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Weak C–H···O and C–H···N interactions in nitropyrazoles

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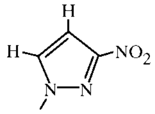
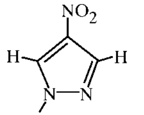
The structures of 1-methyl-3-nitropyrazole and 1-methyl-4-nitropyrazole, $C_4H_5N_3O_2$, have been determined. The 3-nitro derivative has crystallographic *m*-symmetry while the 4-nitro compound has no imposed symmetry. The significant differences in bond distances and angles between the structures are ascribable to the electron-withdrawing effects of the nitro group attached to C3 or C4, respectively. In both structures, the molecules are organized into layers by an extensive network of C—H···O or C—H···N hydrogen interactions. Within a layer, the molecules are arranged in a similar way, although differences of up to 0.3 Å in the analogous H···O or H···N intermolecular distances are observed. The cohesion of the layers is due to van der Waals and C—H···O contacts.

Comment

As part of our ongoing study of the relationship between the molecular and crystal structures of pyrazole derivatives, crystal structure determinations of 1-methyl-3-nitropyrazole, (I), and 1-methyl-4-nitropyrazole, (II), have been undertaken.



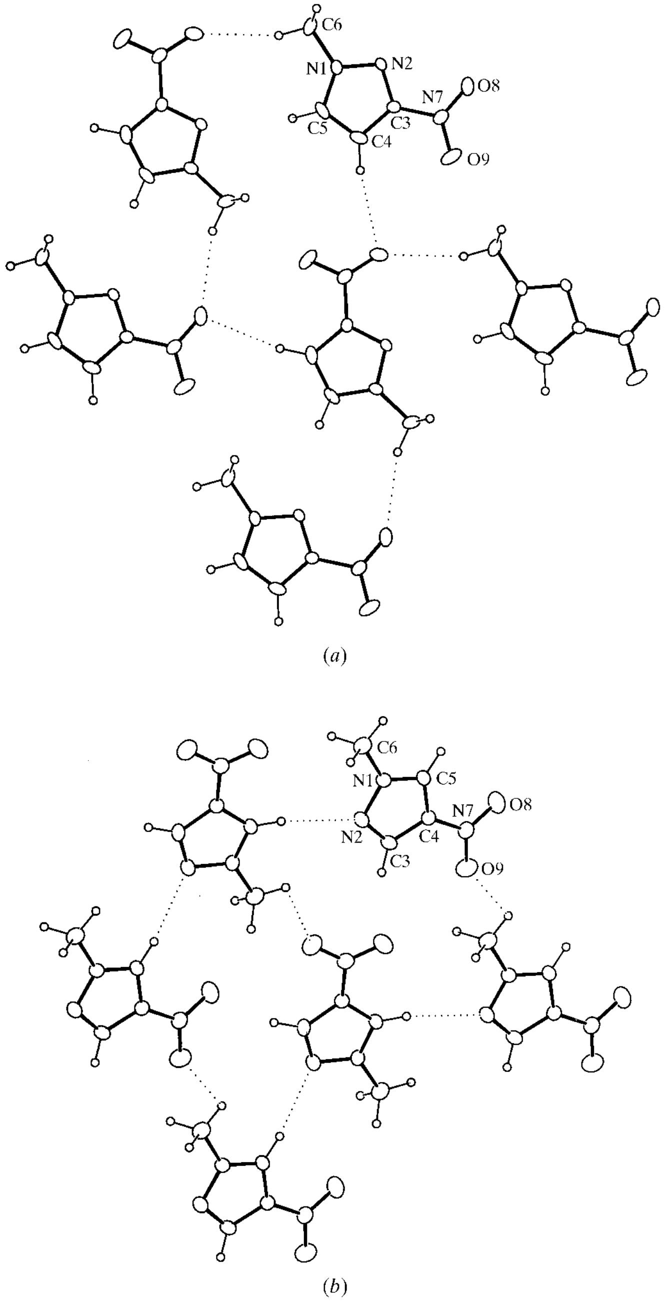
(I)



(II)

N-unsubstituted pyrazoles with only one potential donor and one potential acceptor in the ring form dimers, trimers, tetramers or catemers through N—H···N hydrogen bonds. In the nitropyrazole derivatives already studied (Llamas-Saiz *et al.*, 1994; Foces-Foces *et al.*, 1994, 1997), C—H···O interactions are responsible for the cohesion of these motifs, giving rise to the formation of layered structures. The main aim of this work is to study the influence of the nitro group, not only on the molecular structure but also on the crystal packing, when there are several hydrogen-bond acceptors in the molecule and the only hydrogen-bond donor in the pyrazole (N—H) has been replaced by a methyl group.

