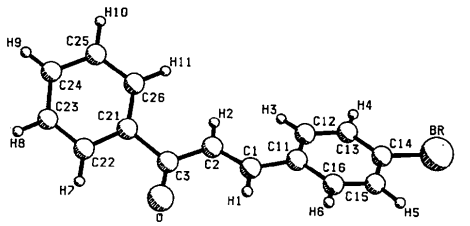

Fig. 1. The molecular structure of the title compound.

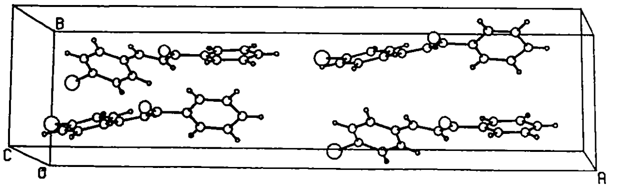

Fig. 2. The packing of the title compound in the unit cell.

Generally, bond lengths in conjugated systems are longer than double bonds and shorter than single bonds. Indeed, for the title compound, C(1)—C(11) and C(2)—C(3) are shorter than a typical single bond, and C(1)—C(2) and C(3)—O are slightly shorter than a typical double bond. It is therefore suggested that an extended π-electron conjugated system is induced in the $BrC_6H_4C_2H_2CO$ group. The bond length C(3)—C(21) is 1.53 Å, which is a typical single bond. This implies that the conjugation of the molecule is interrupted and no intramolecular charge transfer over the whole molecule is expected. Therefore, the molecular dipole axis must lie close to the BrC(14)–C(11)C(1) axis in the molecule. The latter axis is inclined at about ±70° to the b axis in the unit cell, see Fig. 2. The theoretically optimal angle between the two axes is 54.74° for non-linear optical effects to take place (Chemla & Zyss, 1987). The observation of efficient SHG shows that the packing of the molecules in the crystal is favorable for non-linear optical properties. The molecule consists of the phenyl ring C(11)–C(16), Br; the C(1), C(2), C(3), C(11) group; the C(3), O, C(21), C(2) group; and the phenyl ring C(21)–C(26), which are non-coplanar (Table 3). The dihedral angle between the phenyl rings is 48.4°. It is significant that the π-electron conjugated system is disturbed by the non-planarity of the molecule. This will produce a large hypsochromic shift of the cutoff wavelength of transmission. The cutoff wavelength is 380 nm (Goto, 1989).

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Structure of 3,5-Pyrazoledimethanol: an X-ray and ^{13}C Solid-State NMR Study

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Abstract. $C_5H_8N_2O_2$, $M_r = 128.1$, monoclinic, $C2/c$, $a = 12.9884\ (5)$, $b = 4.6517\ (1)$, $c = 20.7870\ (11)$ Å, $\beta = 102.436\ (3)°$, $V = 1226.44\ (9)$ Å^3, $Z = 8$, $D_x = 1.388$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 0.877$ mm^{-1}, $F(000) = 544$, $T = 293$ K, $R = 0.051$ for 900 observed reflections The hydroxyl groups are

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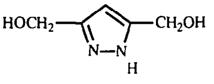
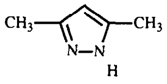
situated almost perpendicular to the pyrazole ring. The crystal structure is stabilized by strong linear N—H···N, N—H···O, O—H···N and O—H···O hydrogen bonds. Although two identical tautomers are present in the crystal, no dynamic behaviour was observed by NMR (^{13}C CP/MAS technique) proving that the disorder is static.

Introduction. The search for pyrazoles showing prototropy in the solid state (Baldy, Elguero, Faure, Pierrot & Vincent, 1985; Smith *et al.*, 1989) led us to prepare 3,5-pyrazoledimethanol (I).



(I)



(II)

The examination of a large number of structures of *N*-unsubstituted pyrazoles, either determined by us (Foces-Foces, Cano, Llamas-Saiz, Meutermans, Toiron & Elguero, 1991) or from the Cambridge Structural Database (CSD, 1991 release) (Allen, Kennard & Taylor, 1983), showed that only those pyrazoles with indentical substituents at positions 3 and 5 could present this dynamic behaviour. One such compound is the 3,5-dimethylpyrazole (II). From this, the dimethanol (I) is derived for which a more complex hydrogen-bond network is expected. To differentiate between static and dynamic disorder in the crystal we used ^{13}C NMR with the cross polarization/magic-angle-spinning technique (CP/MAS) (Faure, Vincent, Rousseau, Claramunt & Elguero, 1988).

