

Table 3. Although there is extensive hydrogen bonding between the water molecules (Fig. 3) and also between the HA-966 molecules (Table 3) there is only a single hydrogen bond [O(3)—H(10)···O(2)] linking the water molecules with the HA-966 molecules. This may explain the highly efflorescent nature of the crystals. Two of the three water molecules of the asymmetric unit furnish four hydrogen bonds, in common with ordinary ice (Pauling, 1960), and O(2) of the HA-966 molecule furnishes two hydrogen bonds.

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## Structure of Dimethyl 4,4'-Methylenebis(phenylcarbamate): a Model for MDI Units in Polyurethane Hard Segments

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**Abstract.**  $C_{17}H_{18}N_2O_4$ , monoclinic,  $P2_1/b$ ,  $a = 5.157$  (3),  $b = 9.800$  (3),  $c = 31.472$  (11) Å,  $\gamma = 93.90$  (3)°,  $Z = 4$ ,  $D_m = 1.30$ ,  $D_c = 1.316$  Mg m<sup>-3</sup>. The structure was refined to  $R = 0.06$  based on diffractometer data collected at 258 K. The molecule is V-shaped with a C—CH<sub>2</sub>—C angle of 114.5 (4)°. The angle between the phenyl-ring planes is 90.0° and the planes of the urethane groups are at angles of 10.2 and 39.4° to their adjacent phenyl rings. The molecules are linked into sheets by C=O···H—N hydrogen bonds between the urethane groups. The title compound furnishes a conformational model for the diol-linked 4,4'-methylenediphenyl diisocyanate (MDI) units in the hard segments of certain polyurethane elastomers.

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**Introduction.** Polyurethane elastomers are block copolymers composed of alternating hard (urethane) and soft (polyester or polyether) segments. The elastomeric properties of these materials are attributed to microphase separation: the urethane segments segregate to form crystalline domains which serve as crosslinks between the soft-segment chains. One commercially important polyurethane system has hard segments composed of diol-linked 4,4'-methylenediphenyl diisocyanate (MDI). The structure of the hard domains has not been determined by direct study of the polymer, due to the low quality of the X-ray diffraction data, but it is believed that hydrogen bonding between the urethane groups is an important factor in the virtual (non-covalent) crosslinking of the chains (Bonart, Morbitzer & Muller, 1974). The title compound is methanol-capped MDI, and its structure has been determined as a model for the structure of the polymer system.

Clear, colorless, thin platelets were grown by slow evaporation from saturated ethanol solution at 278 K. A crystal of dimensions 0.40 × 0.14 × 0.06 mm was used for the structure determination. Data were collected on a Syntex P3 diffractometer, with the crystal cooled to 258 K, using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). Systematic absences of  $hk0$  ( $k = 2n + 1$ ) and  $00l$  ( $l = 2n + 1$ ) defined the space group as  $P2_1/b$ . The unit-cell dimensions were refined from the Bragg angles (determined by the Syntex centering routine) for 36 reflections in the range  $14^\circ < 2\theta < 23^\circ$ . The unit-cell volume, 1587 Å<sup>3</sup>, yields a calculated density of 1.316 Mg m<sup>-3</sup> for  $Z = 4$ , which compares well with the observed density of 1.30 Mg m<sup>-3</sup>. Intensity data for 2085 reflections were collected using the  $\omega$ -scan technique ( $4^\circ < 2\theta < 45^\circ$ ; scan width of  $1.0^\circ$ ; variable scan rate of  $2.0$ – $5.0^\circ$  min<sup>-1</sup>; background measurements at both ends of the scan for a total time equal to the scan time). The intensities of four reflections were monitored after every 100 measurements and showed no change.

Solution and refinement of the structure were carried out using modified versions of programs supplied by Enraf-Nonius Corporation (Frenz, 1978). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). In the least-squares refinement the function minimized was  $\sum w(|F_o| - |F_c|)^2$  with the weights  $w = 1/\sigma^2(F_o)$ ; the standard deviations of the observed structure factors,  $\sigma(F_o)$ , were based on counting statistics and on an 'ignorance factor' ( $p$ ) of 0.02 (Corfield, Doedens & Ibers, 1967).

