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3(5),4-Dimethyl- and 3,4,5-trimethylpyrazole at 200 K. X-ray crystallography and quantum-chemical analysis

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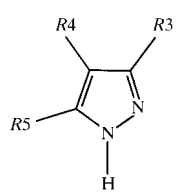
Abstract

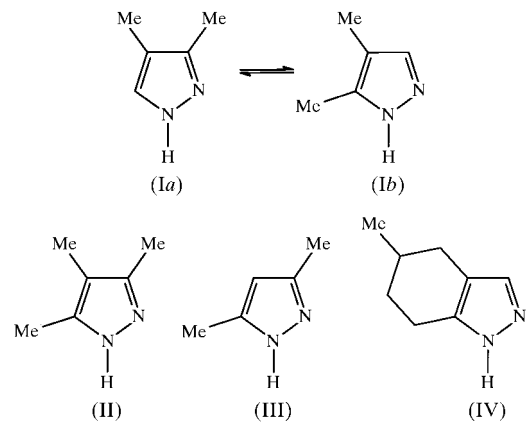
The crystal and molecular structures of 3(5),4-dimethylpyrazole, $C_5H_8N_2$, (I), and of 3,4,5-trimethylpyrazole, $C_6H_{10}N_2$, (II), have been determined at 200 K. In (I) the 4,5-dimethylpyrazole tautomer is present in the solid state and the six independent molecules in the asymmetric unit form trimers *via* NH···N hydrogen bonds related by a pseudo centre of symmetry. The asymmetric unit of (II) contains one and a half molecules: these exhibit NH proton disorder and are hydrogen bonded to each other *via* their respective NH groups to form chains. *Ab initio* calculations at HF and B3LYP/6-31G** levels indicate that the 3,4-dimethylpyrazole tautomer is more stable than the 4,5-dimethylpyrazole tautomer by only approximately 0.5 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}).

1. Introduction

The present work forms part of a series of reports on hydrogen bonding in NH pyrazoles. The pyrazole derivatives reported so far (Elguero *et al.*, 1994) crystallize in chains (catemers) and in cyclic structures: dimers, trimers and tetramers. These compounds quite often present disordered structures corresponding to static or dynamic disorder of the NH proton. The disorder is dynamic only in some cyclic structures with the same or similar substituents at C3 and at C5 (*R*3 and *R*5 in the scheme below)



as proved by CP-MAS NMR spectroscopy (Baldy *et al.*, 1985; Smith *et al.*, 1989; Aguilar-Parrilla *et al.*, 1992). We report here the low-temperature structures of 3(5),4-dimethyl-, (I), and 3,4,5-trimethylpyrazole, (II), in order to establish their secondary structure and the potential for dynamic disorder. The title compounds were selected by analogy with two of the few pyrazoles that present dynamic disorder, namely 3,5-dimethylpyrazole, (III), (Baldy *et al.*, 1985) and the tetrahydroindazole (IV) (Foces-Foces, Hager *et al.*, 1997).



2. Experimental

The compounds were synthesized and crystallized as reported by Elguero & Jacquier (1966). Details of the crystal data, data collection and structure refinement for (I) and (II) are given in Table 1.† The crystals were sealed in Lindemann glass capillary tubes and the data were collected at 200 K using an Oxford Cryosystem Cooler (Cosier & Glazer, 1986). In spite of the large number of independent molecules [Z = 12 for (I*b*) and (II)] no reduction of the unit cells could be obtained (Zimmermann & Burzlaff, 1985). However, this is quite common in pyrazole-derivative structures (Foces-Foces, Llamas-Saiz *et al.*, 1997; Foces-Foces *et al.*, 1994, and references therein). Both structures were solved by direct methods (Altomare *et al.*, 1994) and the numbering schemes are shown in Figs. 1 and 2. In (II), the refinements were carried out in both *I*2/*a* and *Ia* with the asymmetric unit comprising one and a half independent molecules [one molecule in this group (see Fig.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0017). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

