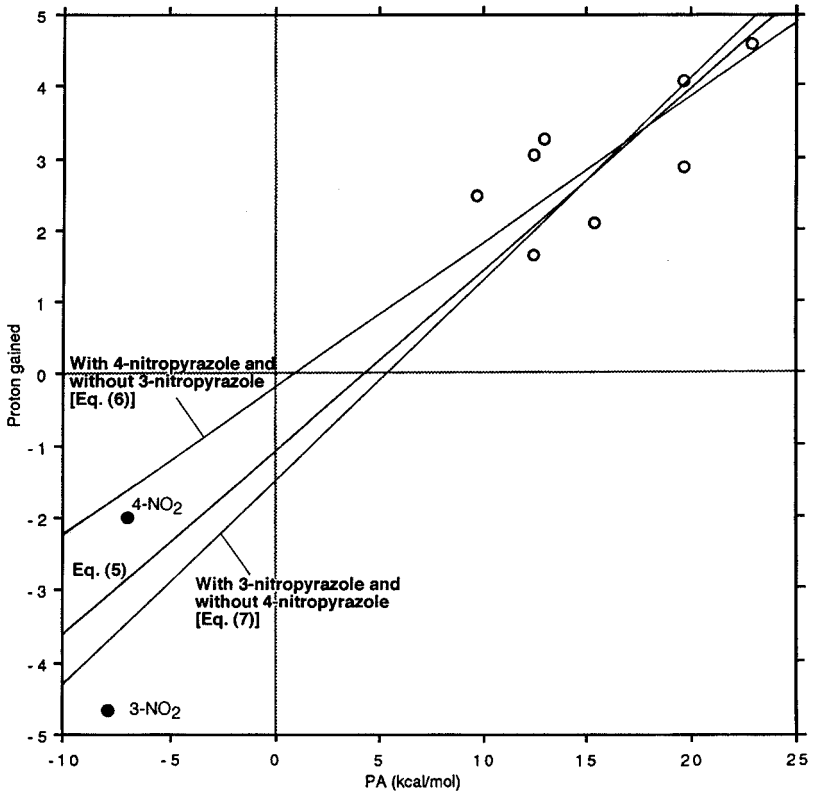


Figure 2. Plot of pK_a(basic) *vs* proton affinity (in kcal mol^{-1})

mol^{-1})

$$n=10,\ r^2=0{\cdot}888 \qquad (5)$$

Following the same strategy, we will remove alternatively the points corresponding to 3-nitro- [equation (6)] and to 4-nitropyrazole [equation (7)]:

pK_a (proton gained) $=(-0{\cdot}2\pm0{\cdot}5)+(0{\cdot}20\pm0{\cdot}03)PA$ (kcal mol^{-1})

$$n=9,\ r^2=0{\cdot}863 \qquad (6)$$

pK_a (proton gained) $=(-1{\cdot}6\pm0{\cdot}6)+(0{\cdot}28\pm0{\cdot}04)\ PA$ (kcal mol^{-1})

$$n=9,\ r^2=0.882 \qquad (7)$$

Again, it appears that compounds **1** and **4** have similar gas-phase basicities [**1**, $GB=-7{\cdot}2$ kcal mol^{-1}; **4**, $-7{\cdot}0$ kcal mol^{-1} (1 kcal = 4·184 kJ)] but very different aqueous basicities. It remains impossible at this level to decide whether the 'anomaly' lies in **1** or in **4**, but it seems that it is the aqueous basicities and not the corresponding aqueous acidities.

EXPERIMENTAL

Materials. 3(5)-Nitropyrazole (**1**) was prepared according to Habraken and Janssen.[15] It was purified by crystallization in water. The same sample from which a single crystal was collected for crystallography was used for the pK_a determination.

