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Diethyl 2-Benzimidazol-1-ylsuccinate–Picric Acid (1/1) – An Inclusion Molecular Complex

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Abstract

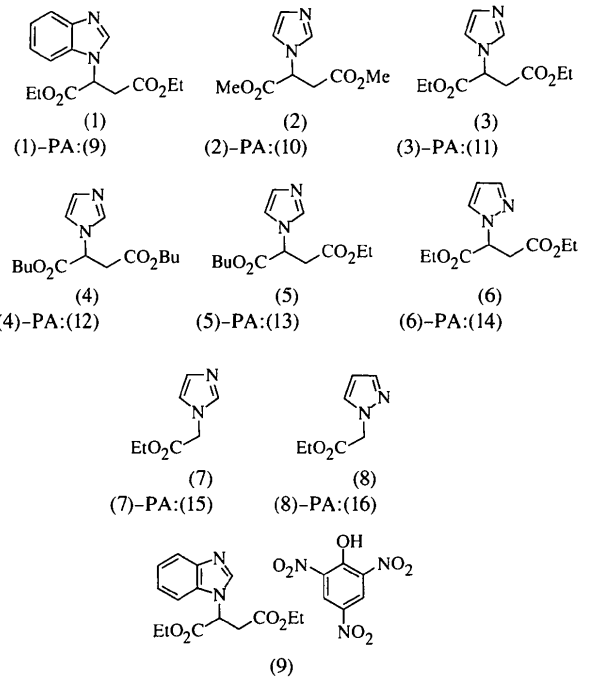
The crystal structure of the diethyl 2-benzimidazol-1-ylsuccinate–picric acid (1/1) molecular complex has been determined by X-ray diffraction analysis. Diethyl 2-benzimidazol-1-ylsuccinate molecules form channels along the *a* axis, in which the picric acid molecules are located. The benzimidazole moiety and the phenol group are held together by hydrogen bonding between the hydrogen of the phenol and the N3 atom of benzimidazole. Additionally, this hydrogen forms an intramolecular hydrogen bond with one O atom of the *ortho*-nitro group, thus producing a bifurcated hydrogen bond. ^{1}H NMR spectra in DMSO-d_6 solution and CP/MAS solid ^{13}C NMR studies of this 2-benzimidazol-1-ylsuccinate–picric acid (1/1) molecular complex, as well as those of dimethyl, diethyl, di-*n*-butyl and 1-*n*-butyl-4-ethyl 2-imidazol-1-ylsuccinates, diethyl 2-pyrazol-1-ylsuccinate, ethyl imidazol-1-ylacetate, ethyl pyrazol-1-ylacetate and ethyl pyrazol-1-ylsuccinate, suggest that the picric acid linkage depends on the nature of the azole. Actual proton transfer is deduced for the imidazole derivatives, but only weak hydrogen bonding could be inferred for pyrazole derivatives.

1. Introduction

The formation of picrates is a common method for the conversion of liquids into stable, tractable solid compounds. Although picrates have long been used, controversy still exists regarding their structures. In many cases the bonding of these electron donor–acceptor (EDA) picric acid complexes strongly depends on the nature of the partners. The linkage could involve not only electrostatic attractions, but also the formation of molecular complexes.

We have recently described the synthesis and neutral hydrolysis of a series of azol-1-ylsuccinic and acetic esters (1)–(8) (Gil, Cruz, Cerdán & Ballesteros, 1992; Gil, Zaderenko, Cruz, Cerdán & Ballesteros, 1994; Zaderenko, Gil, Ballesteros & Cerdán, 1994; Zaderenko, López & Ballesteros, 1996). These products form crystalline 1:1 addition compounds (9)–(16) with picric acid (PA).

In this study we have established the structure of (9) in the solid state by X-ray diffraction analysis. The observed linkage is compared with those presented by other complexes (10)–(16) using NMR studies both in the solid state and in DMSO-d_6 solution.