The structure was solved by direct methods. The positions of all the H atoms were determined by

difference Fourier techniques. Full-matrix least-squares refinement of all the positional and thermal parameters (anisotropic for C, N, and O; isotropic for H) using 1167 reflections with  $I > 2\sigma(I)$  converged at  $R = 0.060$  and  $R_w = 0.045$ . The final atomic coordinates are listed in Table 1.\*

\* Lists of structure factors, thermal parameters, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35216 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

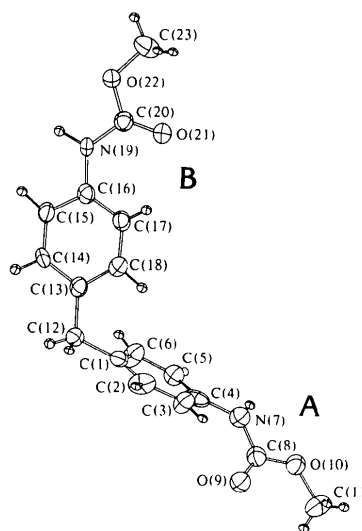


Fig. 1. Molecular structure showing thermal ellipsoids and atomic numbering.

Table 1. Fractional atomic coordinates and their standard deviations

	x	y	z		x	y	z
C(1)	0.1667 (10)	0.0861 (5)	0.0980 (2)	N(7)	0.1913 (7)	0.4999 (4)	0.0589 (1)
C(2)	0.3647 (9)	0.1774 (5)	0.1115 (2)	N(19)	-0.6492 (8)	-0.1986 (4)	0.2357 (1)
C(3)	0.3757 (10)	0.3144 (5)	0.0992 (2)	H(2)	0.498 (8)	0.154 (5)	0.131 (1)
C(4)	0.1899 (9)	0.3605 (5)	0.0720 (2)	H(3)	0.509 (8)	0.379 (4)	0.109 (1)
C(5)	-0.0055 (10)	0.2700 (5)	0.0584 (2)	H(5)	-0.129 (9)	0.301 (5)	0.042 (1)
C(6)	-0.0183 (10)	0.1343 (5)	0.0711 (2)	H(6)	-0.178 (8)	0.075 (4)	0.063 (1)
C(8)	0.4059 (9)	0.5805 (5)	0.0496 (2)	H(7)	0.048 (9)	0.520 (5)	0.051 (1)
C(11)	0.5429 (11)	0.8045 (5)	0.0262 (2)	H(11A)	0.476 (13)	0.884 (6)	0.020 (2)
C(12)	0.1490 (10)	-0.0615 (5)	0.1125 (2)	H(11B)	0.617 (11)	0.785 (6)	0.003 (2)
C(13)	-0.0583 (9)	-0.0955 (5)	0.1452 (2)	H(11C)	0.643 (11)	0.826 (5)	0.054 (2)
C(14)	-0.1198 (10)	-0.0022 (5)	0.1766 (2)	H(12A)	0.119 (7)	-0.125 (4)	0.086 (1)
C(15)	-0.3121 (10)	-0.0317 (5)	0.2068 (2)	H(12B)	0.314 (7)	-0.070 (4)	0.125 (1)
C(16)	-0.4495 (9)	-0.1579 (4)	0.2064 (2)	H(14)	-0.016 (7)	0.086 (4)	0.176 (1)
C(17)	-0.3883 (10)	-0.2533 (5)	0.1757 (2)	H(15)	-0.336 (0)	0.029 (0)	0.227 (0)
C(18)	-0.1985 (10)	-0.2224 (5)	0.1458 (2)	H(17)	-0.494 (7)	-0.342 (4)	0.176 (1)
C(20)	-0.7669 (10)	-0.1164 (5)	0.2630 (2)	H(18)	-0.172 (7)	-0.291 (4)	0.124 (1)
C(23)	-1.1047 (11)	-0.1161 (6)	0.3142 (2)	H(19)	-0.722 (11)	-0.292 (6)	0.234 (2)
O(9)	0.6288 (6)	0.5515 (3)	0.0526 (1)	H(23A)	-1.234 (10)	-0.178 (5)	0.326 (2)
O(10)	0.3317 (6)	0.7049 (3)	0.0368 (1)	H(23B)	-1.179 (13)	-0.033 (7)	0.300 (2)
O(21)	-0.7197 (7)	0.0056 (3)	0.2686 (1)	H(23C)	-0.994 (11)	-0.085 (6)	0.335 (2)
O(22)	-0.9569 (7)	-0.1905 (3)	0.2839 (1)				