Spectrophotometric determination of the pK_a (proton gained) of 3-nitropyrazole. The pK_a (proton gained) of 3(5)-nitropyrazole was determined spectrophotometrically using a Cary 210 (Varian) instrument, assuming that it is a Hammett base. The spectrum of 3(5)-nitropyrazole was recorded from 300 to 200 nm in different aqueous solutions of sulfuric acid with acidities which, expressed as the Hammett function H_0,[16] ranged from $-0{\cdot}22$ to $-7{\cdot}86$. We verified that the family of spectral curves passed through the isosbestic point. The pK_a (proton gained) value was determined from the absorption variation at 258 nm by a non-linear least-squares fitting of the protonation curve in terms of equation (8), using data at 35 different concentrations of sulfuric acid:

Table 1. Crystal analysis parameters at room temperature

Crystal data	
Formula	$C_3H_3N_3O_2$
Crystal habit	Colourless, hexagonal prism
Crystal size (mm)	0·43×0·20×0·23
Symmetry	Triclinic, *P*-1
Unit cell determination:	Least-squares fit from 36 reflections (θ<45°)
Unit cell dimensions (Å, °)	a=10·1023(12) α=100·257(13) b=12·5014(20) β=104·407(12) c=13·1190(17) γ=111·315(13)
Packing: V (Å^3), Z	1438·5(4), 12
D_c(g cm^{-3}), M, F(000)	1·566, 113·076,696
μ (cm^{-1})	11·67
Experimental data	
Technique	Seifert XRD3000-S four circle diffractometer, bisecting geometry· Graphite oriented monochromator, $\omega/2\theta$ scans· Detector apertures 1×1°, 1 min reflection· Radiation Cu Kα· Scan width: 1·7°, θ_{max}=67·5°
Number of reflections:	
Independent	4785
Observed	2578 [2$\sigma(I)$ criterion]
Standard reflections	2 reflections every 90 mins· No variation
Solution and refinements	
Solution	Direct methods: Sir92
Refinement:	
Least-squares on F_0	Full matrix
Parameters:	
Number of variables	505
Degrees of freedom	2073
Ratio of freedom	5·1
Final shift/error	0·02
H atoms	From difference synthesis
Weighting-scheme	Empirical as to give no trends in $<\omega\Delta^2F>$ vs $<\|F_{obs}\|>$ and $<\sin\phi/\lambda>$
Max, thermal value (Å^2)	U22[O(27)]=0·159(3)
Final ΔF peaks (e Å^{-3})	0·26
Final R and Rw	0·038, 0·054

$$A^{258}(H_0)=A^{258}(B)\{[A^{258}(BH^+)-A^{258}(B)]/[1+(K_{BH+}/10^{-H0})]\} \quad (8)$$

where $A^{258}(H_0)$, A^{258}(B) and $A^{258}(BH^+)$ are the absorbances at 258 nm for a solution of acidity H_0, for the deprotonated base and for the protonated form, respectively, and K_{BH+} is the basicity constant. As control, the dissociation constant of 2,3-dichloro-6-nitroaniline was also determined. The pK_a (proton gained) of 3(5)-nitropyrazole was determined to be −4·85±0·10. Using the same experimental approach, a value of −3·46±0·18 was obtained for 2,4-dichloro-6-nitroaniline, in good agreement with data reported in the literature.[16]

X-ray crystallography. The experimental details and the most relevant parameters of the refinement are given in Table 1. The structure was solved by direct methods, Sir92.[17] In spite of the large number of independent molecules, no reduction of the unit cell could be obtained. Usually pyrazole derivatives crystallize with several independent molecules in the asymmetric unit.[18] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included as isotropic. Most of the calculations were carried out with the XTAL3.2[19] and PARST[20] set of programs. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*, Vol. IV.[21]

Theoretical calculations. The *ab initio* optimized geometry, energy and frequency analysis were calculated by means of the Gaussian94 program[22] at several levels of theory, Hf/6–31G, HF/6–31G** and MP2/6–31G**. The zero-point energy correction was taken into account in all

Table 2. Selected geometrical parameters (Å, °). $i=1$ to 6 refers to the six independent molecules, i.e.: $i=2$ and N(1)—N(2) means N(21)—N(22) in Fig. 3 and so on.