	(I*b*)	(II)
Crystal data		
Chemical formula	$C_5H_8N_2$	$C_6H_{10}N_2$
Chemical formula weight	96.132	110.2
Crystal class	Triclinic	Monoclinic
Space group	$P\bar{1}$	$I2/a$
a (Å)	14.417 (1)	14.1911 (9)
b (Å)	12.020 (1)	8.2520 (6)
c (Å)	12.042 (1)	16.7382 (19)
α (°)	119.990 (7)	—
β (°)	105.991 (7)	90.696 (9)
γ (°)	87.224 (10)	—
V (Å^3)	1727.5 (3)	1960.0 (3)
Z	12	12
D_x (Mg m^{-3})	1.109	1.120
Radiation type	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418
No. of reflections for cell parameters	74	43
θ range (°)	4.2–44.1	5.2–45.0
μ (mm^{-1})	0.556	0.546
Temperature (K)	200	200
Crystal form	Sheet	Rectangular prism
Crystal size (mm)	0.60 × 0.40 × 0.17	0.67 × 0.27 × 0.17
Crystal colour	Colourless	Colourless
Crystal source	Elguero & Jacquier (1966)	Elguero & Jacquier (1966)
Data collection		
Diffractometer	Philips PW1100 diffractometer	Philips PW1100 diffractometer
Data collection method	$\omega/2\theta$ scan	$\omega/2\theta$ scan
Absorption correction	None	None
No. of measured reflections	5733	1863
No. of independent reflections	5733	1680
No. of observed reflections	4543	1372
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	–	0.024
θ_{max} (°)	64.84	65.08
Range of h, k, l	$-16 \rightarrow h \rightarrow 16$ $-13 \rightarrow k \rightarrow 12$ $0 \rightarrow l \rightarrow 12$	$-16 \rightarrow h \rightarrow 16$ $0 \rightarrow k \rightarrow 9$ $0 \rightarrow l \rightarrow 19$
No. of standard reflections	2	2
Frequency of standard reflections	Every 90 min	Every 90 min
Intensity decay (%)	0	0
Refinement		
Refinement on	F	F
R	0.075	0.048
wR	0.092	0.054
S	0.848	0.887
No. of reflections used in refinement	4543	1366
No. of parameters used	571	182
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = k/\{(A + BF_o)^2[C + D(\sin\theta)/\lambda]\}$	$w = k/\{(A + BF_o)^2[C + D(\sin\theta)/\lambda]\}$
$(\Delta/\sigma)_{max}$	0.03	0.07
$\Delta\rho_{max}$ (e Å^{-3})	0.30	0.22
$\Delta\rho_{min}$ (e Å^{-3})	−0.416	−0.198
Extinction method	Zachariasen (1967)	Zachariasen (1967)
Extinction coefficient	8.4 (2) × 10^2	3.9 (1) × 10^2
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)
Computer programs		
Data collection	Philips PW1100 (Hornstra & Vossers, 1973)	Philips PW1100 (Hornstra & Vossers, 1973)
Cell refinement	*LSUCRE* (Appleman, 1984)	*LSUCRE* (Appleman, 1984)
Data reduction	*Xtal*3.5 (Hall *et al.*, 1997)	*Xtal*3.5 (Hall *et al.*, 1997)
Structure solution	*SIR*92 (Altomare *et al.*, 1994)	*SIR*92 (Altomare *et al.*, 1994)
Structure refinement	*Xtal*3.5 (Hall *et al.*, 1997)	*Xtal*3.5 (Hall *et al.*, 1997)
Preparation of material for publication	*Xtal*3.5 (Hall *et al.*, 1997)	*Xtal*3.5 (Hall *et al.*, 1997)

Table 2. *Average experimental bond distances and angles for (Ib) and (II) (Å, °)*

An estimation of the weighted population deviation for each value is given in parentheses. The geometry of pyrazole at low temperature (La Cour & Rasmussen, 1973) is also included for comparison purposes. In the atom labelling *x*, denoting the molecule number in Figs. 1 and 2, has been omitted.