2. Experimental

Compounds (1)–(8) were prepared as described previously (Gil, Cruz, Cerdán & Ballesteros, 1992; Gil, Zaderenko, Cruz, Cerdán & Ballesteros, 1994; Zaderenko, Gil, Ballesteros & Cerdán, 1994; Zaderenko, López & Ballesteros, 1996). PA complexes (9)–(16) were prepared by adding a solution containing a slight excess of picric acid in absolute ethanol to (1)–(8) dissolved in the minimal amount of absolute ethanol. Compounds (9)–(16) crystallized from the cold solution and were recrystallized from absolute ethanol. (3).HBF$_4$ was prepared by treatment of (3) with a 54% diethyl ether solution of fluoroboric acid.

Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_{15}H_{18}N_2O_4.C_6H_3N_3O_7$
Chemical formula weight	519.43
Cell setting	Orthorhombic
Space group	$Pna2_1$
a (Å)	11.310 (1)
b (Å)	23.183 (4)
c (Å)	9.462 (1)
V (Å^3)	2480.9 (5)
Z	4
D_x (Mg m^{-3})	1.391
Radiation type	Cu $K\alpha$
Wavelength (Å)	1.5418
No. of reflections for cell parameters	53
θ range (°)	3–25
μ (mm^{-1})	0.985
Temperature (K)	293 (2)
Crystal form	Prism
Crystal size (mm)	0.35 × 0.24 × 0.21
Crystal colour	Colourless
Data collection	
Diffractometer	Philips PW1100
Data collection method	ω–2θ scans
Absorption correction	None
No. of measured reflections	2241
No. of independent reflections	2241
No. of observed reflections	1683
Criterion for observed reflections	$I > 2\sigma(I)$
θ_{max} (°)	64.80
Range of h, k, l	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 27$ $0 \rightarrow l \rightarrow 11$
No. of standard reflections	2
Frequency of standard reflections (min)	90
Intensity decay (%)	None
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0785
$wR(F^2)$	0.2160
S	1.135
No. of reflections used in refinement	2241
No. of parameters used	334
H-atom treatment	H atoms refined isotropically
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0844P)^2 + 2.4124P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.316
$\Delta\rho_{min}$ (e Å^{-3})	−0.224
Extinction method	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)
Absolute configuration	Flack (1983)
Computer programs	
Data collection	Philips PW1100
Cell refinement	*LSUCRE* (Appleman, 1996)
Data reduction	*XRAY*80 *System* (Stewart, Kundell & Baldwin, 1980)
Structure solution	*SIR*92 (Altomare *et al.*, 1992)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)

Table 2. *Selected geometric parameters (Å, °)*

N1—C2	1.347 (9)	C32—N33	1.440 (13)
N1—C7a	1.375 (9)	N33—O34	1.171 (15)
C2—N3	1.316 (10)	N33—O35	1.179 (13)
N3—C3a	1.376 (9)	C37—N38	1.471 (12)
C3a—C7a	1.415 (10)	N38—O39	1.166 (19)
O10—C12	1.433 (10)	N38—O40	1.276 (20)
C12—C13	1.458 (15)	C42—N43	1.441 (12)
O17—C18	1.474 (12)	N43—O44	1.202 (11)
C18—C19	1.443 (20)	N43—O45	1.220 (11)
C2—N1—C7a	108.1 (6)	N1—C7a—C3a	106.0 (6)
N3—C2—N1	110.7 (7)	O34—N33—O35	121.0 (13)
C2—N3—C3a	108.5 (6)	O39—N38—O40	125.3 (11)
N3—C3a—C7a	106.8 (6)	O44—N43—O45	119.2 (10)

Table 3. *Hydrogen-bond geometries (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O31—H31···O45	0.820 (10)	1.963 (11)	2.659 (11)	142.3 (9)
O31—H31···N3	0.820 (10)	2.044 (11)	2.556 (10)	120.1 (9)

2.1. *Crystal structure determination*

Crystals of (9) were obtained from absolute ethanol. Crystal and experimental data are given in Table 1.† The intensities were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods. The C-, O- and N-atom positions were refined with anisotropic displacement parameters. Hydroxyl and some other H atoms were unambiguously located from a difference map. Only H8, H122, H182, H192, H193 and H41 were fixed at ideal geometries and refined using a riding model with fixed isotropic displacement parameters. The H atom attached to O31 was refined as an OH-idealized group with an *X*—O—H tetrehedral angle. Several cycles of least-squares refinement converged to $R = 0.0785$ and $wR = 0.189$; the rather high R values may contain contributions from general uncertainties in the data and the high displacement parameters for the nitro groups of picric acid.

