

AROMATIC PROPELLENES. PART 3. NMR, X-RAY CRYSTALLOGRAPHY AND SEMI-EMPIRICAL CALCULATIONS ON THE CONFORMATIONAL ISOMERISM OF 1,2,4,5-TETRAKIS (PYRAZOL-1'-YL)-3,6-BIS(3'',5''-DIMETHYLPYRAZOL-1'-YL) BENZENE

CONCEPCION FOCES-FOCES* AND CRISTINA FERNÁNDEZ-CASTAÑO

Departamento de Cristalografía, Instituto de Química Física 'Rocasolano', CSIC, Serrano 119, E-28006 Madrid, Spain

ROSA MARÍA CLARAMUNT* AND CONSUELO ESCOLÁSTICO

Departamento de Química Orgánica y Biología, UNED, Senda del Rey s/n, E-28040 Madrid, Spain

AND

JOSÉ ELGUERO

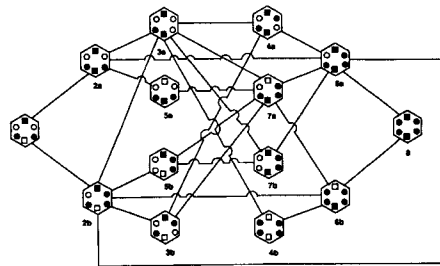
Instituto de Química Médica, Centro de Química Orgánica 'Manuel Lora Tamayo,' CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain

The molecular and crystal structures of two crystalline forms of 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1'-yl) benzene and one inclusion complex with two molecules of acetic acid were determined by x-ray analysis. The acetic acid forms dimers through symmetry centers and the only interactions in the structures are mainly due to weak C—H...N interactions. All 14 possible conformations of the pyrazole with regard to the benzene ring were explored by means of AM1 semi-empirical calculations. The observed conformation in the crystal structures agrees fairly well with the most stable conformation which presents the pyrazole rings with the N(2) alternating between both sides of the phenyl plane. These calculations allow one to identify the minor isomer present in solution together with the major isomer corresponding to the crystal structure.

INTRODUCTION

In Parts 1 and 2, we reported the study of the conformational isomerism of hexa(3',5'-dimethylpyrazol-1'-yl)benzene [(dmpz)₆bz]¹ and hexa(pyrazol-1'-yl)benzene [(pz)₆bz].² We now discuss 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1'-yl)benzene [(pz)₄(dmpz)₂bz] (1). The fact that there are two different pyrazoles in a kind of *para* situation makes the number of conformational isomers increase from 8 (9 counting enantiomerism) to 14 (15 taking into account that they are two enantiomers in the case of 3a) and that the graph representing all the single inter-conversion paths (see Scheme 1) becomes much more

complex. As in the previous papers,^{1,2} black represents *up* (*u*) and white represents *down* (*d*) and circles and squares correspond to pz^{1,2} and dmpz (this work), respectively.



Scheme 1

* Authors for correspondence.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra in solution were recorded on a Bruker AC200 instrument operating at 200.13 and 50.32 MHz, respectively. The ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectrum of **1b** was recorded on the same instrument using the conditions described elsewhere.³

Materials. Pyrazole (23.67 mmol) in 20 ml of anhydrous THF was placed in a three-necked round-bottomed flask provided with a reflux refrigerator, argon

atmosphere and magnetic stirring. To this solution, 23.67 mmol of NaH (60% oil dispersion) were added in small portions and the reaction mixture was heated at 65 °C for 1 h. After cooling, 5.92 mmol of 1,4-bis(3',5'-dimethylpyrazol-1'-yl)-2,3,5,6-tetrafluorobenzene were added and the mixture was heated under reflux for 6 h. A white precipitate of 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1'-yl)benzene (**1**) was formed, which, after filtration, was rinsed first with 20 ml of water and then with 20 ml of THF: yield 95%, $R_f = 0.44$ [dichloromethane-ethanol (95:5)], m.p. by differential scanning calorimetry.