Experimental. Compound (I) has been described in the literature (as a hydrochloride) where its preparation was by reduction of 3,5-dimethoxycarbonylpyrazole with LiAlH$_4$ in dry ether (Schenck *et al.*, 1985). Using this method but with the ethyl ester (Elguero, Navarro & Rodriguez-Franco, 1984), the diol was obtained in 60% yield. In a three-necked flask, 8.2 g (0.22 mol) of LiAlH$_4$ was suspended in 550 ml dry ether. To this flask a soxhlet was connected. 10.2 g (0.048 mol) of 3,5-diethoxycarbonylpyrazole was weighed in the paper thimble of the soxhlet. The ether was refluxed for 24 h. At the end 27 ml of H$_2$O was added dropwise. The ether was removed and the resulting solid suspended in methanol (550 ml). The methanolic solution was treated for 10 min with CO$_2$(gas) and then refluxed for 6 h. After filtration the solvent was evaporated and the resulting oil was left standing with 100 ml ethyl acetate. After a few days the solid was filtered and dried yielding 3.7 g of diol (60% yield); m.p. 364–365 K. ^{1}H NMR (DMSO-d_6, p.p.m.): 12.4 (*s*, 1H, N—H), 6.1 (*s*, 1H, H$_4$), 5.0 (*t*, 2H, OH) (^2J = 6 Hz), 4.4 (*d*, 4H, —CH$_2$—). ^{13}C NMR (DMSO-d_6, p.p.m.): 56.2 (CH$_2$), 101.9 (C4), 148.5 (C3 and C5). Suitable monocrystals were obtained by slow evaporation of an ethyl acetate solution. The solid-state NMR spectrum was recorded on a Bruker CXP400.

The main characteristics of the structural determination and the final atomic coordinates for the non-H atoms are given in Tables 1 and 2, respectively. Refinements were carried out in space groups *C*2/*c* and *Cc*, showing high correlation-matrix elements and unreasonable geometry for the latter. All H atoms were located in a difference synthesis and were refined isotropically. The proton at the N atom, as well as that at O9, appears to be disordered in two positions. The temperature factors of these disordered atoms were kept fixed. Almost all the calculations were performed using *SIR*88 (Burla *et al.*, 1989) and the *XRAY*80 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a VAX 6410 computer. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).*

Discussion. The most relevant geometrical characteristics of the title compound are reported in Table 3, following the numbering system given in Fig. 1 (Hall & Stewart, 1990). Bond distances, angles and torsion angles are indicative of a pseudo-twofold axis through C4 and the midpoint of the N1—N2 bond. This pseudosymmetry was also present in 3,5-dimethylpyrazole (I) (Smith *et al.*, 1989) and in 3(5)-methyl-5(3)-phenylpyrazole (CSD refcode: MEPHPY01). The substituents at C3 and C5 have rather unsymmetrical geometries (C4—C3/C5—*R* > N—C3/C5—*R*, Table 3). The molecular conformation is characterized by a planar ring from which the hydroxyl groups, O7H and O9H, are twisted with regard to C4 by 95.7 (3) and 79.4 (3)°, respectively.

The crystal can be considered to be built of layers of molecules parallel to the *ab* plane. These layers are connected through strong O7—H7···O7 hydrogen bonds, Fig. 1. Because of proton disorder, two types of layers (50% each) have to be considered. Within each layer, pairs of molecules bearing the N—H···N interaction are linked together through N2—H2···O9, and through O9—H9*B*···N2 and O9—H9*A*···O9 hydrogen bonds along the *a* and *b* axes, respectively. The packing diagram showing one of these types of layers is represented in Fig. 2. By changing the

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* Lists of structure factors, anisotropic thermal parameters for the non-H atoms, bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54678 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference AL0499]

donor–aceptor interactions of all the hydrogen bonds (X—H···Y by X···H—Y) the other type of layer is obtained. Both layers are related like two pyrazole tautomers, *i.e.* atoms N1 and N2, on one hand, and C3 and C5, on the other, exchange their relative position (in standard pyrazole numbering N1 is always the atom bearing the substituent, in this case a proton).

To distinguish between static and dynamic disorder the ^{13}C CP/MAS NMR spectrum of compound (II) was recorded at 100 MHz. The following signals were observed: 53.2 (CH_2), 104.1 (C4), 143.2 (C5) and 150.8 and 153.4 p.p.m. (C3). All signals are narrow, thus excluding dynamic behaviour ($E_a \gg 50$ kJ mol^{-1}) (Faure *et al.* 1988). The splitting of C3 (ratio 1:2) is probably a result of dipolar coupling with ^{14}N2. The average of the C3 and C5 signals, 147.6 p.p.m., is near the observed solution signal for both C atoms, 148.5 p.p.m.