	(I*b*)	(II)	Pyrazole
N1—N2	1.355 (4)	1.351 (10)	1.352 (3)
N2—C3	1.336 (6)	1.338 (4)	1.328 (10)
C3—C4	1.391 (6)	1.389 (1)	1.389 (13)
C4—C5	1.381 (5)	1.387 (4)	1.371 (15)
C5—N1	1.344 (6)	1.338 (4)	1.337 (5)
C3—*R*3	—	1.491 (8)	—
C4—*R*4	1.501 (1)	1.498 (6)	—
C5—*R*5	1.497 (4)	1.490 (6)	—
C5—N1—N2	110.7 (6)	108.5 (1)	113.0 (5)
N1—N2—C3	105.6 (5)	108.3 (4)	103.7 (5)
N2—C3—C4	111.2 (3)	109.2 (2)	111.8 (6)
C3—C4—C5	104.5 (2)	104.8 (1)	105.1 (7)
C4—C5—N1	108.0 (4)	109.2 (1)	106.3 (7)
N2—C3—*R*3	—	121.4 (5)	—
C4—C3—*R*3	—	129.4 (3)	—
C3—C4—*R*4	127.8 (5)	127.7 (1)	—
C5—C4—*R*4	127.9 (6)	127.6 (1)	—
N1—C5—*R*5	121.8 (4)	121.8 (2)	—
C4—C5—*R*5	130.3 (5)	129.1 (3)	—

2) is located on a crystallographic twofold axis] and three molecules, respectively. The space group *I*2/*a* was chosen because of the more satisfactory refinement attained: neither correlation parameters nor unreliable geometry were observed, as seen for *Ia*. However, the H atoms of the NH and the C17 methyl groups (x = 1 in Fig. 2) had to be modelled as disordered over two sites according to the peaks in a difference synthesis (occupancy factor = 0.5). Empirical weighting schemes were computed so as to give no trends in $<w\Delta^2F>$ *versus* $<|F_o|>$ or $<\sin\theta/\lambda>$ (*PESOS*; Martínez-Ripoll & Cano, 1975). The *A*, *B*, *C* and *D* parameters were adjusted to flatten the initial trends. Energy minimization with complete optimization of the geometry was performed at HF and B3LYP/6-31G** levels using the *GAUSSIAN*94 program (Frisch *et al.*, 1995).

3. Results and discussion

3.1. *X-ray analysis*

For compound (I), the structure determination shows that the 4,5-dimethylpyrazole tautomer (I*b*) was present in the crystal. As the asymmetric units of (I*b*) and (II) consist of several [six in (I*b*) and one and a half in (II) (Figs. 1 and 2)] independent but closely similar molecules (Abrahams & Keve, 1971), the average molecular geometries are given in Table 2. (In Figs. 1 and 2 x denotes the number of the molecule, so atom Nx1 in molecule 1 is atom N11 in Tables 3 and 4.) The six independent molecules in (I*b*) are joined through N—H···N hydrogen bonds forming two trimers *A* and *B* (Fig. 1), which are related by a pseudo centre of symmetry at [0.251 (4), 0.449 (1), 0.495 (2)] (Nardelli, 1983). Within each trimer, the pseudo six-membered ring formed by the N atoms (N11—N12···N31—N32···N21—N22 and N61—N62···N51—N52···N41—N42) adopts (Table 3) slightly puckered [Q_T = 0.147 (3) and 0.124 (3) Å] boat conformations distorted towards skews [φ_2 and θ = 46 (1), 97 (1)° and 55 (1), 85 (1)° *versus* 60/30, 90° for the undistorted boat and skew conformations (Cremer & Pople, 1975)].

The hydrogen bonds which form the trimers in (I*b*) are quite strong as measured by the N···N distances, which are close to the lower end of the 2.851 (7)–2.978 (4) Å range for this motif in pyrazoles (Foces-Foces, Hager *et al.*, 1997; Foces-Foces, Llamas-Saiz *et al.*, 1997). The crystal is built up of alternating sheets, each