In the present compounds, the nitro group attached to either the C3 atom, (I), or the C4 atom, (II), of the pyrazole ring (Fig. 1*a* and Fig. 1*b*) mainly affects the molecular structure, while the crystal packing, in layers, is similar. The differences at the molecular level concern the bond distance and angle patterns and the planarity of the molecule as a whole. In (I), all non-H atoms are coplanar (the molecules lie on mirror planes), while in (II) the pyrazole and the nitro group are slightly twisted with respect to each other, the angle between their planes being 4.5 (2)°. The significant differences



(*a*)

(*b*)

Figure 1
The molecular arrangement of molecules within a layer (*a*) in (I) and (*b*) in (II), showing the atom-numbering schemes. The displacement ellipsoids are drawn at the 30% probability level. Dotted lines represent the shortest hydrogen contacts, H···O/N < 2.7 Å.

in bond lengths and angles in the pyrazole ring (Tables 1 and 3) can be ascribed to the electron properties of the nitro group, resulting in an opening of the corresponding internal angle of the pyrazole and a closing of the adjacent ones. These angular deformations are in good agreement with those observed for nitrobenzenes and nitropyrazoles from an experimental and theoretical (*ab initio*) point of view (Domenicano & Murray-Rust, 1979; Llamas-Saiz *et al.*, 1994; Foces-Foces *et al.*, 1997).

A search of the Cambridge Structural Database (CSD; Allen *et al.*, 1991, version of April 1999) for 3- or 4-nitropyrazole derivatives yields just a few organic structures without disorder, three and ten structures (nine and 18 fragments), respectively. The molecules reported so far (CSD) display the following features. Firstly, the 3-nitro derivatives display a different bonding pattern from that of the 4-nitro ones and both patterns agree with those found in (I) and (II), respectively. Secondly, the nitro group is almost coplanar with the pyrazole ring, although it can be twisted by up to 87° (CSD reference TASJEC; Dalinger *et al.*, 1996) to lessen the steric interactions when substituents other than H atoms are placed in adjacent positions. Thirdly, in spite of the dispersion of the samples, the C—N(NO_2) distance appears to be longer in the 3-nitro than in the 4-nitro derivatives reported so far, and this may be due to steric hindrance [1.447 (22) and 1.431 (13) Å, respectively, for the average and the standard deviation of the sample]. This distance is significantly longer in (I) (C3—N7) than in (II) (C4—N7); see Tables 1 and 3. Fourthly, for either the 3- or 4-nitro, treated individually, the C—N(NO_2) distance is correlated with the twist of the nitro group with respect to the pyrazole: the greater the N—C—N—O or C—C—N—O angle, the larger the C—N distance. This observation is consistent with the theoretical *ab initio* results on 4-nitropyrazole (Llamas-Saiz *et al.*, 1994) as a consequence of the resonance interaction. Finally, in the 3-nitro derivatives, the C4—C3—N7 angle is significantly widened, reducing the corresponding N2—C3—N7 angle. In the 4-nitro derivatives both angles are quite similar.

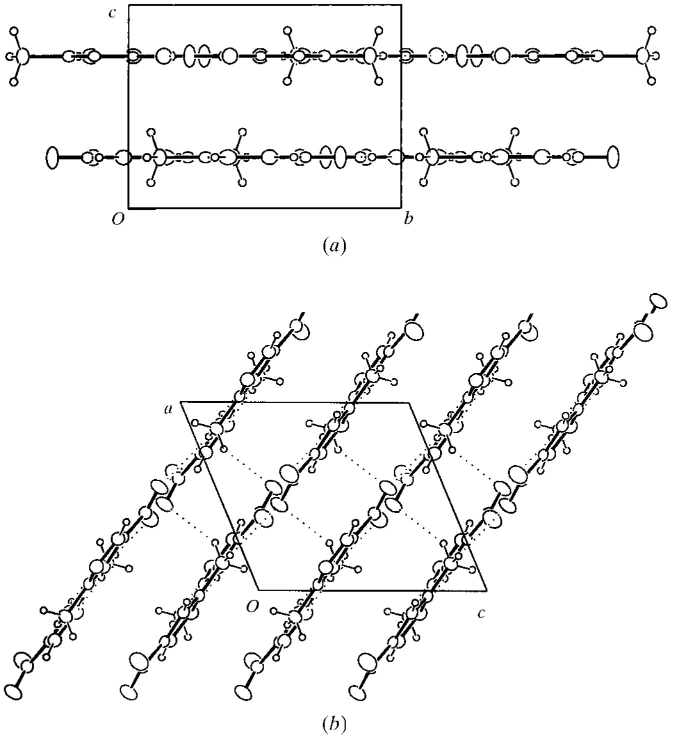


Figure 2
The crystal packing of (*a*) (I) along the *a* axis and (*b*) (II) along the *b* axis, showing the layered structures. Dotted lines represent the shortest hydrogen contacts, H···O/N < 2.7 Å.