Table 1. Crystal analysis parameters at room temperature

	1a	1b	1 · 2AcOH
Crystal data			
Formula	$\text{C}_{28}\text{H}_{26}\text{N}_{12}$	$\text{C}_{28}\text{H}_{26}\text{N}_{12}$	$\text{C}_{28}\text{H}_{26}\text{N}_{12} \cdot 2\text{C}_2\text{H}_4\text{O}_2$
Crystal habit	Colorless, prism	Colorless, prism	Colorless, plate
Crystal size (mm)	0.50 × 0.16 × 0.13	0.24 × 0.13 × 0.13	0.47 × 0.33 × 0.07
Symmetry	Triclinic, <i>P</i> -1	Monoclinic, <i>C2/m</i>	Triclinic, <i>P</i> -1
Unit cell determination:	Least-squares fit from 68 reflections ($\theta < 45^\circ$)	Least-squares fit from 68 reflections ($\theta < 45^\circ$)	Least-squares fit from 70 reflections ($\theta < 45^\circ$)
Unit cell dimensions (Å , °)	$a = 10.501(6)$ $b = 14.3411(24)$ $c = 11.0770(11)$ 112.134(10) 113.529(6) 95.321(4)	$a = 14.3565(10)$ $b = 14.6551(7)$ $c = 6.4408(2)$ 90 99.110(4) 90	$a = 11.2133(15)$ $b = 10.7153(7)$ $c = 8.3867(7)$ 112.416(8) 77.589(7) 116.219(10)
Packing: V (Å^3), Z	1366.2(3), 2	1338.0(1), 2	834.4(2), 1
D_c (g cm^{-3}), M , $F(000)$	1.290, 530.59, 556	1.317, 530.59, 556	1.295, 650.70, 342
μ (cm^{-1})	6.75	6.89	7.42
Experimental data			
Technique	Philips PW1100 four-circle diffractometer, bisecting geometry. Graphite-oriented monochromator. $\omega/2\theta$ scans. Detector apertures $1 \times 1^\circ$. 1 min/reflection. Radiation: Cu K α		
Scan width (°)	1.5	1.5	1.6
θ_{max} (°)	65	65	65
Number of reflections:			
Independent	4468	1196	2807
Observed	3602 [$2\sigma(I)$ criterion]	1051 [$2\sigma(I)$ criterion]	2336 [$2\sigma(I)$ criterion]
Standard reflections	2 reflections every 90 minutes. No variation		
Solution and refinement			
Solution		Direct methods: Sir92	
Refinement:		Full matrix	
Least-squares on F_o			
Parameters:			
Number of variables	466	133	286
Degrees of freedom	3136	918	2050
Ratio of freedom	7.7	7.9	8.2
Final shift/error	0.01	0.08	0.03
Secondary extinction (10^4)	0.20(2)	0.25(3)	0.27(4)
H atoms		From difference synthesis	
Weighting scheme	Empirical as to give no trends in $\langle \omega \Delta^2 F \rangle$ vs $\langle F_o \rangle$ and $\Gamma \sin \theta / \lambda$		
Max. thermal value (Å^2)	U11[C(33)]mol.2] = 0.106(3)	U33[C(14)] = 0.138(3)	U22[C(26)] = 0.124(4)
Final ΔF peaks (e Å^{-3})	0.22	0.19	0.24
Final R and R_w	0.053, 0.058	0.042, 0.053	0.048, 0.051 * 97

metry (DSC) 344.7 °C (from dichloromethane–hexane) (**1a**). The samples recrystallized from ethanol (**1b**) and acetic acid showed by DSC the same melting point; in the case of the latter crystals the loss of the acetic acid was observed at 111 °C. IR (KBr), ν (cm⁻¹): 3125, 3105, 2915, 1605, 1555, 1520, 1480, 1395, 1335, 1305, 1200, 1185, 1130, 1105, 1080, 1050, 1035, 1020, 950, 930, 915, 895, 855, 790, 765, 665, 640, 625. MS, m/z (relative intensity, %): 532 ($M^+ + 2$, 10), 531 ($M^+ + 1$, 48), 530 (M^+ , 100), 476 (13), 475 (41), 463 (30), 462 (32), 395 (15), 265 (16), 80 (110), 79 (10), 68 (12). Elemental analysis: calculated for C₂₈H₂₆N₁₂, C 63.38, H 4.94, N 31.68; found, C 63.63, H 4.91, N 31.23%.

X-ray crystallography. Details of data collection and processing are presented in Table 1. Polymorphs **1a** and **1b** were obtained by slow evaporation of saturated solutions in dichloromethane–hexane and in ethanol, respectively. The structures were solved by direct methods (Sir92).⁴ The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included as isotropic. Most of the calculations were performed on a VAX6410 computer using the Xtal System.⁵ The atomic scattering factors were taken from Ref. 6.

Semi-empirical calculations. The molecular structures for the fourteen possible combinations of *up* and *down* pyrazoles (Scheme 1) were optimized using the AM1 parametrizations of the Hamiltonian as implemented in the MOPAC6.0 package.⁷ The only restriction imposed was the planarity of the pyrazole and benzene rings. The calculations were performed on an ALPHA3000–300X DEC station.

RESULTS AND DISCUSSION

Syntheses

The synthesis of 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3", 5"-dimethylpyrazol-1"-yl)benzene (**1**) has been achieved

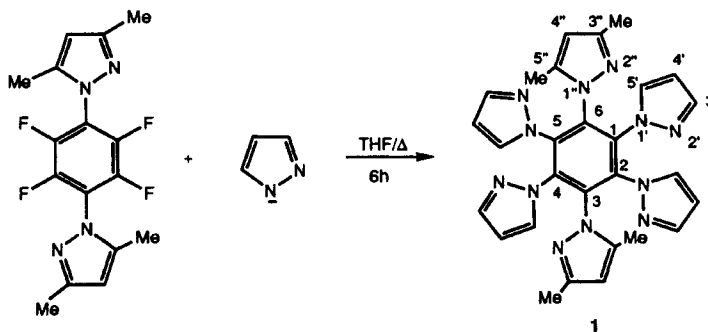
by the reaction of 1,4-bis(3',5'-dimethylpyrazol-1'-yl)-2,3,5,6 tetrafluorobenzene³ with the pyrazole anion in a molar ratio 1 : 4 with a 95% yield (Scheme 2).