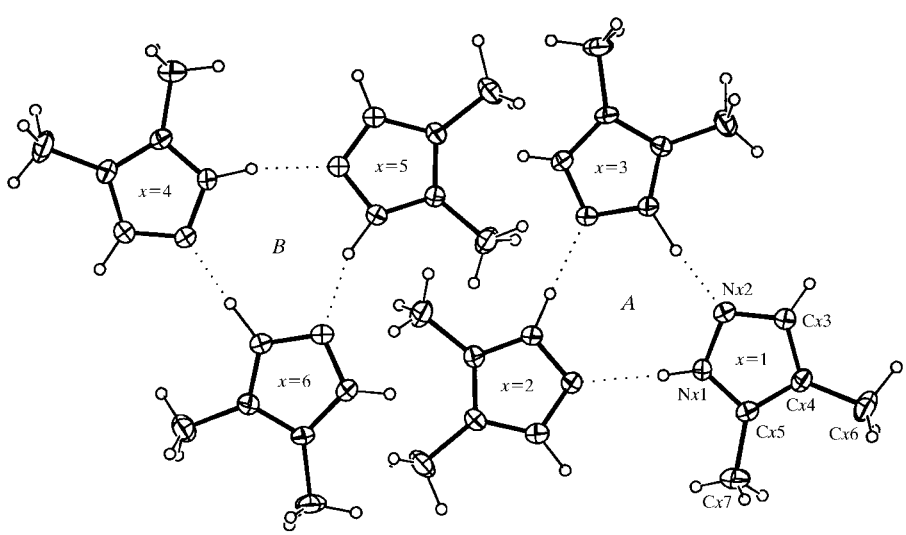


Fig. 1. The pair of 4,5-dimethylpyrazole (I*b*) trimers in the asymmetric unit showing the atomic numbering scheme with displacement ellipsoids drawn at the 30% probability level for non-H atoms. Dotted lines represent hydrogen bonds.

Table 3. *Pseudotorsion angles (°) describing the conformation of the ring in (Ib) formed by the N—H···N hydrogen bonds*

N11—N12···N31—N32	6.1 (3)	N61—N62···N51—N52	8.4 (3)
N12···N31—N32···N21	4.1 (3)	N62···N51—N52···N41	0.2 (3)
N31—N32···N21—N22	−11.5 (3)	N51—N52···N41—N42	−6.9 (3)
N32···N21—N22···N11	8.7 (3)	N52···N41—N42···N61	6.4 (3)
N21—N22···N11—N12	0.5 (4)	N41—N42···N61—N62	1.4 (3)
N22···N11—N12···N31	−8.8 (3)	N42···N61—N62···N51	−8.8 (3)

Table 4. *Hydrogen-bonding geometry for (Ib) (Å, °)*

CEN*x* represents the centroid of the pyrazole ring in molecule *x*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···N22	0.87 (5)	2.01 (5)	2.869 (3)	171 (4)
N21—H21···N32	1.00 (8)	1.88 (8)	2.871 (5)	173 (5)
N31—H31···N12	1.17 (9)	1.71 (8)	2.870 (3)	173 (9)
N41—H41···N52	0.98 (6)	1.92 (6)	2.877 (3)	167 (5)
N51—H51···N62	1.04 (9)	1.86 (9)	2.868 (5)	162 (4)
N61—H61···N42	1.12 (7)	1.78 (8)	2.867 (3)	163 (6)
C46—H462···CEN2^{i}	1.01 (8)	2.86 (10)	3.678 (5)	139 (7)
C67—H673···CEN3^{ii}	1.04 (9)	2.84 (7)	3.725 (4)	142 (6)
C16—H163···CEN5^{iii}	0.96 (6)	2.85 (6)	3.702 (4)	148 (6)
C26—H262···CEN3^{iv}	1.05 (7)	2.68 (8)	3.620 (4)	149 (6)
C66—H663···CEN4^{v}	1.02 (6)	2.79 (5)	3.627 (4)	140 (5)
C57—H572···CEN5^{vi}	1.00 (6)	2.91 (6)	3.776 (4)	146 (6)

Symmetry codes: (i) $x, y-1, z-1$; (ii) $x, y-1, z$; (iii) $x, 1+y, 1+z$; (iv) $-x, 1-y, 1-z$; (v) $1-x, -y, 1-z$; (vi) $1-x, 1-y, 1-z$.

of which is derived exclusively from one trimer (Fig. 3*a*). There are no contacts between sheets derived from the same trimer, but weak C—H···π(pyrazole ring) interactions link sheets composed of different trimers (*A* and *B*) along the [100] direction [symmetry operations (i), (ii) and (iii) in Table 4] and with the centrosymmetrically related ones (Fig. 3*b*). The methyl- and/or nitropyrazole derivatives [*R*3 = *R*5 = Me, *R*4 = H; *R*3 = *R*5 = H, *R*4 = NO_2 (Llamas-Saiz *et al.*, 1994); *R*3 = H, *R*4 = NO_2, *R*5 = Me (Foces-Foces *et al.*, 1994); *R*3 = NO_2, *R*4 = *R*5 = H (Foces-Foces, Llamas-Saiz *et al.*, 1997)] present a similar secondary structure of trimers and analogous packing of layers. However, the topology within each layer is different depending on the type of weak interactions involved.