The crystal packing in the two structures is remarkably similar. The molecules pack in layers (Fig. 2*a* and Fig. 2*b*), although the planarity of these layers is slightly different, as seen in Fig. 1. The two-dimensional network is formed by C—H···N and C—H···O interactions, in which the closest intermolecular interaction occurs between the methyl group and O9 (Tables 2 and 4). In this contact, the C···O distance is *ca* 0.2 Å shorter than the sum of the corresponding van der Waals radii [*rw*(C) = 1.70 and *rw*(O) = 1.52 Å; Vainshtein *et al.*, 1982], although the angle at H is very narrow. The differences within the layers concern their planarity and the disposition of the donor (*A*) and acceptor groups (*D*) in the molecule. In (I), the molecules lie on planes perpendicular to the *c* axis (Fig. 2*a*) and all donor groups, and therefore all acceptor groups, are located on one side or the other of the molecule following the sequence *DDD* or *AAA*, respectively (Fig. 1*a*). In (II), the molecules forming a sheet lie approximately in planes perpendicular to the *ac* plane and contiguous molecules make angles of 15.7 (1)° (Fig. 2*b*). In addition, the donor–acceptor sequences are *DAD* or *ADA* (Fig. 1*b*), which could be coincident with those for (I) if the N2 and C5 atoms interchanged their positions in the pyrazole ring. However, differences of up to 0.3 Å in the equivalent H···O and H···N distances are observed, for instance H5···N2, H62···O9, H4···O8 and H61···O8 in (I), and the equivalent ones H5···N2, H62···O9, H3···O8 and H61···O8 in (II) (Tables 2 and 4). The layers in (I) are connected only by van der Waals interactions, whereas in (II) the O9 atom links layers through C—H···O contacts (Table 4); the lack of this interaction in (I) could be due to gliding between layers. The thickness of the layers in (I) is 3.178 Å (*c*/2), while in (II) it is 3.289 Å, computed from the number of sheets along the (*a*–*c*) diagonal distance (Fig. 2*b*).

In summary, comparing the crystal structures of (I) and (II), the positioning of the nitro group at C3 [(I)] instead of at C4 [(II)] is accompanied by an increase of the symmetry within the layers (molecules on mirror planes), which implies a change from a monoclinic [(II)] to an orthorhombic lattice [(I)], followed by an increase of the beta angle; the *n*-glide plane perpendicular to the 10 Å axis, as well as the twofold screw axis parallel to it, are maintained in both structures.

Experimental

Compounds (I) and (II) were prepared according to the method of Luitjen & van Thuijl (1979). Crystals of (I) and (II) were obtained by recrystallization from EtOAc.

Compound (I)

Crystal data

$C_4H_5N_3O_2$
$M_r = 127.1$
Orthorhombic, *Pnam*
$a = 10.5062$ (5) Å
$b = 8.5940$ (4) Å
$c = 6.3562$ (3) Å
$V = 573.90$ (5) Å^3
$Z = 4$
$D_x = 1.471$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 69 reflections
$\theta = 2$–45°
$\mu = 1.038$ mm^{-1}
$T = 293$ K
Rectangular prism, colourless
0.60 × 0.50 × 0.23 mm

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ-scan (North *et al.*, 1968)
$T_{min} = 0.518$, $T_{max} = 0.788$
1164 measured reflections
571 independent reflections
571 reflections with $I > 0$
$R_{int} = 0.044$
$\theta_{max} = 67.46°$
$h = 0 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 7$
2 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
$R = 0.043$
$wR = 0.045$
$S = 1.016$
571 reflections
56 parameters
H-atom parameters not refined
$w = k/\{(A+BF_o)^2[C+D(\sin\theta)/\lambda]\}$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: (Zachariasen, 1967)
Extinction coefficient: 16 (6)

Table 1
Selected geometric parameters (Å, °) for (I).