¹H NMR spectra of a freshly prepared solution of **1** and its evolution with time in solvents such as CDCl₃ and methanol-*d*₄ were recorded [see Table 2 and Figure 1(a) and (b)]. The spectra of the freshly prepared solutions show signals which correspond to a single isomer, after 24 h the presence of a minor new rotational isomer is detected and the proportion does not change with time, the initial conformer being the majority component with a ratio of 9 : 1. We succeeded in isolating a mixture enriched in the minor isomer; its ¹H NMR spectrum was recorded and after 24 h the same equilibrium mixture was obtained.

The ¹³C NMR spectra are reported in Table 3. The ¹³C CP/MAS NMR spectra of **1** (polymorphs **1a** and **1b**) and its acetic acid complex show data which agree with the existence of **1** in the solid state as only one conformer [see Figure 2(a) and (b)] but with two different structures: in **1a** there are two kinds of dmpz whereas in **1b** there is only one kind. The corresponding inclusion compound **1**·2AcOH shows the signals of acetic acid in a 2 : 1 ratio and only one kind of dmpz [Figure 2c)].

X-ray analysis

Crystals of the two polymorphic forms **1a** and **1b** and of the inclusion complex **1**·2AcOH were obtained in dichloromethane–hexane, ethanol and acetic acid, respectively. Table 4 summarizes the main geometric characteristics of the molecular structures according to the numbering scheme shown in Figure 3. All molecules were located on inversion centers: two independent halves are present in **1a** and half a host and one acetic acid molecule in the complex. In the **1b** form, the host molecule shows higher symmetry than in the two others since the 3,5-dimethylpyrazole (dmpz) rings are on mirror planes and the molecule also exhibits a twofold axis perpendicular to it (C_{2v}). These results are in



Scheme 2

Table 2. ¹H NMR chemical shifts (δ , ppm) and coupling constants (J , Hz) of 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1''-yl)benzene

Compound	H-3'	H-4'	H-5'	H-4''	CH ₃ -3''	CH ₃ -5''	Solvent
1 ^a	7.35 (dd)	6.11 (dd)	7.36 (dd)	5.61 (s)	2.10 (s)	1.82 (s)	CDCl ₃
	7.41 (dd)	6.11 (dd)	7.11 (dd)	5.64 (s)	2.03 (s)	1.97 (s)	
	$J_{H3',H4'} = 1.9$ $J_{H3',H5'} = 0.5$	$J_{H3',H4'} = 1.8$ $J_{H4',H5'} = 2.5$	$J_{H3',H5'} = 0.5$ $J_{H4',H5'} = 2.5$				
1 ^a	7.36 (dd)	6.17 (dd)	7.41 (dd)	5.71 (s)	2.05 (s)	1.86 (s)	Methanol- <i>d</i> ₄
	7.38 (dd)	6.17 (dd)	7.29 (dd)	5.74 (s)	1.99 (s)	1.99 (s)	
	$J_{H3',H4'} = 1.9$ $J_{H3',H5'} = 0.5$	$J_{H3',H4'} = 1.9$ $J_{H4',H5'} = 2.6$	$J_{H4',H5'} = 2.4$				

^aThe signals of the major isomer are given first.

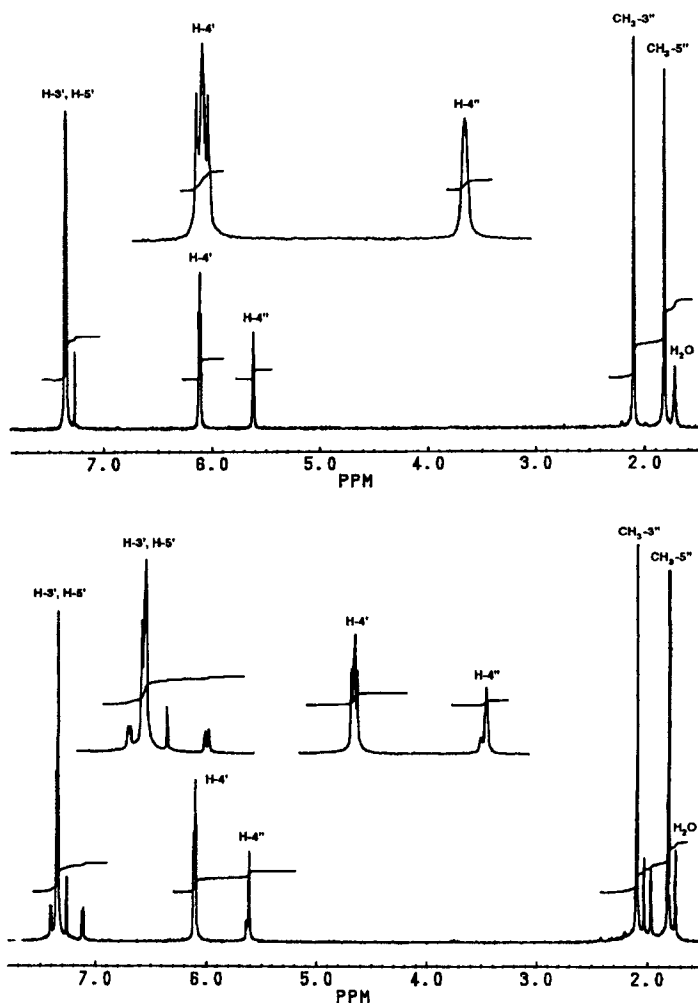


Figure 1. ¹H NMR spectra of (a) a freshly prepared solution in CDCl₃ of 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1''-yl)benzene and (b) a solution in CDCl₃ of 1,2,4,5-tetrakis(pyrazol-1''-yl)-3,6-bis(3'',5''-dimethylpyrazol-1''-yl)benzene after standing for 24 hours