Apart from the secondary structure (Figs. 1 and 2), (I*b*) and (II) differ from each other in certain geometrical features such as the pattern of bond distances and angles (Table 2). The disorder of the NH group observed in (II) leads to a symmetrical pyrazole not only in molecule 1 (located on a crystallographic twofold axis), but in molecule 2 as previously observed in related structures (Llamas-Saiz *et al.*, 1994). The molecules are also linked by N—H···N hydrogen bonds into strands

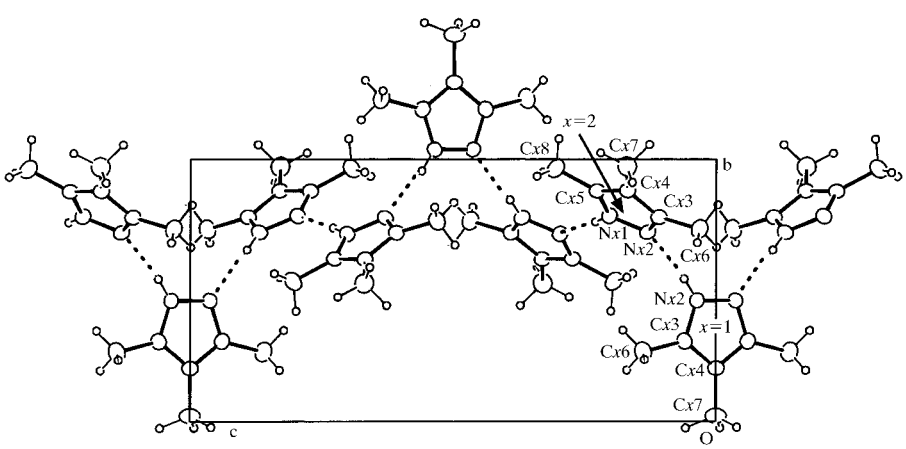


Fig. 2. View of a chain in 3,4,5-trimethylpyrazole, (II), showing the atomic numbering scheme with displacement ellipsoids drawn at the 30% probability level for non-H atoms. Only one component of the disorder model is shown.

Table 5. *Hydrogen-bonding geometry for (II) (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N12—H12···N21	0.81 (4)	2.13 (4)	2.920 (2)	165 (4)
N21—H21···N12	0.81 (5)	2.12 (5)	2.920 (2)	168 (4)
N22—H22···N22^{i}	0.89 (5)	2.03 (5)	2.921 (2)	176 (4)

Symmetry code: (i) $\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}-z$.

Table 6. *Optimized (ab initio calculations) bond distances and angles (Å, °) for several methyl pyrazole derivatives*

The geometry of pyrazole already reported has been included for comparison purposes (Llamas-Saiz *et al.*, 1995). Energies E are given in hartrees (1 hartree = 627.5095 kcal mol^{-1}).