N1—N2	1.335 (2)	C3—C4	1.383 (3)
N1—C5	1.344 (3)	C3—N7	1.445 (3)
N1—C6	1.450 (3)	C4—C5	1.358 (4)
N2—C3	1.319 (3)		
N2—N1—C5	112.3 (2)	C4—C3—N7	127.1 (2)
C3—N2—N1	103.2 (2)	C5—C4—C3	103.0 (2)
N2—C3—C4	113.8 (2)	N1—C5—C4	107.7 (2)
N2—C3—N7	119.2 (2)		
N2—N1—C6—H61	180	N2—C3—N7—O8	0.0 (2)
N2—N1—C6—H62	60		

Table 2
Hydrogen-bonding and short-contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O8^{i}	0.97	2.57	3.527 (3)	170
C6—H61···O8^{ii}	0.97	2.55	3.489 (3)	163
C5—H5···N2^{ii}	0.92	2.75	3.649 (3)	169
C6—H62···O9^{iii}	0.97	2.75	3.000 (3)	95

Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $x, y-1, z$.

Compound (II)

Crystal data

$C_4H_5N_3O_2$
$M_r = 127.1$
Monoclinic, $P2_1/c$
$a = 7.4197$ (8) Å
$b = 10.1803$ (15) Å
$c = 8.3529$ (10) Å
$\beta = 112.924$ (8)°
$V = 581.11$ (13) Å^3
$Z = 4$
$D_x = 1.453$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 49 reflections
$\theta = 2$–45°
$\mu = 1.026$ mm^{-1}
$T = 293$ K
Rhombohedral prism, colourless
0.50 × 0.33 × 0.23 mm

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ-scan (North *et al.*, 1968)
$T_{min} = 0.569$, $T_{max} = 0.790$
1181 measured reflections
1011 independent reflections
854 reflections with $I > 0.75\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 67.46°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 9$
2 standard reflections
frequency: 90 min
intensity decay: 5.8%

Refinement

Refinement on F
$R = 0.071$
$wR = 0.08$
$S = 1.005$
854 reflections
83 parameters
H-atom parameters not refined
$w = k/\{(A+BF_o)^2[C+D(\sin\theta)/\lambda]\}$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: (Zachariasen, 1967)
Extinction coefficient: 154 (22)

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C5	1.323 (4)	C3—C4	1.397 (4)
N1—N2	1.360 (4)	C4—C5	1.369 (4)
N1—C6	1.453 (4)	C4—N7	1.412 (4)
N2—C3	1.315 (4)		
C5—N1—N2	112.4 (2)	C5—C4—N7	126.4 (3)
C3—N2—N1	105.2 (2)	C3—C4—N7	127.7 (2)
N2—C3—C4	110.3 (3)	N1—C5—C4	106.3 (3)
C5—C4—C3	105.9 (2)		
N2—N1—C6—H61	−52	C3—C4—N7—O9	−5.7 (6)
N2—N1—C6—H62	170	C5—C4—N7—O8	−3.4 (6)
N2—N1—C6—H63	47		

Table 4
Hydrogen-bonding and short-contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···N2^{i}	0.93	2.56	3.465 (3)	164
C6—H61···O9^{ii}	1.00	2.63	3.538 (5)	151
C6—H61···O8^{iii}	1.00	2.85	3.460 (5)	120
C6—H62···O9^{iv}	0.99	2.59	3.041 (4)	108
C3—H3···O8^{v}	0.95	2.73	3.614 (4)	155

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x-1, y, z-1$; (v) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

In (I), the structure was solved in the centrosymmetric space group since the intensity statistics indicate the space group *Pnam*. As the molecules are placed on mirror planes and the nitro groups are slightly twisted in these kinds of compounds (Allen *et al.*, 1991), refinements in the $Pna2_1$ space group, also compatible with the systematic absences, were also carried out. The structure can be better described in the centrosymmetric space group since the refinement proceeded well in this group, *i.e.* similar geometrical parameters and slightly lower isotropic displacement parameters for atom O9.

Data collection: Philips PW1100 software (Hornstra & Vossers, 1973) for compound (I), *CRYSOM* (Seifert, 1996) for compound (II); for both compounds, cell refinement: *LSUCRE* (Appleman, 1984); data reduction: *Xtal*3.2 (Hall *et al.*, 1992); program(s) used to solve structure: *Xtal*3.2; program(s) used to refine structure: *Xtal*3.2; molecular graphics: *Xtal*3.2; software used to prepare material for publication: *Xtal*3.2.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1434). Services for accessing these data are described at the back of the journal.

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