Table 3. ^{13}C NMR chemical shifts (δ , ppm) and coupling constants (J , Hz) of 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1''-yl)benzene

Compound	C-1	C-2	C-3	C-3'	C-4'	C-5'	C-3''	C-4''	C-5''	CH ₃ -3''	CH ₃ -5''
1^a	137.2	137.2	135.1	141.4	106.7	132.0	150.4	105.5	143.1	13.4	10.5
				$^1J_{\text{H}3'} = 186.6$ $^2J_{\text{H}4'} = 5.9$ $^3J_{\text{H}5'} = 8.4$	$^1J_{\text{H}4'} = 178.5$ $^2J_{\text{H}3'} = 10.2$ $^2J_{\text{H}5'} = 8.9$ 107.1	$^1J_{\text{H}5'} = 191.9$ $^2J_{\text{H}4'} = 9.4$ $^3J_{\text{H}3'} = 4.6$		$^1J_{\text{H}4''} = 174.1$		$^1J = 127.4$	$^1J = 129.2$
1^b	137.2	137.2	135.4	141.4	107.1	131.1	150.5	105.5	143.3	13.4	10.5
1^ab	138.7	138.7	136.7	140.8	108.3	131.2	148.3	107.1	142.2	13.0	9.7
						131.7	151.4			14.1	10.8
1^b	138.1	138.1	138.1	138.1	107.0	130.9	148.1	105.0	142.6	15.0	11.5
1 · 2AcOH^{b,c}	137.5	137.5	133.7	141.5	107.0	131.8	148.9	106.3	141.5	13.3	10.3

^a The signals of the major isomer are given first (solvent: CDCl₃).^b CP MAS.^c Acetic acid: 21.7 (CH₃), 179.7 (C=O).

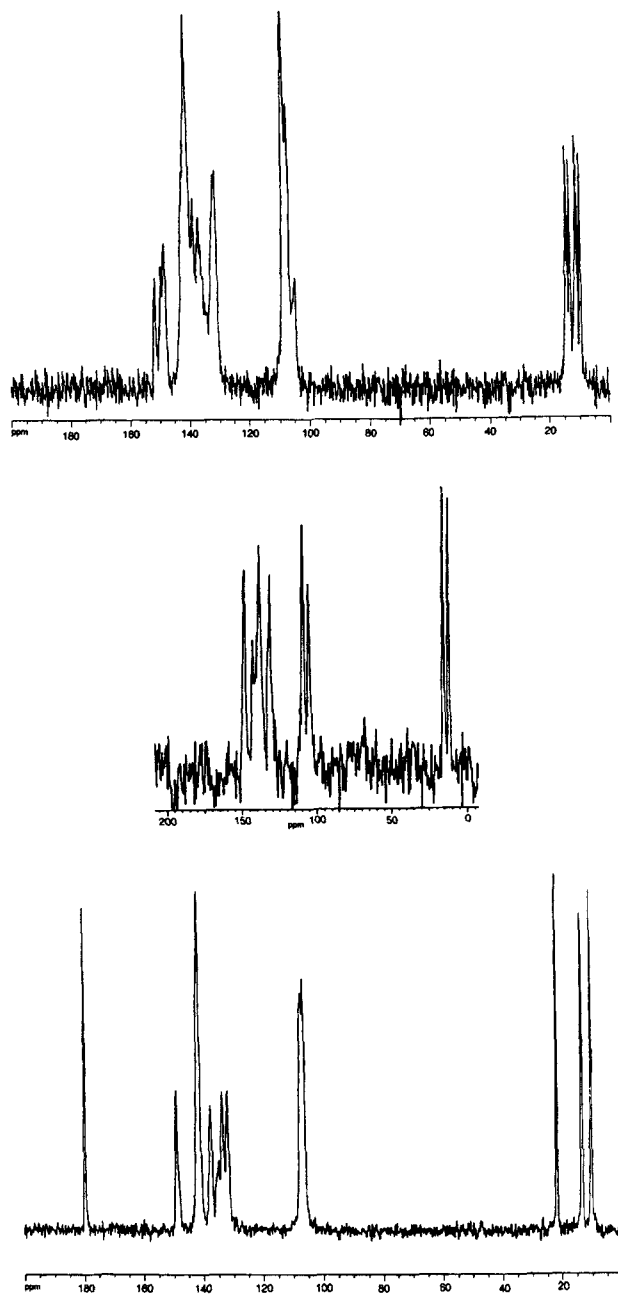


Figure 2. ^{13}C NMR spectra in the solid state of (a) 1,2,4,5-tetrakis(pyrazol-1'-yl)-m3,6-bis(3'',5''-dimethylpyrazol-1''-yl)benzene (polymorph **1a**) (75 MHz), (b) 1,2,4,5-tetrakis(pyrazol-1'-yl)-3,6-bis(3'',5''-dimethylpyrazol-1''-yl)benzene (polymorph **1b**) (50 MHz) and (c) inclusion compound **1** · 2AcOH (75 MHz)

