

Fig. 2. A stereoview of the extended structure.

This mode of motion causes the distance between the mean atomic positions to be less than the corresponding mean interatomic separation, which is the quantity of chemical significance (Johnson, 1970). The rather high temperature factors of many atoms of the molecule are probably the reason for the low percentage of observed reflections collected.

A stereopicture of the extended structure is shown in Fig. 2. The benzene rings of all molecules in the unit cell are pointing inwards along the *b* direction while the carbon chains are located along the *a* direction near the edge of the cell. This arrangement favours an intermolecular hydrogen-bond interaction between O(1) acting as donor and O(2) as acceptor. The relevant interatomic distance is 2.768 (6) Å. The benzene rings of neighbouring molecules are almost parallel with a dihedral angle of 2.8° and a mean interplanar distance

of 3.66 Å. In a direction normal to the benzene-ring plane, there is no overlap between neighbouring rings which indicates that an eventual π - π intermolecular interaction is not favoured; the packing seems to be dominated by the steric requirements of the hydrogen-bonding scheme.

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The Structure of Bis(4-hydroxybutyl) 4,4'-Methylenebis(phenylcarbamate): a Model Compound for Diol-Linked MDI Units in Polyurethane Elastomers

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Abstract. $C_{23}H_{30}N_2O_6$, orthorhombic, $P2_12_12$, $a = 16.511$ (1), $b = 13.970$ (1), $c = 4.778$ (1) Å, $Z = 2$, $D_m = 1.29$, $D_c = 1.296$ Mg m⁻³. The structure was refined to $R = 0.075$ ($R_w = 0.068$), based on diffractometer data collected at room temperature. The two halves of the molecule are related by a twofold axis through the central CH_2 . The central C- CH_2 -C bridge angle is 105.2 (1.0)°, and the planes of the phenyl

rings are mutually inclined at 98.2°. The urethane groups are planar and are inclined at 13.6° to their adjacent phenyl rings. The $(CH_2)_4$ chains are also planar (all *trans*), and are approximately *gauche* to the adjacent urethane. The terminal OH groups form hydrogen bonds to the C=O and N-H groups of different neighboring molecules, leading to a chain of hydrogen bonds along the *b* axis. The title compound serves as a model for the diol-linked 4,4'-methylenediphenyl diisocyanate (MDI) units which form the hard segments in certain polyurethane elastomers.

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Introduction. We are determining the structures of derivatives of 4,4'-methylenediphenyl diisocyanate (MDI) as model compounds for our studies of the structures of polyurethane elastomers, in which the hard domains are polymers formed by diol-linked MDI units. In previous work (Blackwell & Gardner, 1979; Gardner & Blackwell, 1980) we have determined the structure of methanol-capped MDI [MeMMe; $\text{CH}_2\text{C}_6\text{H}_4(\text{NHCOOCH}_3)_2$], and the structure of a second crystalline form of this compound has been determined by Born, Hocker, Paulus & Wolfel (1980). These two structures will be designated MeMMeI and MeMMeII respectively; a preliminary report of the MeMMeII structure is given by Hocker & Born (1979). We have now determined the structure of butanediol-capped MDI (HO-BMB-OH, the title compound). Butanediol is the most frequently used diol in commercial preparations of polyurethane elastomers, and this derivative will give information on the conformation of the butanediol unit, which is not available from the MeMMe structures.

Clear, colorless crystals were grown by slow evaporation from saturated ethanol solutions at room temperature. A crystal with dimensions $0.87 \times 0.20 \times$

0.20 mm was mounted on a Picker FACS-I automated diffractometer, with the c axis parallel to the φ rotation axis. Graphite-monochromated $\text{Cu } K\alpha$ radiation was used to measure the intensities at a scan rate of 2° min^{-1} for $2\theta < 90^\circ$; 984 reflections were measured, of which 512 had $I < 3\sigma(I)$. Systematic absences of $h00$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$) were observed, and the space group is $P2_12_12$. The structure was solved by direct (*MULTAN*; Germain, Main & Woolfson, 1971) and Fourier methods, and refined by least squares, using programs written for the Xerox Sigma 2 system by Dr R. F. Bryan of the University of Virginia. The coordinates for the H atoms attached to the C atoms were calculated from the refined coordinates for the latter atoms, at C-H distances of 1.0 \AA ; the amine and hydroxyl H atoms were located from difference Fourier syntheses. An anisotropic temperature factor of $B = 10.0 \text{ \AA}^2$ was assigned to the H atoms. Full-matrix refinement of the atomic coordinates, and anisotropic thermal parameters for the heavier atoms, led to a structure with an R value of 0.075 ; $R_w = 0.068$, based on assigned weights of $1/\sigma^2(F_{\text{obs}})$ (Corfield, Doedens & Ibers, 1967). The final atomic coordinates are listed in Table 1.* The molecular structure and the ab projection of the crystal structure are shown in Figs. 1 and 2 respectively, and pertinent bond lengths and angles are given in Table 2.