	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$
N(1)—N(2)	1·341(5)	1·346(5)	1·329(4)	1·334(5)	1·340(5)	1·334(4)
N(1)—C(5)	1·335(6)	1·343(6)	1·345(6)	1·349(6)	1·336(5)	1·340(6)
N(2)—C(3)	1·329(5)	1·318(5)	1·334(6)	1·323(4)	1·321(5)	1·330(5)
C(3)—C(4)	1·369(6)	1·375(6)	1·387(6)	1·379(6)	1·379(5)	1·372(6)
C(4)—C(5)	1·367(7)	1·342(7)	1·352(7)	1·345(6)	1·364(6)	1·361(6)
N(6)—C(3)	1·453(4)	1·448(5)	1·429(5)	1·436(5)	1·443(5)	1·436(6)
N(6)—O(7)	1·213(4)	1·217(6)	1·219(6)	1·223(5)	1·217(5)	1·223(5)
N(6)—O(8)	1·220(4)	1·218(5)	1·229(5)	1·224(4)	1·214(5)	1·226(5)
N(2)—N(1)—C(5)	113·3(3)	111·9(3)	112·6(4)	112·1(3)	112·9(3)	113·0(3)
N(1)—N(2)—C(3)	101·7(3)	102·5(3)	103·4(3)	103·1(3)	102·7(2)	102·5(3)
N(2)—C(3)—C(4)	114·8(4)	114·0(3)	112·8(4)	113·4(3)	113·9(3)	113·8(3)
C(3)—C(4)—C(5)	102·9(4)	103·5(4)	104·0(4)	103·8(3)	103·3(4)	103·5(4)
N(1)—C(5)—C(4)	107·3(4)	108·0(4)	107·3(4)	107·6(4)	107·2(3)	107·2(4)
N(2)—C(3)—N(6)	116·9(3)	117·8(4)	118·3(3)	118·4(3)	117·8(3)	117·9(3)
C(4)—C(3)—N(6)	128·2(3)	128·1(4)	129·0(4)	128·3(3)	128·4(4)	128·3(4)
C(3)—N(6)—O(7)	118·3(3)	118·3(4)	119·4(4)	118·4(3)	118·6(4)	118·8(3)
C(3)—N(6)—O(8)	117·2(3)	117·0(4)	117·2(3)	117·1(3)	116·9(4)	117·2(3)
O(7)—N(6)—O(8)	124·2(4)	124·4(4)	123·5(4)	124·5(4)	124·5(4)	123·9(3)
N(2)—C(4)—N(6)—O(7)	−9·9(5)	0·7(6)	−1·8(6)	−7·7(5)	0·1(5)	2·3(5)
N(2)—C(4)—N(6)—O(8)	168·2(3)	179·6(4)	178·0(4)	173·2(3)	179·8(3)	−177·8(3)

Pesudo-rings		Cremer and Pople parameters
N(11)—N(12)···N(21)—N(22)	8·9(4)	$q_2=0·062(3)$
N(12)···N(21)—N(22)···N(31)	−2·3(3)	$q_3=0·083(3)$
N(21)—N(22)···N(31)—N(32)	4·6(4)	$\Phi_2=-6(3)$
N(22)···N(31)—N(32)···N(11)	−7·4(4)	$Q=0·104(3)$
N(31)—N(32)···N(11)—N(12)	12·1(4)	$\theta_2=37(2)$
N(32)···N(11)—N(12)···N(21)	−10·5(4)	
N(41)—N(42)···N(61)—N(62)	−7·7(4)	$q_2=0·025(3)$
N(42)···N(61)—N(62)···N(51)	5·9(3)	$q_3=-0·056(3)$
N(61)—N(62)···N(51)—N(52)	−5·6(4)	$\Phi_2=-74(6)$
N(62)···N(51)—N(52)···N(41)	2·9(3)	$Q=0·063(3)$
N(51)—N(52)···N(41)—N(42)	−4·4(4)	$\theta_2=157(2)$
N(52)···N(41)—N(42)···N(61)	5·2(3)	