Substituent *R*3	H	Me	H	H	Me	H	Me	Me
Substituent *R*4	H	H	Me	H	Me	Me	H	Me
Substituent *R*5	H	H	H	Me	H	Me	Me	Me
	(HF/B3LYP)	(HF/B3LYP)	(HF/B3LYP)	(HF/B3LYP)	(HF/B3LYP)	(HF/B3LYP)	(HF/B3LYP)	(HF/B3LYP)
N1—N2	1.330/1.350	1.334/1.353	1.327/1.349	1.335/1.354	1.331/1.351	1.331/1.351	1.339/1.356	1.335/1.354
N2—C3	1.302/1.333	1.303/1.335	1.302/1.332	1.300/1.331	1.302/1.334	1.299/1.331	1.300/1.333	1.299/1.332
C3—C4	1.413/1.414	1.419/1.420	1.418/1.419	1.414/1.414	1.424/1.425	1.418/1.417	1.420/1.420	1.425/1.425
C4—C5	1.363/1.381	1.361/1.379	1.363/1.383	1.365/1.384	1.362/1.381	1.368/1.389	1.364/1.382	1.366/1.387
C5—N1	1.341/1.359	1.340/1.358	1.345/1.360	1.344/1.363	1.343/1.359	1.348/1.364	1.343/1.362	1.346/1.364
C3—*R*3	—	1.498/1.499	—	—	1.498/1.498	—	1.496/1.499	1.498/1.498
C4—*R*4	—	—	1.500/1.500	—	1.500/1.499	1.501/1.500	—	1.501/1.499
C5—*R*5	—	—	—	1.496/1.496	—	1.497/1.496	1.498/1.496	1.497/1.496
C5—N1—N2	112.8/113.3	112.5/113.1	112.6/113.1	113.3/113.9	112.3/112.9	113.2/113.8	113.0/113.6	113.0/113.6
N1—N2—C3	105.0/103.9	105.5/104.6	105.0/103.9	104.8/103.7	105.5/104.5	104.6/103.6	105.3/104.4	105.2/104.2
N2—C3—C4	111.7/112.1	110.9/111.1	112.1/112.6	111.7/112.1	111.3/111.7	112.2/112.7	110.9/111.1	111.4/111.7
C3—C4—C5	103.9/104.5	104.4/105.1	103.2/103.6	104.5/105.1	103.7/104.2	103.7/104.2	104.9/105.7	104.1/104.8
C4—C5—N1	106.6/106.1	106.7/106.1	107.2/106.8	105.9/105.2	107.2/106.7	106.3/105.7	105.9/105.2	106.3/105.7
N2—C3—*R*3	—	121.2/120.3	—	—	121.2/120.5	—	121.2/120.4	121.2/120.6
C4—C3—*R*3	—	128.0/128.5	—	—	127.6/127.8	—	127.9/128.6	127.4/127.7
C3—C4—*R*4	—	—	128.2/128.4	—	127.8/127.7	127.1/127.9	—	126.6/126.8
C5—C4—*R*4	—	—	128.6/128.0	—	128.5/128.1	129.2/128.0	—	129.3/128.4
N1—C5—*R*5	—	—	—	122.5/122.8	—	121.6/122.5	122.5/122.9	121.4/122.2
C4—C5—*R*5	—	—	—	131.6/131.9	—	132.2/131.7	131.6/131.9	132.3/132.1
E(HF)	—	−263.8475	−263.8438	−263.8476	−302.8881	−302.8870	−302.8920	−341.9314
E(B3LYP)	—	−265.5305	−265.5276	−265.5304	−304.8513	−304.8506	−304.8540	−344.1743

extending in the [001] direction (molecules: 1, 2, 2′, 1′, 2″, and so on). The N···N values (Table 5) are within the 2.821 (3)–3.133 (5) Å range found for pyrazole catemers (Domiano & Musatti, 1974; Llamas-Saiz *et al.*, 1994; Claramunt *et al.*, 1997, and references therein). Only one component of the disorder model is represented in Fig. 2. There are no interactions between chains other than van der Waals contacts (Fig. 4). As we have explained, for the disorder to be dynamic the hydrogen-bond network should involve cyclic structures [for instance, compound (I*b*) which crystallizes in trimers], this being a necessary but not sufficient condition. Since in compound (II) the structure corresponds to a catemer, the disorder must be static in order to be consistent with failure to observe a signal from this compound by ^{15}N CP-MAS NMR spectroscopy (Aguilar-Parrilla *et al.*, 1994).

There are no voids in the structures and the total packing coefficients are 0.638 and 0.646 for (I*b*) and (II), respectively (Cano & Martínez-Ripoll, 1992).

3.2. *Molecular orbital calculations*

Theoretical studies [*ab initio* molecular orbital calculations at the HF and B3LYP/6-31G** levels; Frisch *et al.*, 1995] on isolated 3,4-dimethyl- (I*a*) and 4,5-dimethyl- (I*b*) pyrazoles predict a greater stability, but only by 0.69 and 0.44 kcal mol^{-1}, respectively, of the 3,4-dimethyl tautomer, in accordance with the value of 0.55 kcal mol^{-1} previously reported from a calculation carried out at the 3-21G level (Alcamí *et al.*, 1990).