2.2. *NMR determinations*

^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.33 MHz) spectra were recorded with freshly prepared DMSO-d_6 solutions on a Bruker AC200 spectrometer. Chemical shifts are expressed in p.p.m. relative to tetramethylsilane. ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were obtained at 50.33 MHz on a Bruker CP-200 spectrometer. Samples were rotated at 3.5 or 2.5 kHz in a 7 mm ZrO_2 rotor; the initial contact

† Lists of atomic coordinates, anisotropic displacement parameters, complete geometry, structure factors and ^{1}H NMR data have been deposited with the IUCr (Reference: BM0007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

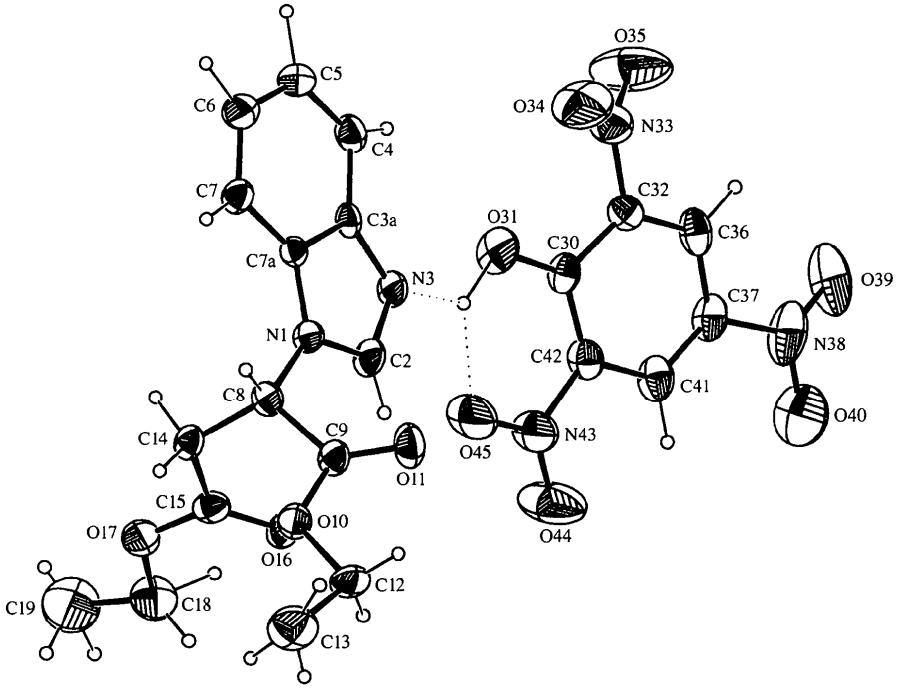
time was 1 ms; 90° pulse lengths for protons were 7 μs; a 4 s delay between scans and 200 transients were used.

Chemical shifts were measured relative to the glycine resonance at 176.1 p.p.m. as an external reference.

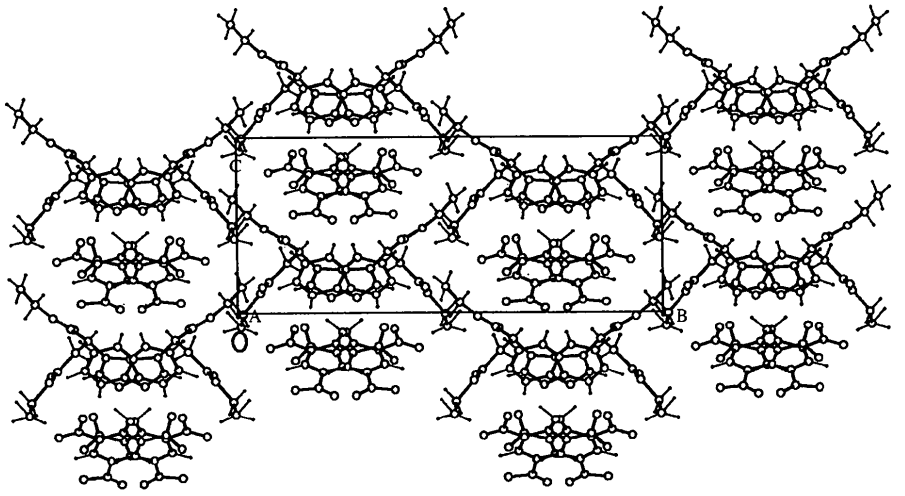
3. Results and discussion

The geometric features of (9) are shown in Tables 2 and 3. The asymmetric unit contains one molecule of diethyl (±)-benzimidazol-1-ylsuccinate (1) and one molecule of picric acid (PA).