Hydrogen interactions	D—H	H···A	D···A	D—H···A
N(11)—H(11)···N(32)	0·79(5)	2·16(5)	2·929(5)	168(5)
N(21)—H(21)···N(12)	0·97(5)	1·98(4)	2·928(4)	164(4)
N(31)—H(31)···N(22)	0·93(4)	2·03(4)	2·933(5)	164(3)
N(41)—H(41)···N(52)	0·90(4)	2·03(4)	2·919(4)	170(4)
N(51)—H(51)···N(62)	0·89(4)	2·01(4)	2·892(5)	170(3)
N(61)—H(61)···N(42)	0·87(4)	2·07(4)	2·931(5)	170(4)
N(11)—H(11)···O(37)	0·79(5)	2·64(5)	3·170(5)	126(4)
N(21)—H(21)···O(17)	0·97(5)	2·44(5)	3·001(5)	116(3)
N(31)—H(31)···O(27)	0·93(4)	2·48(4)	3·101(5)	125(3)
N(41)—H(41)···O(57)	0·90(4)	2·50(4)	3·043(5)	120(3)
N(51)—H(51)···O(67)	0·89(4)	2·59(4)	3·141(5)	121(3)
N(61)—H(61)···O(47)	0·87(4)	2·56(4)	3·098(5)	121(3)
C(44)—H(44)···O(18)	0·92(4)	2·51(4)	3·381(5)	158(3)
C(64)—H(64)···O(17)(−x, 2−y, l−z)	0·89(5)	2·57(5)	3·434(6)	163(3)
C(45)—H(45)···O(38)(1−x, 1−y, 2−z)	0·95(4)	2·60(4)	3·394(6)	141(3)
C(65)—H(65)···O(68)(−x, 2−y, 1−z)	0·91(4)	2·50(3)	3·370(5)	160(4)
C(34)—H(34)···O(57)(1−x, 1−y, 2−z)	0·96(5)	2·53(5)	3·484(7)	173(4)
C(15)—H(15)···O(58)(−x, 1−y, 2−z)	0·96(4)	2·61(4)	3·356(6)	135(4)
C(55)—H(55)···O(67)(−2−x, 1−y, 1−z)	1·05(5)	2·50(4)	3·335(7)	137(3)
C(25)—H(25)···O(68)(−x, 2−y, 1−z)	0·90(5)	2·68(5)	3·334(6)	131(3)

Table 3. *Ab initio* MP2/6–31G** geometrical parameters (Å, °)[a]

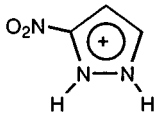
	5	**1a**	**1b**	**4**	**5H$^+$**	**1H$^+$**	**4H$^+$**
N(1)—N(2)	1·348	1·346	1·346	1·351	1·339	1·336	1·341
N(1)—C(5)	1·360	1·361	1·353	1·355	1·349	1·353	1·347
N(2)—C(3)	1·347	1·342	1·353	1·343	1·349	1·347	1·347
C(3)—C(4)	1·406	1·402	1·401	1·403	1·391	1·389	1·388
C(4)—C(5)	1·385	1·384	1·386	1·383	1·391	1·392	1·388
N(6)—C(i)	–	1·446	1·431	1·435	–	1·447	1·452
N(6)—O(7)	–	1·240	1·247	1·243	–	1·242	1·237
N(6)—O(8)	–	1·245	1·241	1·243	–	1·237	1·237
C(2)—N(1)—C(5)	113·9	114·4	112·4	114·5	109·3	109·6	109·8
N(1)—N(2)—C(3)	103·4	101·9	103·8	104·1	109·3	108·0	109·8
N(2)—C(3)—C(4)	112·1	114·1	112·7	110·3	107·5	109·4	106·1
C(3)—C(4)—C(5)	104·9	103·4	103·2	107·0	106·5	105·0	108·3
N(1)—C(5)—C(4)	105·7	106·1	107·9	104·1	107·5	108·0	106·1
X(*i*-1)—C)(*i*)—N(6)	–	119·9	131·9	127·3	–	118·5	125·8
Y(*i*+1)—C)(*i*)—N(6)	–	126·0	120·2	125·7	–	132·1	125·8
C(*i*)—N(6)—O(7)	–	118·3	116·5	117·1	–	115·0	115·7
C(*i*)—N(6)—O(8)	–	115·7	117·2	117·3	–	115·9	115·7
O(7)—N(6)—O(8)	–	126·0	126·2	125·7	–	129·1	128·6

[a]For all compounds the nitro group is coplanar with the pyrazole ring· *i*=3, 4 or 5 for **1a**, **4** or **1b** derivatives; X, Y=C or N and Y (*i*+)=N(1) for **1b**·

cases and the scaling was carried out following Scott and Radom[23] (for 6–31G calculations, the scaling factor used, 0·9135, was that of 6–31G*). Appropriate thermal corrections were applied. All the calculations were carried out on a DEC3000–300X workstation.