In order to estimate the influence of the methyl substitution on the geometry of the pyrazole, we have optimized the geometries of the 3-methyl-, 4-methyl-

and 5-methylpyrazoles at the same level and compared them with that of pyrazole (Llamas-Saiz *et al.*, 1995) and those of the dimethyl- and trimethylpyrazole (Table 6). The effects due to two or more substituents can be superimposed and the methyl group closes the *ipso* angle by 0.9° and opens the contiguous ones by 0.6°, on average, *versus* 1.9 and −1.0° found in benzenes (Domenicano & Murray-Rust, 1979). Comparison of the optimized geometries (Table 6) with the experimental ones (Table 2) reveals that as far as the bond distances are concerned [neglecting compound (II) because of disorder] better agreement is obtained when electronic correlation effects are considered (B3LYP method). However, the disagreement in the bond angles could be an indication of a small percentage of disorder in (I*b*) (not observed in the X-ray analysis) that tends to close and open the angles at N*x*1 and N*x*2. The difference between the values of the internal angle at N*x*1 and at N*x*2 becomes negligible when the population parameter is 0.50 as in compound (II) (Table 2). This fact is also noteworthy when the values in (I*b*) are compared with those of the pyrazole itself (La Cour & Rasmussen, 1973).

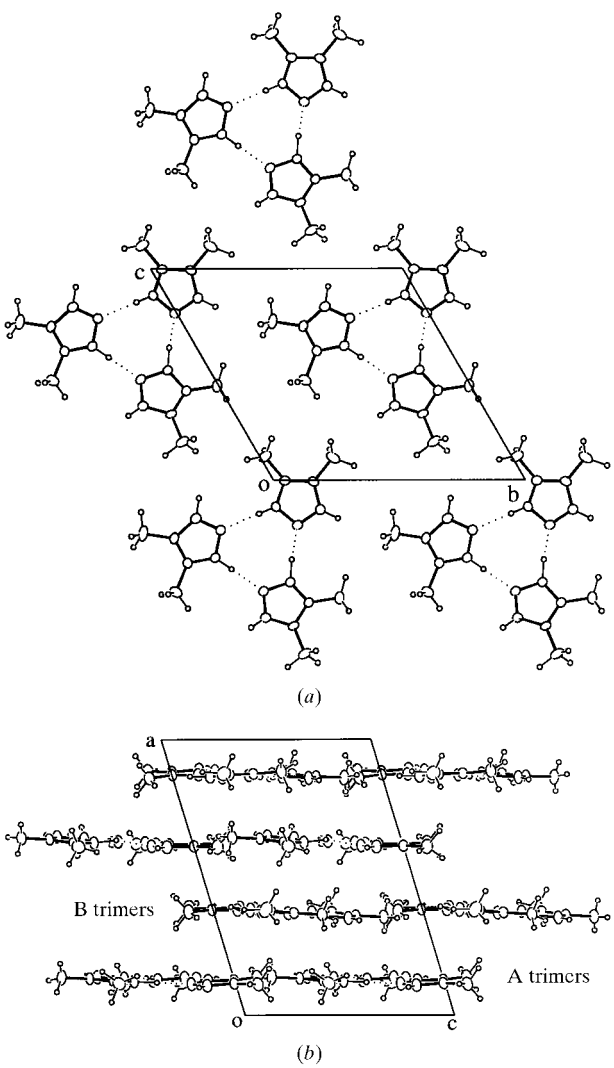


Fig. 3. (*a*) View of a layer of *A* trimers in (I*b*) along the *a* axis. (*b*) The crystal packing in (I*b*) along the *b* axis.

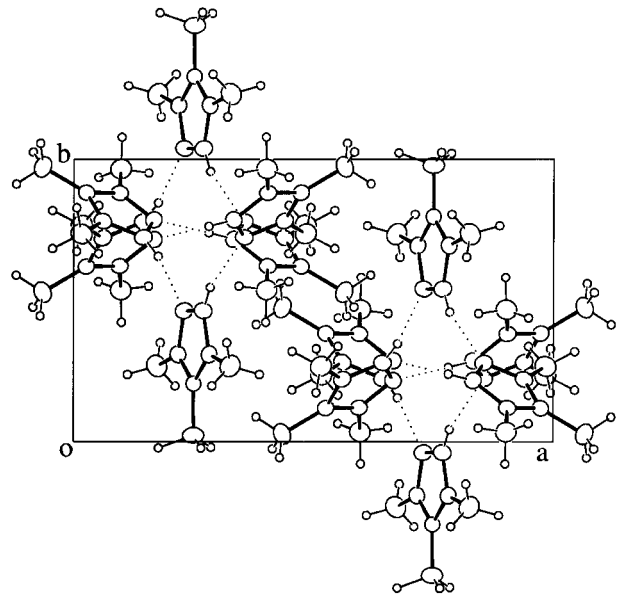


Fig. 4. The crystal packing of (II) viewed down the *c* axis.

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