Table 4. Selected geometric parameters (Å, °)^a

	Compound 1a					
	Molecule 1			Molecule 2		
	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3
N(<i>i</i> 1)—N(<i>i</i> 2)	1.355(4)	1.374(3)	1.363(2)	1.355(3)	1.370(3)	1.348(5)
N(<i>i</i> 1)—C(<i>i</i> 5)	1.355(4)	1.351(4)	1.351(4)	1.339(4)	1.355(3)	1.344(4)
N(<i>i</i> 2)—C(<i>i</i> 3)	1.312(4)	1.327(5)	1.319(4)	1.317(5)	1.326(3)	1.333(6)
C(<i>i</i> 3)—C(<i>i</i> 4)	1.384(6)	1.393(4)	1.391(5)	1.370(6)	1.393(4)	1.369(6)
C(<i>i</i> 4)—C(<i>i</i> 5)	1.345(5)	1.362(5)	1.356(3)	1.360(5)	1.359(4)	1.352(6)
N(<i>i</i> 2)—N(<i>i</i> 1)—C(<i>i</i> 5)	111.1(3)	112.6(2)	112.2(2)	111.9(3)	112.4(2)	112.4(3)
N(<i>i</i> 1)—N(<i>i</i> 2)—C(<i>i</i> 3)	104.2(3)	104.0(2)	103.6(2)	103.6(3)	104.0(2)	102.8(3)
N(<i>i</i> 2)—C(<i>i</i> 3)—C(<i>i</i> 4)	112.5(4)	111.0(3)	112.4(3)	112.8(4)	111.2(3)	113.0(4)
C(<i>i</i> 3)—C(<i>i</i> 4)—C(<i>i</i> 5)	105.0(3)	107.0(3)	105.3(3)	104.9(4)	106.7(3)	104.8(3)
N(<i>i</i> 1)—C(<i>i</i> 5)—C(<i>i</i> 4)	107.3(3)	105.4(2)	106.6(3)	106.8(3)	105.6(2)	107.0(3)
N(<i>i</i> 2)—N(<i>i</i> 1)—C(<i>i</i>)—C(<i>i</i> - 1)	52.8(4)	-87.8(3)	120.5(3)	58.1(4)	-90.3(3)	113.9(3)
	Compound 1b			Compound 1 · 2AcOH		
	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3
N(<i>i</i> 1)—N(<i>i</i> 2)	1.356(3)	1.371(3)	1.356(3)	1.354(3)	1.374(3)	1.357(3)
N(<i>i</i> 1)—C(<i>i</i> 5)	1.352(3)	1.359(3)	1.352(3)	1.352(3)	1.348(4)	1.340(3)
N(<i>i</i> 2)—C(<i>i</i> 3)	1.317(3)	1.327(3)	1.317(3)	1.325(3)	1.325(4)	1.325(4)
C(<i>i</i> 3)—C(<i>i</i> 4)	1.368(5)	1.397(4)	1.368(5)	1.377(4)	1.388(5)	1.377(4)
C(<i>i</i> 4)—C(<i>i</i> 5)	1.365(4)	1.368(3)	1.365(4)	1.361(3)	1.375(4)	1.360(5)
N(<i>i</i> 2)—N(<i>i</i> 1)—C(<i>i</i> 5)	112.0(2)	112.8(2)	112.0(2)	112.8(2)	113.0(3)	112.1(2)
N(<i>i</i> 1)—N(<i>i</i> 2)—C(<i>i</i> 3)	103.9(2)	103.8(2)	103.9(2)	103.1(2)	103.7(2)	103.1(2)
N(<i>i</i> 2)—C(<i>i</i> 3)—C(<i>i</i> 4)	112.4(2)	111.7(2)	112.4(2)	112.7(3)	111.6(3)	113.1(3)
C(<i>i</i> 3)—C(<i>i</i> 4)—C(<i>i</i> 5)	105.9(3)	106.3(2)	105.9(3)	105.5(3)	106.6(3)	104.4(3)
N(<i>i</i> 1)—C(<i>i</i> 5)—C(<i>i</i> 4)	105.7(2)	105.5(2)	105.7(2)	105.9(3)	105.1(3)	107.3(3)
N(<i>i</i> 2)—N(<i>i</i> 1)—C(<i>i</i>)—C(<i>i</i> - 1)	116.5(2)	-87.4(2)	65.7(2)	57.4(3)	-94.5(3)	114.9(3)

^aFor comparison purposes and owing to the symmetry in compound 1b, column *i* = 3 is equivalent to *i* = 1.

perfect agreement with the solid-state NMR results: triclinic polymorph **1a** two independent halves, that is, two dmpz; monoclinic polymorph **1b** one quarter of an independent molecule, that is, one dmpz; acetic acid complex half an independent molecule (one dmpz) and one acetic acid molecule (stoichiometry 1 : 2).