RESULTS AND DISCUSSION

In view of the possible 'anomaly' in the basicity of compounds **1** and **4**, and since the x-ray structures of 4-nitropyrazoles do not present anything unexpected,[5] we decided to undertake a careful study of 3-nitropyrazole (**1**), first to check that the literature value for the pK_a (proton gained) was correct,[14] then to determine its x-ray structure to verify that no anomaly was present and finally to carry out some calculations on **1a** and **1b** and the common cation **1H$^+$**.



1H$^+$

The experimental pK_a (proton gained) of compound **1** is $-4{\cdot}85\pm0{\cdot}10$, which agress with the value reported by Dumanovic *et al*.[14] ($-4{\cdot}66$). Then, since the 'anomaly' was not due to an experimental error, the following x-ray analysis and theoretical calculations were carried out.

X-ray analysis

Bond distances and angles among the six independent molecules are nearly identical according to half normal probability plots.[24] The differences are confined to the twist of the nitro group that presents the greatest deviation from planarity in molecules **1** and **4** (Table 2).

The experimental geometry shows the same pattern as that obtained from *ab initio* calculations at the MP2/6–31G** level,[22] although all the computed bond lengths appear to be elongated with respect to the experimental values. These differences could be expected when comparing the internuclear distances displayed by the equilibrium structure with the distances between the centroids of the electronic cloud obtained experimentally.[25] However, both methods reflect the influence of the NO_2 substitution that widen the endocyclic *ipso* (α) and *meta* (γ) angles and close the *ortho* (β) angles, analogously to what happens in benzene derivatives.[26] The values for the angular distortion $\Delta\alpha=2{\cdot}1(1)^\circ$, $\Delta\beta=-1{\cdot}6(1)^\circ$ and $\Delta\gamma=0{\cdot}5(1)^\circ$ were computed (on average) by comparing the *ab initio* geometry of the neutral and the protonated pyrazole (**5** and **5H$^+$**, respectively) with the corresponding neutral and protonated nitro derivatives (Table 3).

The six independent molecules are arranged in two trimers (Figure 3) via N—H···N hydrogen bonds. The trimer as a whole is not planar and the central ring adopts a flattened [$Q=0{\cdot}104(3)$ and $0{\cdot}063(3)$ Å] envelope conformation distorted towards a chair. This fact, together with the almost coplanarity of the nitro group with the pyrazole ring, places the O(7) atom close to the H(1) atom of the

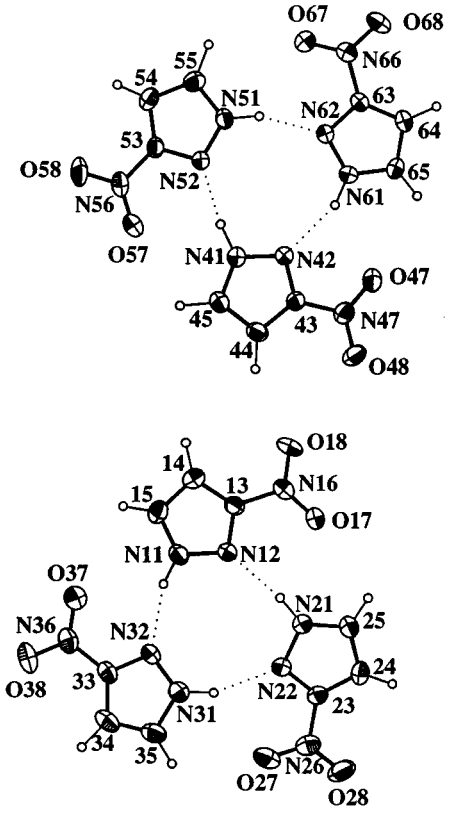
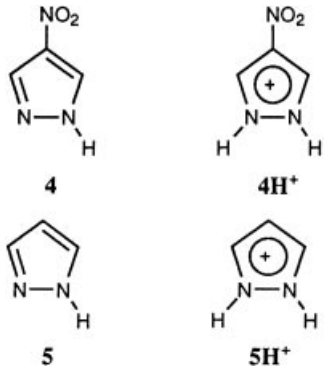