The benzimidazole ring is planar, with no atom deviating from the mean plane by more than 0.027 (10) Å; the value of the dihedral angle being 0.8 (2)°. The geometry of the ring is similar to that found in the literature (Dik-Edixhoven, Schenk & van der Meer, 1973; Toffoli, Rodier, Ceolin, Doung & Joannic, 1990; Duesler, Engelmann, Curtin & Paul, 1978). The side chains lie above and below the heterocycle and their planes form angles of 51.3 (3) and 69.9 (3)° with the plane of the ring. The aromatic ring of picric acid is also planar, with no atom deviating from this mean plane by



(*a*)



(*b*)

Fig. 1. (*a*) *ORTEP* (Hall & Stewart, 1990) view of (9), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level; (*b*) packing of molecules of (9) viewed down the *c* axis.

Table 4. *Selected ^1H NMR chemical shifts (δ, p.p.m.) in DMSO-d_6 of (1)–(6) and (8) and their PA complexes (9)–(14) and (16)*

Assigments have been made on the basis of reported data: Gil, Cruz, Cerdán & Ballesteros (1992); Gil, Zaderenko, Cruz, Cerdán & Ballesteros (1994); Zaderenko, Gil, Ballesteros & Cerdán (1994). In some cases COSY 2D (two-dimensional) NMR experiments have been carried out; s: singlet; bs: broad signal; vbs: very broad singlet. ^1H NMR of PA in DMSO-d_6: H3(5): 8.55 (s); OH: 11.10 (s) p.p.m.

Compound	CH	CH_2	Azole	PA
(1)	5.83	3.36	7.17–7.29 (H5,H6)	
			7.55–7.67 (H4,H7)	
			8.84 (H2)	
(9)	6.19	3.49	7.56–7.60 (H5,H6)	8.58
			7.83–7.98 (H4)	
			8.00–8.02 (H7)	
			9.56 (H2)	
Δδ [δ(9)–δ(1)]	0.36	0.13	0.35 (H5,H6)	
			0.29 (H4)	
			0.40 (H7)	
			0.72 (H2)	
(2)	5.50	3.21	6.88 (H4)	
			7.23 (H5)	
			7.72 (H2)	
(10)	5.86	3.41	7.71 (H4)	8.58
			7.86 (H5)	
			9.21 (H2)	
Δδ [δ(10)–δ(2)]	0.36	0.20	0.83 (H4)	
			0.64 (H5)	
			1.49 (H2)	
(3)	5.45	3.17	6.87 (H4)	
			7.23 (H5)	
			7.71 (H2)	
(11)	5.83	3.38	7.72 (H4)	8.58
			7.87 (H5)	OH: 13.50 (vbs)
			9.21 (H2)	
Δδ [δ(11)–δ(3)]	0.38	0.21	0.85 (H4)	
			0.64 (H5)	
			1.50 (H2)	
(3).HBF_4	5.82	3.34	7.70 (H4)	
			7.89 (H5)	
			9.21 (H2)	
Δδ [δ(3).HBF_4–δ(3)]	0.37	0.17	0.83 (H4)	
			0.66 (H5)	
			1.50 (H2)	
(4)	5.47	3.18	6.87 (H4)	
			7.23 (H5)	
			7.72 (H2)	
(12)	5.84	3.39	7.70 (H4)	8.58
			7.86 (H5)	OH: 14.52 (vbs)
			9.18 (H2)	
Δδ [δ(12)–δ(4)]	0.37	0.21	0.83 (H4)	
			0.63 (H5)	
			1.46 (H2)	
(5)	5.47	3.18	6.87 (H4)	
			7.24 (H5)	
			7.73 (H2)	
(13)	5.83	3.37	7.70 (H4)	8.58
			7.86 (H5)	OH: 14.44 (vbs)
			9.18 (H2)	
Δδ [δ(13)–δ(5)]	0.37	0.21	0.83 (H4)	
			0.63 (H5)	
			1.46 (H2)	
(6)	5.49	3.16	6.25 (H4)	
			7.46 (H3)	
			7.84 (H5)	
(14)	5.49	3.16	6.25 (H4)	8.58
			7.46 (H3)	OH: 8.52 (bs)
			7.84 (H5)	
Δδ [δ(14)–δ(6)]	0.00	0.00	0.00 (H4)	
			0.00 (H3)	
			0.00 (H5)	
(8)		5.04	6.26 (H4)	
			7.45 (H3)	
			7.71 (H5)	
(16)		5.04	6.26 (H4)	8.58
			7.45 (H3)	OH: 10.78(s)
			7.71 (H5)	
Δδ [δ(16)–δ(8)]	0.00	0.00	0.00 (H4)	
			0.00 (H3)	
			0.00 (H5)	