The molecules in **1a**, **1b** and **1 · 2AcOH** have essentially the conformation labelled **1** in Scheme 1. All the nitrogen [N(*i*2)] of the pyrazole rings are placed, alternately, *up* (*u*) and *down* (*d*) with respect to the benzene ring^{1,2} giving rise to the *ududud* conformation (see semi-empirical calculations and Scheme 1). In all of them, the dmpz rings appear to be almost perpendicular to the benzene ring while the pz rings make angles of 60° with it [torsion angles close to 60 or 120° using an anticlockwise definition in the benzene ring (Table 4 and Figure 4)]. The lowest N(*i*2)—N(*i*1)—C—C torsion angles presented by the pz rings are counterbalanced by the presence of C(*i*5)—H(*i*5)···N

intramolecular distances shorter than the sum of van der Waals radii⁸ of 3.28 Å, as in **1a** with C(*i*5)—H(*i*5)···N(22) [*i* = 1, 3 in molecule 1, 3.191(4), 3.238(4); *i* = 1 in molecule 2, 3.196(4) Å] or in **1 · 2AcOH** [*i* = 1, 3.203(3) Å]. These distances correspond to torsion angles <60° or greater >120° (Table 4).

The crystal packing of **1a** [Figure 4(a)] consists of piles of alternating independent molecules along the *b* axis. The benzene rings are mutually rotated 24° on average as measured by the lowest Cphenyl1···Cent1···Cent2···Cphenyl2 pseudo-torsion angle (Cent = centroid of the phenyl ring). The benzene plane makes an angle of 13.1(2)° and their centroids are *b*/2 Å apart. In **1b**, only piles of identical molecules along the *c* axis are observed so that the benzene rings are parallel and the centroid separation is shorter than in **1a** (*c* parameter in **1b** < *b*/2 in **1a**).

In **1 · 2AcOH**, the acetic acid molecules are arranged in centrosymmetric dimers [O···O = 2.671(3) Å and

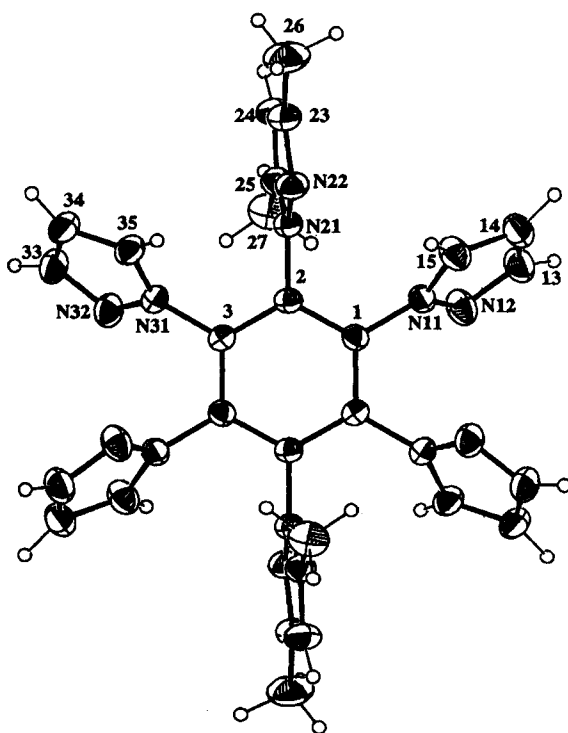


Figure 3. ORTEP⁵ view of compound **1** · 2AcOH with the host projected on the benzene ring showing the numbering system using in the three structures. Ellipsoids are drawn at the 30% probability level

O—H...O = 172(8)°]. The packing is analogous to that of polymorph **1a** [Figure 4(a) and (c)] where one molecule of the two different ones has been replaced by the dimer. This resulted in a shortening of the axis of the columns. The formation of acetic acid dimers is unusual since it has been observed previously only in four structures (CSD⁹ refcodes: COVFUO, PEHYUW, VEVLOX and VUSLIE).

No intermolecular contacts shorter than the sum of van der Waals radii⁸ has been detected.

NMR spectroscopy and the structure of the minor isomer

An important fact in Table 2 must be stressed: the minor isomer shows only the signals for *one* pz and *one* dmpz (ratio 4:2) and this in different solvents. Hence the following criteria are to be used to establish the structure of the minor isomer:

(1) the isomer must have a symmetry consistent with only one dmpz and one pz in ¹H NMR; this criterion is excluding;

(2) according to the results obtained in Parts 1 and 2,^{1,2} the number of *uu* (*dd*) interactions has to be the least possible;

(3) a minor condition is that the number of *uuu* (or *ddd*) situations should also be the least possible. The possible situations for three adjacent pyrazoles are *udu* (*dud*), *duu* (*udd*) and *uuu* (*ddd*), which we have called V-shaped (V), L-shaped (L) and horizontal-shaped (H). We have summarized in Table 5 and Scheme 3 these criteria for the 14 isomers.