Figure 3. The pair of 3-nitropyrazole trimers in the asymmetric unit[18] displaying the numbering scheme with displacement parameters drawn at the 30% probability level

neighbouring, hence this hydrogen atom is involved in a second and weaker interaction that could be responsible for the low puckering of the pseudo-rings. The N···N distances range from 2·892(5) to 2·933(5) Å, which are longer than those presented by 4-nitro-5-methylpyrazole[27] and 4-nitropyrazole[5] trimers. Centrosymmetric related trimers held by C–H···O interactions form layers of molecules that are also centrosymmetrically related to each other and constitute the whole crystal (Table 2 and Figure 4). There are no voids in the structure and the total packing coefficient is 0·70 ($C_k^{all} = V_{molecules}$/unit cell volume).[28]

Ab initio calculations

Assuming that the protonation always takes place on the pyrazole nitrogen atom, we performed *ab initio* calculations at different levels up to MP2/6–31G** on the following neutral molecules: pyrazole itself (**5**), the two tautomers of 3(5)-nitropyrazole (**1a** and **1b**) and 4-nitropyrazole (**4**) and their corresponding cations. ($\mathbf{5H}^+$, $\mathbf{1H}^+$ and $\mathbf{4H}^+$) (Table 4).



The zero-point energy (ZPE, scaled)[23] correction produces an appreciable effect although the values without and with correction are linearly related ($r^2 = 1{\cdot}000$). Assuming that the best values are the MP2/6–31G** + ZPE, then it appears that they reproduce conveniently the experimental values [note that the experimental value for both tautomers of 3(5)-nitropyrazole are identical because the method cannot distinguish between them]:

$$PA\ (\text{exp.}) = (1{\cdot}029 \pm 0{\cdot}002)\, PA\ (\text{MP2/6–31G**} + \text{ZPE}) \quad n = 4,\ r^2 = 1{\cdot}000 \qquad (9)$$

where values are in kcal mol^{-1}.

Concerning the difference in energy between **1a** and **1b**, the results in Table 5 show that the difference in favour of the 3-nitro tautomer **1a** is very small and becomes zero for the highest level calculations. We recorded the UV spectra of compound **1** and those of its two *N*-methyl derivatives in cyclohexane as an approximation to the gas phase. The following results were obtained: 3(5)-nitropyrazole (**1**), 255·2 nm, 1-methyl-3-nitropyrazole 251.1 nm and 1-methyl-5-nitropyrazole 273.3 nm (another band at 222.1 nm). Clearly, the absorption of compound **1** is much more similar to that of 1-methyl-3-nitropyrazole, but taking into account the results of the *ab initio* calculations (Table 5) it is possible that the absorptions of both tautomers should be similar and that the very different spectrum of 1-methyl-5-nitropyrazole is due to a steric interaction between the nitro and methyl groups which twists the first one out of plane.

CONCLUSIONS

Since 3(5)- and 4-nitropyrazoles have very similar intrinsic basicities (experimental and calculated) and also similar aqueous acidities, the large difference in aqueous basicities should be an effect of the solvent (water). Either the intrinsic basicity of 4-nitropyrazole (**4**) is greatly enhanced by solvation or that of 3(5)-pyrazole (**1**) is greatly lowered by solvation. It is not easy to answer this question, although the 4-nitro group lowers the basicity of pyrazole by 4·5 units while the 3(5)-nitro group produces an effect of $-7{\cdot}3$ pK_a