Table 1. *Crystal analysis parameters at room temperature*

Crystal data	
Crystal habit	Transparent colourless plate
Crystal size (mm)	0.03 × 0.17 × 0.50
Unit-cell determination	Least-squares fit from 53 reflections ($\theta < 45°$)
Experimental data	
Technique	Philips PW1100 four-circle diffractometer, bisecting geometry, Cu $K\alpha$, graphite-orientated monochromator, $\omega/2\theta$ scans, scan width 1.5°, $\theta_{max} = 65°$, 1 min per reflection
$+h$, $+k$, $\pm l$ range	14, 5, 24
Number of reflections	
Measured	1257
Independent	1052
Observed	900 [$3\sigma(I)$ criterion]
R_{int}	0.012
Standard reflections	Two reflections every 90 min, no variation
Absorption	No correction applied
Solution and refinement	
Solution	Direct methods
Refinement	Full-matrix least squares on F_o
Parameters	
Number of variables	118 (anisotropic for non-H and isotropic for H, see text)
Degrees of freedom	782
Ratio of freedom	7.6
Goodness of fit	1.1
H atoms	Difference synthesis
Final shift/e.s.d.	0.05
Maximum shift/e.s.d.	0.42
Weighting scheme	Empirical as to give no trends in $w\Delta^2F$ *vs* $\lvert F_{obs}\rvert$ and $\sin\theta/\lambda$
Maximum thermal value (Å^2)	U_{22}(O9) = 0.074 (1)
Final $\Delta\rho$ peaks (e Å^{-3})	±0.19
Final R and wR	0.051, 0.054

Table 2. *Final atomic coordinates and thermal parameters* (Å^2 × 10^4)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(a_ia_j)$$

	x	y	z	U_{eq}
N1	0.49614 (15)	0.1537 (5)	0.06082 (10)	384 (6)
N2	0.56968 (15)	0.3478 (5)	0.08868 (10)	394 (6)
C3	0.54757 (17)	0.4408 (5)	0.14505 (11)	349 (7)
C4	0.45677 (18)	0.3027 (5)	0.15391 (11)	367 (7)
C5	0.42705 (16)	0.1247 (5)	0.09991 (11)	331 (7)
C6	0.61388 (21)	0.6622 (6)	0.18576 (14)	455 (8)
O7	0.70020 (16)	0.5326 (4)	0.22905 (10)	561 (7)
C8	0.33439 (18)	−0.0714 (6)	0.08105 (14)	435 (8)
O9	0.24273 (14)	0.0870 (5)	0.05209 (10)	559 (7)

Table 3. *Main geometrical characteristics* (Å, °)

N1—N2	1.351 (3)	N1—C5	1.341 (3)
N2—C3	1.337 (3)	C3—C4	1.390 (3)
C4—C5	1.382 (3)	C3—C6	1.485 (3)
C6—O7	1.413 (3)	C5—C8	1.494 (3)
C8—O9	1.419 (3)		
C5—N1—N2	108.1 (2)	N1—N2—C3	109.1 (2)
N2—C3—C4	108.4 (2)	C3—C4—C5	105.4 (2)
N1—C5—C4	109.0 (2)	C4—C3—C6	130.5 (2)
N2—C3—C6	121.1 (2)	C4—C5—C8	130.4 (2)
N1—C5—C8	120.6 (2)	C3—C6—O7	110.5 (2)
C5—C8—O9	110.5 (2)		
N1—N2—C3—C6	−178.5 (2)	C4—C3—C6—O7	95.7 (3)
N2—N1—C5—C8	178.4 (2)	C4—C5—C8—O9	79.4 (3)

X—H···Y	X—H	X···Y	H···Y	X—H···Y
N1—H1···N1^{i}	0.96 (7)	2.925 (3)	1.97 (7)	171 (6)
N2—H2···O9^{ii}	0.88 (8)	2.758 (3)	1.90 (8)	168 (6)
O7—H7···O7^{iii}	0.88 (5)	2.712 (3)	1.85 (5)	165 (4)
O9—H9A···O9^{iv}	0.96 (9)	2.683 (3)	1.74 (9)	168 (9)
O9—H9B···N2^{v}	0.77 (10)	2.758 (3)	2.06 (10)	151 (9)

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

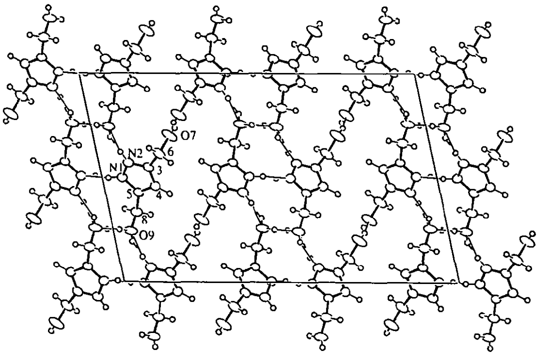

Fig. 1. Crystal-packing view as projected along the b axis together with the numbering system (50% ellipsoids).