more than 0.016 (11) Å. Bond distances and angles have normal values within experimental error (Hall & Stewart 1990). The twist angles of the three nitro groups from the phenyl ring are 36 (2), 8 (2) and 2 (2)°. The wide range of N—O distances [1.166 (19)–1.276 (20) Å] is probably due to the large temperature factors of the O atoms. All attempts to find a model for the disorder failed.

Proton transfer from the phenol group towards the benzimidazole ring does not occur. The benzimidazole moiety of the molecules forms channels along the *a* axis within which the picric acid molecules are located, forming an inclusion molecular complex (Fig. 1*b*). The benzimidazole ring and the picric acid are held together by hydrogen bonding through the hydrogen of the phenol and the N3 atom of the benzimidazole ring (Table 3). Furthermore, this hydrogen forms a bifurcated intramolecular hydrogen bond with the O45 atom of the *ortho*-nitro group of the picric acid. Similar interactions have been reported in tryptophan metabolite–picric acid molecular complexes (Nagata, In, Doi, Ishida & Wakahara, 1995). No stacking interactions between benzimidazole rings have been observed (Albert & Cano, 1991). Although the nearest-neighbour intermolecular distance between ring centroids was 4.96 Å, the angle (17.6°) between the planes did not allow the ring interactions (Desiraju, 1989).

These results combined with NMR data of molecular complexes (9)–(16) in solution and the solid state provide valuable information about the nature of the linkage in the molecular complex.

Table 5. *^{13}C chemical shifts (δ, p.p.m.) in DMSO-d_6 and CP/MAS of (1), (3), (6), (8), PA and the PA complexes (9), (11), (14), (15) and (16)*

		Heterocyclic carbons								Picric acid carbons			
Compound	Conditions	C2	C3	C3a	C4	C5	C6	C7	C7a	C_{ipso}	C_o	C_m	C_p
(1)	DMSO-d_6	143.6		143.3	119.6	121.9	122.6	110.7	133.4				
(9)	DMSO-d_6	142.4		131.5	115.6	126.1	126.2	113.4	131.2	160.8	141.8	125.2	124.8
	CP/MAS	143.3		†	114.7	126.4	126.4	110.8	†	161.3	†	126.4	†
(3)	DMSO-d_6	137.6			128.3	118.8							
(11)	DMSO-d_6	136.5			122.0	119.9				160.9	141.8	125.2	124.4
(3).HBF_4	DMSO-d_6	136.5			122.0	119.9							
(6)	DMSO-d_6		139.3		105.6	131.3							
(14)	DMSO-d_6		139.4		105.5	131.1				160.5	141.9	125.3	124.8
	CP/MAS		‡		108.7	‡				161.7	142.0	125.6	†
(8)	DMSO-d_6		139.3		105.6	131.3							
(16)	DMSO-d_6		139.1		106.0	132.1				160.3	141.9	125.4	125.5
	CP/MAS		138.0		110.4	135.0				160.7	142.2	127.6	†
(15)	DMSO-d_6	136.9			123.5	119.7				167.1	141.9	125.4	124.2
	CP/MAS	136.4			†	120.2				162.4	146.6	126.1	†
PA	DMSO-d_6									159.0	142.0	125.9	132.3

† Overlapped by C5, C6 or C_m of PA. ‡ C3 and C5 are overlapped at −139 p.p.m..