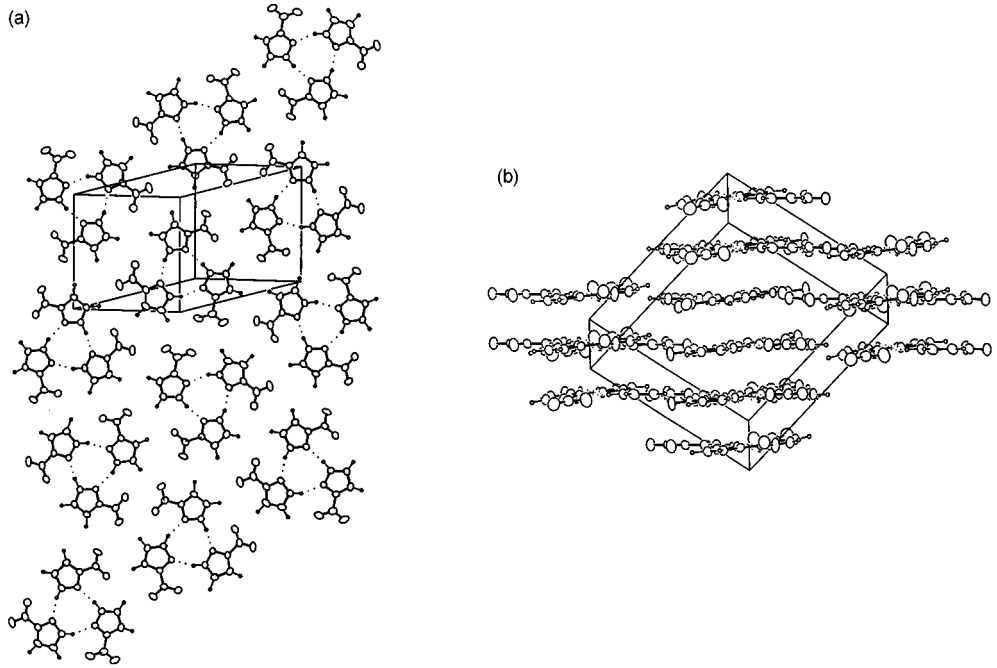


Figure 4. (a) Partial packing diagram showing one layer of centrosymmetric trimers; (b) view of the arrangement of layers in the crystal

Table 4. *Ab initio* calculations (all values in hartree[a]) of pyrazole **5** and nitropyrazoles **1** and **4** with thermal corrections included

Compound	6–13G	6–31G + ZPE	6–31G**	6–31G** + ZPE	MP2/6–31G**	MP2/6–31G** + ZPE
5	-224·6386	-224·5673	-224·7525	-224·6818	-225·4906	-225·4211
5H$^+$	-224·9951	-224·9106	-225·1015	-225·0214	-225·8336	-225·7511
1a	-427·9832	-427·9092	-428·2164	-428·1419	-429·4887	-429·4166
1b	-427·9822	-427·9085	-428·2148	-428·1403	-429·4886	-429·4165
1H$^+$	-428·2991	-428·2126	-428·5338	-428·4471	-429·8065	-429·7222
4	-427·9912	-427·9171	-428·2214	-428·1467	-429·4881	-429·4158
4H$^+$	-428·3100	-428·2231	-428·5407	-428·4538	-429·8032	-429·7185

[a]1 hartree = 627·51 kcal mol^{-1}·

Table 5· Tautomeric equilibrium ΔG(**1a1b**) values, calculated and experimental proton affinities with thermal correction (all values in kcal mol^{-1})[a]

Compound	6–31G	6–31G + ZPE	6–31G**	6–31G** + ZPE	MP2/6–31G**	MP2/6–31G** + ZPE	Exp· *PA*[8,9,12]
1a/**1b**[b]	0·7	0·5	1·0	1·0	0·0	− 0·1	–[c]
5	223·8	215·5	219·1	213·2	215·3	207·1	213·2
1a	198·2	190·4	199·2	191·6	199·5	191·8	196·7[d]
1b	198·9	190·9	200·2	192·6	199·5	191·9	196·7[d]
4	200·1	192·1	200·4	192·8	197·8	190·0	196·5

[a]*PA*(NH_3) = 204·0 kcal mol^{-1}·
[b]A positive value indicates that the 3-nitro tautomer **1a** is more stable than the 5-nitro tautomer **1b**·
[c]The 3-nitro tautomer predominates in solution.[8,12]
[d]The experimental value corresponds to the mixture of both tautomers·

units. For other azoles, the *C*-nitro effect is as follows: 2-nitroimidazole, −7·8; 4 (5)-nitroimidazole, −6·9; 3(5)-nitro-1,2,4-triazole, −6·1; and 5-nitro-1,2,3,4-tetrazole, −6·6 pK_a units.[11] The anomaly may lie in the 'high' aqueous basicity of 4-nitropyrazole, but this conclusion is only tentative and other possibilities have to be considered.

SUPPLEMENTARY MATERIAL

The following supplementary material is available from C. F.-F on request: list of the structure factors, atomic coordinates and thermal components for the non-hydrogen atoms, hydrogen atom parameters, bond distances and angles and *ab initio* MP2/6–31G** calculated frequencies.

ACKNOWLEDGMENTS

Financial support was provided by the Spanish DGICYT (PB93–0125, PB93–0197–CO2 and PB93–0289–CO2).