**Discussion.** The molecular structure is shown in Fig. 1. Selected interatomic distances, bond angles, and torsion angles for a single molecule are given in Table 2. The halves of the molecule have been labeled *A* and *B* (Fig. 1). The C—CH<sub>2</sub>—C angle is 114.5°, compared to values of 116.7° in 4,4'-methylenedianiline (Swardstrom, Duvall & Miller, 1972) and 119.2° in 4,4'-methylenebis(2,3,5,6-tetramethylphenol) (Chaudhuri & Hargreaves, 1956). The planes of the phenyl rings are mutually inclined at 90.0°. This inclination is not unexpected since it should minimize the  $\pi$ - $\pi$  orbital overlap between the rings, and compares favorably with the values observed in other diphenylmethane structures: 86° in 4,4'-methylenebis(2,3,5,6-tetramethylphenol) (Chaudhuri & Hargreaves, 1956), 104° in 4,4'-methylenebis(2-chlorophenol) (Whittaker, 1953), and 90.0° in 4,4'-methylenedianiline (Swardstrom *et al.*, 1972). The angles between the central C—CH<sub>2</sub>—C plane and the planes of the *A* and *B* phenyl rings are 74.5 and 35.5° respectively. The two urethane groups are planar and mutually inclined at 52.7°; the terminal methyl groups lie in the planes of their respective urethane groups. The angles between the planes of the urethanes and their adjacent phenyl groups are 39.4 (*A*) and 10.2° (*B*). The torsion angles that define the sense of these rotations are given in Table 2. Such conformational asymmetry is not observed in other chemically symmetrical molecules containing the diphenylmethane group (Whittaker, 1953; Chaudhuri & Hargreaves, 1956; Swardstrom *et al.*, 1972), where the two halves of the molecule are related by a twofold axis through the central CH<sub>2</sub> group. It seems likely that the asymmetry of the title

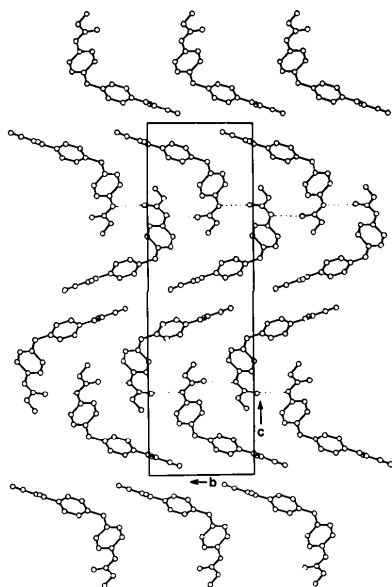


Fig. 2. Packing of molecules in the unit cell (*bc* projection).

Table 2. Selected bond lengths (Å), angles (°), and torsion angles (°) for the non-hydrogen atoms

E.s.d.'s in the torsion angles are not greater than 1.0°.

C(1)—C(12)	1.514 (7)	C(12)—C(13)	1.504 (7)
C(4)—N(7)	1.426 (6)	C(16)—N(19)	1.419 (6)
C(5)—C(6)	1.386 (7)	C(17)—C(18)	1.377 (7)
N(7)—C(8)	1.348 (6)	N(19)—C(20)	1.351 (6)
C(8)—O(9)	1.206 (5)	C(20)—O(21)	1.217 (5)
C(8)—O(10)	1.364 (5)	C(20)—O(22)	1.349 (6)
O(10)—C(11)	1.451 (7)	O(22)—C(23)	1.449 (7)
C(4)—N(7)—C(8)	125.1 (5)	C(1)—C(12)—C(13)	114.5 (4)
N(7)—C(8)—O(9)	127.1 (5)	C(16)—N(19)—C(20)	126.4 (5)
N(7)—C(8)—O(10)	108.6 (5)	N(19)—C(20)—O(21)	127.6 (5)
O(9)—C(8)—O(10)	124.3 (5)	N(19)—C(20)—O(22)	109.2 (4)
C(8)—O(10)—C(11)	115.2 (5)	O(21)—C(20)—O(22)	123.2 (5)
		C(20)—O(22)—C(23)	116.0 (5)
C(1)—C(12)—C(13)—C(14)			-35.6
C(1)—C(12)—C(13)—C(18)			144.7
C(2)—C(1)—C(12)—C(13)			105.1
C(3)—C(4)—N(7)—C(8)			38.6
C(4)—N(7)—C(8)—O(9)			-3.6
C(4)—N(7)—C(8)—O(10)			177.7
C(5)—C(4)—N(7)—C(8)			-143.4
C(6)—C(1)—C(12)—C(13)			-74.0
N(7)—C(8)—O(10)—C(11)			179.2
O(9)—C(8)—O(10)—C(11)			0.5
C(15)—C(16)—N(19)—C(20)			12.4
C(16)—N(19)—C(20)—O(21)			-2.4
C(16)—N(19)—C(20)—O(22)			176.4
C(17)—C(16)—N(19)—C(20)			-168.5
N(19)—C(20)—O(22)—C(23)			-179.3
O(21)—C(20)—O(22)—C(23)			-0.4