As shown in Table 4, the stability of the complexes is different in solution. ^{1}H chemical shifts of imidazole derivatives (10)–(13) and (15) are rather different from those observed for the free ligands (2)–(5) and (7), suggesting a strong bond with picric acid. However, in the pyrazole complexes (6) and (8) the linkage is completely destroyed in DMSO-d_6 solution, and ^{1}H NMR spectra of free ligands (6) and (8) and those from (14) and (16) are identical. The benzimidazole derivative (9), whose crystal structure has been elucidated here, represents an intermediate situation.

These results would suggest that in the case of imidazole derivatives (10)–(13) and (15) an actual proton transfer to N3 of the imidazole ring occurs, producing an ionic linkage which is stable in solution. Unfortunately, the picric acid hydroxyl resonance cannot be used to identify the proton transfer. In most cases this resonance is not visible or appears as a very broad signal, as in the case of (11), (12) and (13). However, the N3 protonation in (10)–(13) and (15) could be clearly observed because of the downfield shifting of H2 (*ca* 1.50 p.p.m.) in all cases. The chemical shifts lie in the same range as observed in the protonated (3).HBF_4 salt (see Table 4). Similar values have been found previously in imidazol-1-ylacetic acid and 2-imidazol-1-yl-3-ethoxycarbonylpropionic acid obtained from neutral hydrolysis of (3) and (7) (Gil, Cruz, Cerdán & Ballesteros, 1992; Gil, Zaderenko, Cruz, Cerdán & Ballesteros, 1994; Zaderenko, Gil, Ballesteros & Cerdán, 1994). These acids show a zwitterionic structure in the solid state and in D_2O solution, with proton transfer from the carboxylic group to the N3 of the imidazole ring (López, Zaderenko, Balcazar, Fonseca, Hernández-Cano & Ballesteros, 1996).

Considering the bond patterns shown by (9) in the solid state, we can suggest that pyrazole derivatives (14) and (16) are linked in a similar manner. However, the poor electron-donor properties of N2 of the pyrazole ring would imply less effective hydrogen bonds (Desiraju, 1995), which are destroyed in solution and are mantained only in the solid state.

To confirm this we compared the ^{13}C chemical shifts of some of the compounds in DMSO-d_6 solution and the solid state by the CP/MAS technique (Table 5). Protonation of N3 of the imidazole ring in (11) is confirmed since the chemical shifts of the corresponding C atoms showed the same values as those of (3).HBF_4. However, ^{13}C data in solutions of (14) and (16) are identical to those of the free ligands. In the solid state the differences between the free ligands (6) and (8) and the corresponding molecular complexes (14) and (16) are clearly observed. The resonances of C4 atoms in (14), and C4 and C5 atoms in (16) are shifted downfield by +3.1, +4.8 and +3.7 p.p.m., respectively.

The above results permit us to establish that the picric acid linkage clearly depends on the nature of the azole, being stronger in the case of imidazole. Its more basic character [pK_a = 6.99, 1.43 pK_a units more basic than benzimidazole and 4.51 pK_a units than pyrazole (Catalán, Abboud & Elguero, 1987)] would allow proton transfer to form an ionic molecular complex. In fact, although we have not determined the pK_a values of all the azol-1-ylalkanoic esters discussed here, we have reported previously the pK_a values in D_2O of (3) (pK_a = 6.02) and methyl imidazol-1-ylacetate (pK_a = 6.35): these esters are 1.12 and 0.79 pK_a units more acidic than imidazole (Gil, Cruz, Cerdán & Ballesteros, 1992; Gil, Zaderenko, Cruz, Cerdán & Ballesteros, 1994). Considering the same relationship for the benzimidazole and pyrazole, it would be possible to estimate that the pK_a of (1) would be *ca* 4.44 and the pK_a of the pyrazole derivatives *ca* 1.36. The validity of this estimation is confirmed by the value obtained for (1) (pK_a = 4.54), calculated according to the reported relationship between the pK_a of azoles and benzazoles in water solution: pK_a(benzazole) = $-1.81 + 1.056$pK_a(azole) (Catalán, Abboud & Elguero, 1987). Thus, these azoles with an intermediate or relatively weak basic character yield picric acid molecular complexes, which are held together by hydrogen bonds involved in the supramolecular construction.

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