REFERENCES

1. A. Harada, Y. Okazaki, K. Kamiyama and S. Umegaki, *Appl. Phys. Lett.* **59**, 1535–1537 (1991).
2. R. D. Miller and O. Reiser, *J. Heterocycl. Chem.* **30**, 755–763 (1993).
3. M. Okazaki, N. Uchino, N. Nozaki and K. Kubo, *Bull. Chem. Soc. Jpn.* **68**, 1024–1029 (1995).
4. C. Foces-Foces, F. H. Cano and J. Elguero, *Gazz. Chim. Ital.* **123**, 477–479 (1993).
5. A. L. Llamas-Saiz, C. Foces-Foces, F. H. Cano, P. Jiménez, J. Laynez, W. Meutermans, J. Elguero, H.-H. Limbach and F. Aguilar-Parrilla, *Acta Crystallogr., Sect B* **50**, 746–762 (1994).
6. J. Elguero, E. Gonzalez and R. Jacquier, *Bull. Soc. Chim. Fr.* 5009–5017 (1968).
7. J. Catalán, M. Menéndez and J. Elguero, *Bull. Soc. Chim. Fr., Ser. 1* 30–33 (1985).
8. J.-L. M. Abboud, P. Cabildo, T. Cañada, J. Catalán, R. M. Claramunt, J.-L. G. de Paz, J. Elguero, H. Homan, R. Notario, C. Toiron and G. I. Yranzo, *J. Org. Chem.* **57**, 3938–3943 (1992).
9. R. Notario, M. Herreros, A. El Hammadi, H. Homan, J.-L. M. Abboud, I. Forfar, R. M. Claramunt and J. Elguero, *J. Phys. Org. Chem.* **7**, 657–662 (1994).
10. J.-L. M. Abboud, C. Foces-Foces, M. Herreros, H. Homan, L. Infantes, R. Notario, A. W. Krebs, J. Neubauer, J. Elguero and N. Jagerovic, *J. Phys. Org. Chem.* **9**, 79–86 (1996).
11. J. Catalán, J.-L. M. Abboud and J. Elguero, *Adv. Heterocycl. Chem.* **41**, 187–274 (1987).
12. A. El Hammadi, M. El Mouhtadi, R. Notario, J.-L. M. Abboud and J. Elguero, *J. Chem. Res. (S)* 172–173, *(M)* 1080–1096 (1995).
13. J. W. A. M. Janssen, C. G. Kruse, H. J. Koeners and C. L. Habraken, *J. Heterocycl. Chem.* **10**, 1055–1058 (1973).
14. D. Dumanovic, J. Ciric, A. Muk and V. Nikolic, *Talanta* **22**, 819–822 (1975).
15. C. L. Habraken and J. W. A. M. Janssen, *J. Org. Chem.* **36**, 3081–3084 (1971).
16. M. A. Paul and F. A. Long, *Chem. Rev.* **51**, 1–44 (1957).
17. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, SIR9′*J. Appl. Crystallogr.* 435–435 (1994).
18. C. Foces-Foces, A. L. Llamas-Saiz, R. M. Claramunt, C. López and J. Elguero, *J. Chem. Soc., Chem. Commun.* 1143–1145 (1994), and references cited therein.
19. S. R. Hall, H. D. Flack and J. M. Stewart, *Xta13.2.* University of Western Australia, Perth (1994).
20. M. Nardelli. *Comput. Chem.* **7**, 95–98 (1983).
21. *International Tables for X-Ray Crystallography*, Vol. IV. Kynoch Press, Birmingham (1974).
22. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Ciolowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian94 (Revision C.3).* Gaussian, Pittsburgh, PA (1995).
23. A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502–16513 (1996).
24. G. A. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A* **27**, 157–165 (1971).
25. A. Domenicano and I. Hargittai (Eds), *Accurate Molecular Structures* (IUC. Monographs on Crystallography). Oxford University Press, Oxford (1992).
26. A. Domenicano and P. Murray-Rust, *Tetrahedron Lett.* **24**, 2283–2286 (1979).
27. C. Foces-Foces, A. L. Llamas-Saiz, R. M. Claramunt, C. López and J. Elguero, *J. Chem. Soc., Chem. Commun.* 1143–1145 (1994).
28. F. H. Cano and M. Martínez-Ripoll, *J. Mol. Struct. (Theochem).* **258**, 139–158 (1992).