compound occurs in order to optimize the hydrogen bonding.

The *bc* projection of the crystal structure is shown in Fig. 2. The molecules are linked by two intermolecular C=O...H—N hydrogen bonds, such that the crystal contains infinite two-dimensional sheets perpendicular to the *c* axis. Molecules related by the *b* glide plane are linked by hydrogen bonds between their *B* urethane groups. Such a bond is shown in Fig. 2, and has an N...O distance of 2.899 (5) Å. The second hydrogen bond is between the *A* urethane groups of successive molecules along the *a* axis, and has an N...O distance of 2.985 (6) Å. The plate-like morphology of the crystal parallels the orientation of the hydrogen-bonded sheets.

We have utilized the conformation determined for this compound to propose a new model for the structure of the MDI—butanediol hard segments of polyurethane elastomers (Blackwell & Gardner, 1979).

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## Cyclizine Hydrochloride\*

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**Abstract.**  $C_{18}H_{23}N_2^+ \cdot Cl^-$ , *Pnma*,  $a = 11.833$  (3),  $b = 13.631$  (3),  $c = 10.023$  (3) Å,  $Z = 4$ ,  $D_c = 1.24$  Mg  $m^{-3}$ ,  $\mu(Mo K\alpha) = 0.191$  mm $^{-1}$ . The molecule lies on a crystallographic plane of symmetry and the crystal structure is held together by van der Waals packing of ion pairs linked by hydrogen bonds. The distance of 6.03 Å between the protonated N atom and the centroid of the phenyl ring is close to those observed in other antihistamines belonging to different chemical classes, but does not correspond to that observed in histamine itself. The final *R* was 0.047.

**Introduction.** Antihistamines, or, more precisely,  $H_1$  histamine receptor antagonists, are a class of drugs able to antagonize competitively the effects of histamine at the  $H_1$  receptor site. In many cases agonists and their competitive antagonists show remarkable chemical similarities, but this similarity has been questioned (Ariens, 1977) for antihistaminic agents, which do not appear to mimic histamine and its agonists. Nevertheless, chemical and stereochemical similarities can be

found among antihistamines themselves, in spite of the fact that they belong to at least five different chemical classes. In general, it is assumed (Witiak, 1970) that the pharmacodynamic part of antihistamines can be reduced to  $Ar_2X-C-C-N^+$  (where  $X = N, C-O$  or  $CH$ ). Reports in the literature suggest (Witiak, Muhi-Eldeen, Mahishi, Sethi & Gerald, 1971) that the presence of two aromatic rings is useful for the enhancement of antihistaminic activity but that strongest antagonism occurs only when at least one ring is able to assume a fixed distance from the amino N atom.

From crystal structure determinations of histadyl hydrochloride (Clark & Palenik, 1972), ( $\pm$ )-brompheniramine maleate (James & Williams, 1971), (+)-chlorpheniramine maleate (James & Williams, 1974a) and triprolidine hydrochloride (James & Williams, 1974b), the distance between the amino N and the centroid of one of the unsaturated rings is found to lie in the range 6–6.40 Å (James & Williams, 1974b). In a recent paper (Bertolasi, Borea, Gilli & Sacerdoti, 1980) we have reported the crystal structure of carbinoxamine maleate, which belongs to the class of the aminoethyl ether derivatives, and have shown that a similar distance of 6.30 Å is found in this molecule.

\* Crystallographic and Conformational Studies on Histamine  $H_1$  Receptor Antagonists. II.