Semi-empirical computations

Semi-empirical AM1 calculations were carried out for the fourteen isomers shown in Scheme 3 and the energies corresponding to the minima are reported in Table 5. Two different conformations similar in energy (0.7 kcal mol⁻¹) were obtained for isomer **1** (starting from one dmpz: -92.0, 115.8, -63.0, 92.0, -115.8, 63.0° and -97.1, 75.0, -65.0, 97.1, -75.0, 65.0°). The more stable conformations correspond, in terms of torsion angles, to those found in the crystal structures of the studied compounds (Table 4). The energies in Table 5 can be analysed using a very simple additive model: $\Delta H = a_0 + a_1(uu) + a_2(uuu)$. The model considered, based on our previous experience, that the disfavorable terms are two or three adjacent pyrazoles with the same orientation *uu* (or *dd*) and *uuu* (or *ddd*). The result of the multiple

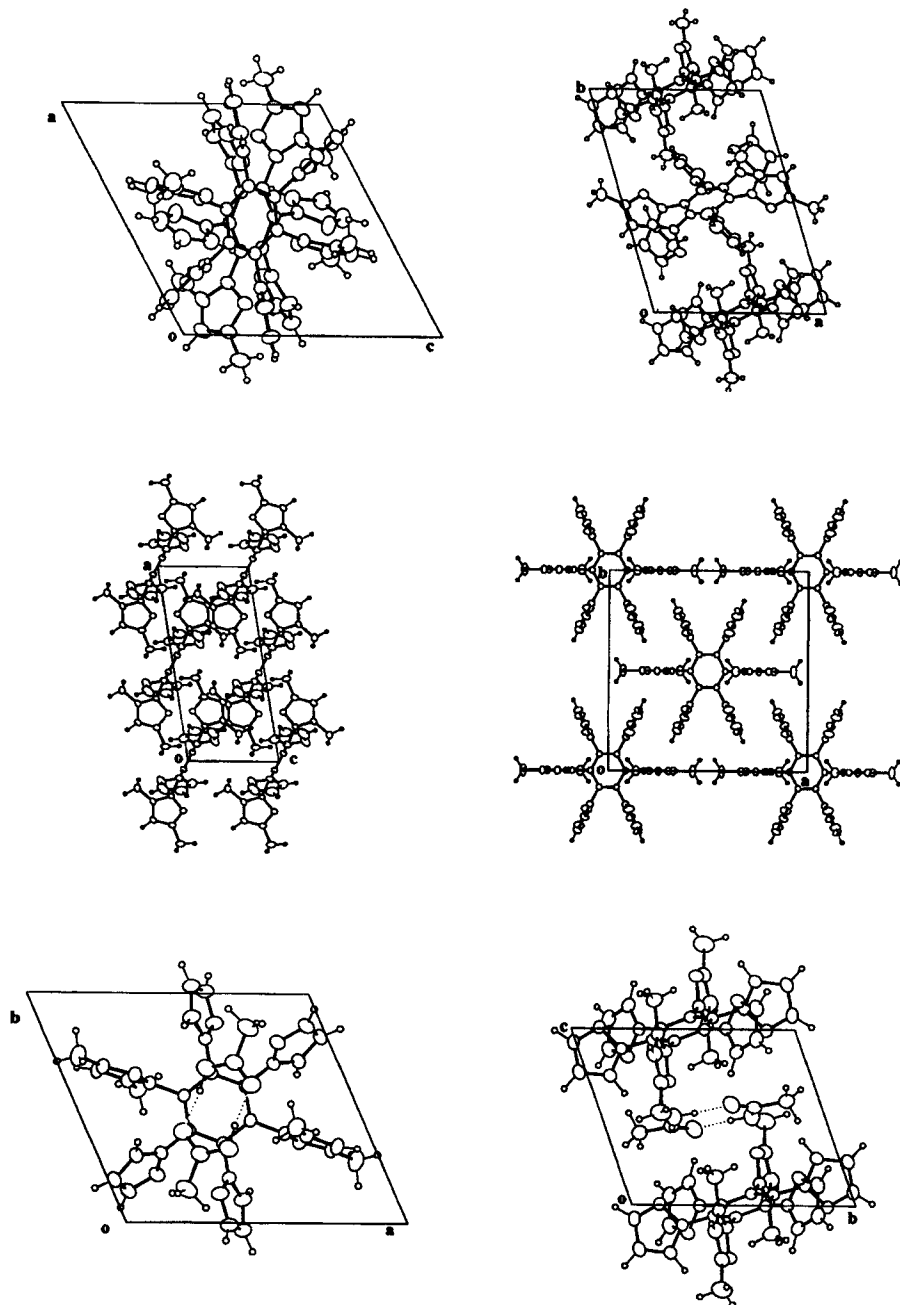
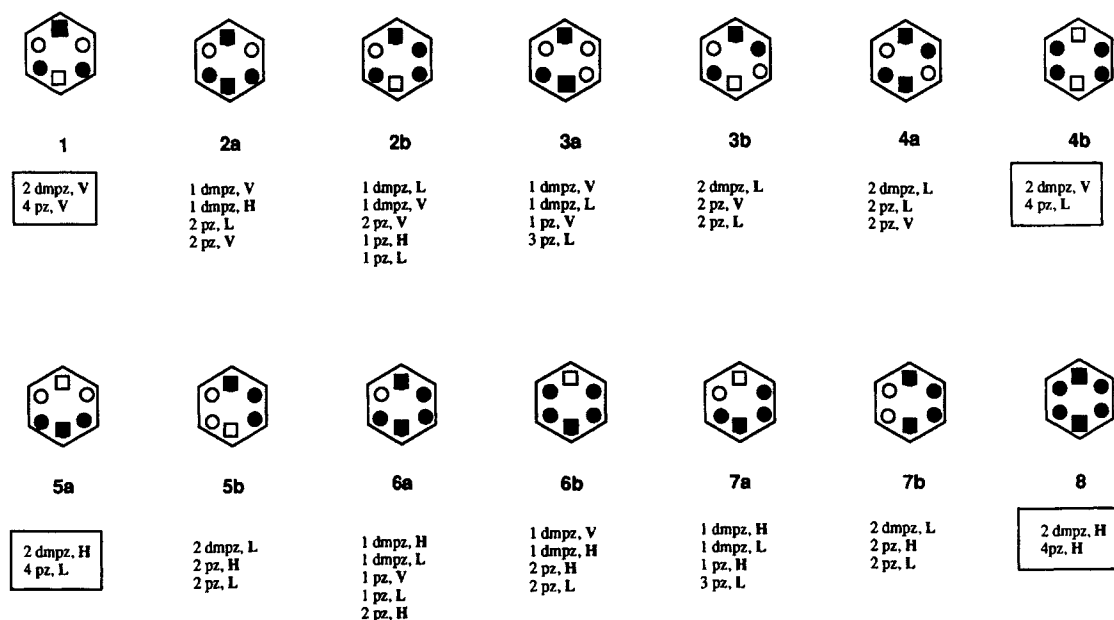