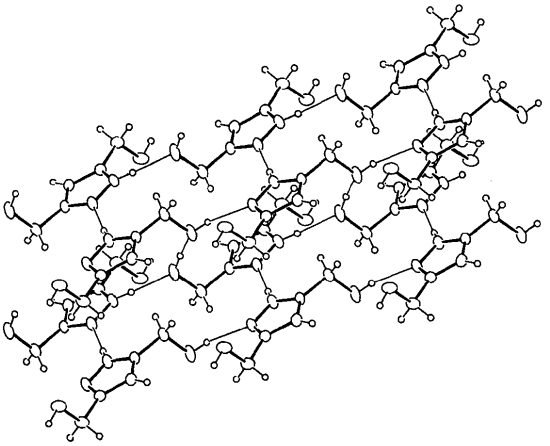

Fig. 2. Packing of one layer of molecules (30% ellipsoids). Half protons arbitrarily located in one of the two possible positions.

In conclusion, even if compound (II) shows half protons and symmetry in crystallography, no dynamic behaviour is observed in the crystals. The reason is probably that in this case tautomerism involves the transformation of a strand of an infinite number of molecules into another strand of the same length, and this requires too much energy.

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Structure of 4-Methoxyphenyl Methyl Sulfone and a Redetermination of the Structure of Methyl Phenyl Sulfone

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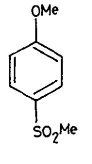
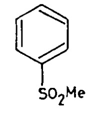
Abstract. $\mathrm{C_8H_{10}O_3S}$, $M_r = 186.2$, monoclinic, $P2_1/c$, $a = 5.638\,(3)$, $b = 7.828\,(2)$, $c = 20.045\,(3)$ Å, $\beta = 95.05\,(2)^\circ$, $V = 881.3$ Å^3, $Z = 4$, $D_x = 1.40\ \mathrm{g\,cm^{-3}}$, monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 3.2\ \mathrm{cm^{-1}}$, $F(000) = 392$, $T = 293$ K, $R = 0.041$ and $wR = 0.055$ for 1499 observed reflections with $|F^2| > 2\sigma(F^2)$. Bond lengths: S—O1 1.431 (2), S—O2 1.437 (2), S—C1 1.761 (2) and S—C7 1.755 (3) Å. $\mathrm{C_7H_8O_2S}$, $M_r = 156.2$, monoclinic, $P2_1/c$, $a = 8.172\,(2)$, $b = 9.095\,(2)$, $c = 10.844\,(13)$ Å, $\beta = 111.66\,(5)^\circ$, $V = 749.0$ Å^3, $Z = 4$, $D_x = 1.39\ \mathrm{g\,cm^{-3}}$, monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 3.5\ \mathrm{cm^{-1}}$, $F(000) = 328$, $T = 293$ K, $R = 0.045$ and $wR = 0.060$ for 1427 observed reflections with $|F^2| > 2\sigma(F^2)$. Bond lengths: S—O1 1.436 (2), S—O2 1.442 (2), S—C1 1.765 (2) and S—C7 1.751 (3) Å.

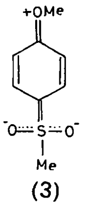
Introduction. In connection with our interest in the preparation of organic materials for non-linear optics, we prepared the chiral sulfoxide (*S*)-4-methoxyphenyl methyl sulfoxide, and obtained, in addition, a small amount of the corresponding sulfone, (1). The structure of the material was determined, and it was thought desirable to compare this with the unsubstituted analogue, methyl phenyl sulfone, (2). This structure has been determined previously (Vorontsova, 1965) but the *R* factor was 19%, so that the bond lengths which were needed for comparison were in some doubt.



(1)



(2)



(3)

Experimental. 4-Methoxyphenyl methyl sulfone, (1), was isolated as a by-product (by flash chromatography, SiO$_2$, cyclohexane/EtOCOMe) from an

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