Figure 4. Crystal packings of (a) **1a** down the *b* and *c* axes, (b) **1b** and (c) **1·2AcOH** down the *c* and *a* axes

Table 5. NMR characteristics of the 14 isomers

Conformer	dmpz	pz	<i>uu</i> (<i>dd</i>) interactions	ΔH (AM1) (kcal mol ⁻¹)
1	1 (2V)	1 (4V)	0	508.7
2a	2 (V, H)	2 (2V, 2L)	2	511.5
2b	2 (L, H)	3 (2V, H, L)	2	511.2
3a ^a	2 (V, L)	2 (1V, 3L)	2	511.3
3b	2 (2L)	2 (2V, 2L)	2	511.4
4a	1 (2L)	2 (2V, 2L)	2	511.5
4b	1 (2V)	1 (4L)	2	511.6
5a	1 (2H)	1 (4L)	4	514.0
5b	1 (2L)	2 (2H, 2L)	4	513.2
6a	2 (L, H)	3 (2H, V, L)	4	514.4
6b	2 (V, H)	2 (2H, 2L)	4	514.5
7a	2 (L, H)	2 (1H, 3L)	4	514.0
7b	1 (2L)	2 (2H, 2L)	4	514.4
8	1 (2H)	1 (4H)	6	517.9

^a This isomer has another enantiomer.



Scheme 3

regression is ΔH (kcal mol⁻¹) = 508.9 ± 0.3 + (1.16 ± 0.15) (*uu*) + (0.29 ± 0.13) (*uuu*), *n* = 14, *r*² = 0.978.

Mixing symmetry and energy considerations (see Scheme 3 and Table 5), the only possible candidate for the minor isomer is **4b** (torsion angles starting from one dmpz: -91.1, 61.9, 61.9, -91.1, 118.1, 118.1°).

Supplementary material

Lists of the structure factors, atomic coordinates and thermal components for the non-hydrogen atoms,

hydrogen atom parameters, bond distances and angles are available from C. F.-F on request.

ACKNOWLEDGEMENTS

Financial support was provided by the Spanish DGI-CYT (PB93-0197-C02 and PB93-0289-C02-m01). C. F.-C. and C. E. thank the Comunidad de Madrid for a fellowship (Acción Especial No AE00067/95). The ¹³C CP/MAS NMR spectra of compounds **1a** and **1·2C₂H₄O₂** were recorded at 75 MHz at Bruker

Analytische Messtechnik by Dr H. Forster; the help of Dr C. Marfisi (Bruker Española) is gratefully acknowledged.

REFERENCES

1. C. Foces-Foces, A. L. Llamas-Saiz, R. M. Claramunt, N. Jagerovic, M. L. Jimeno and J. Elguero, *J. Chem. Soc., Perkin Trans. 2* 1359 (1995).
2. C. Foces-Foces, A. L. Llamas-Saiz, C. Escolastico, R. M. Claramunt and J. Elguero, *J. Phys. Org. Chem.*, **9**, 137 (1996).
3. C. Fernández-Castaño, C. Foces-Foces, F. H. Cano, R. M. Claramunt, C. Escolástico, A. Fruchier and J. Elguero, *New J. Chem.*, in press.
4. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. App. Crystallogr.* **27**, 435 (1994).
5. S. R. Hall, H. D. Flack and J. M. Stewart, *Xtal3.2*. University of Western Australia, Perth (1994).
6. *International Tables for X-Ray Crystallography*, Vol. IV. Kynoch Press, Birmingham (1974).
7. J. J. P. Stewart, *J. Computer-Aided Mol. Des.* **4**, 1 (1990).
8. B. K. Vainshtein, V. M. Fridkin and V. L. Indenbom, *Modern Crystallography II*, p. 87. Springer, Berlin, (1982).
9. F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, J. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.* **31**, 187 (1991).