Table 1. Fractional atomic coordinates ($\times 10^4$) (e.s.d.'s in parentheses)

	x	y	z	U_{eq}^* (\AA^2)
C(1)	5000	5000	9547 (32)	0.0238 (42)
C(2)	4258 (4)	4828 (6)	7549 (19)	0.0226 (28)
C(3)	3929 (5)	3920 (6)	7150 (21)	0.0236 (29)
C(4)	3280 (5)	3764 (6)	5306 (23)	0.0246 (28)
C(5)	2936 (4)	4510 (5)	3897 (20)	0.0185 (27)
C(6)	3242 (4)	5431 (6)	4264 (24)	0.0238 (29)
C(7)	3880 (5)	5599 (6)	6027 (24)	0.0244 (29)
N(8)	2267 (4)	4442 (4)	1997 (16)	0.0223 (21)
C(9)	1999 (4)	3621 (5)	832 (21)	0.0234 (26)
O(10)	2235 (3)	2804 (4)	1358 (14)	0.0282 (18)
O(11)	1367 (3)	3801 (4)	-799 (14)	0.0260 (18)
C(12)	1046 (5)	2983 (6)	-2296 (21)	0.0287 (32)
C(13)	243 (5)	3337 (6)	-3616 (22)	0.0308 (31)
C(14)	-368 (5)	3510 (8)	-1546 (23)	0.0325 (34)
C(15)	-1207 (5)	3791 (6)	-2861 (21)	0.0251 (30)
O(16)	-1768 (3)	3775 (4)	-580 (16)	0.0345 (20)
H(1)	4905	5574	10756	
H(3)	4161	3366	8203	
H(4)	3068	3101	5024	
H(6)	2993	5978	3224	
H(7)	4087	6266	6264	
H(8)	1915	5096	802	
H(12) <i>A</i>	942	2440	-980	
H(12) <i>B</i>	1432	2771	-3785	
H(13) <i>A</i>	42	2840	-4950	
H(13) <i>B</i>	350	3945	-4654	
H(14) <i>A</i>	-441	2916	-407	
H(14) <i>B</i>	-184	4044	-306	
H(15) <i>A</i>	-1369	3318	-4327	
H(15) <i>B</i>	-1180	4445	-3706	
H(16)	-2443	3129	-464	

* U_{eq} calculated from $\frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35625 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

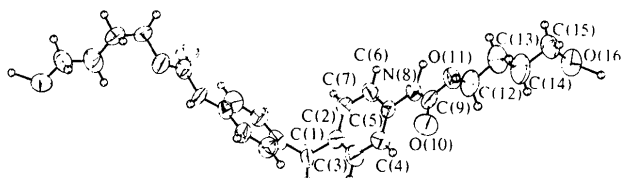


Fig. 1. Molecular structure showing thermal ellipsoids and atomic numbering.

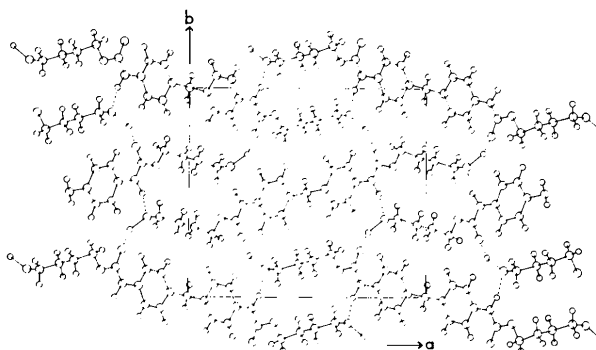


Fig. 2. Packing of the molecules in the unit cell, ab projection.

Table 2. Selected bond distances (Å), bond angles (°) and torsion angles (°)

C(1)—C(2)	1.572 (12)	C(2)—C(1)—C(2')	105.2 (1.0)
C(5)—N(8)	1.433 (10)	C(4)—C(5)—N(8)	125.6 (7)
N(8)—C(9)	1.350 (9)	C(5)—C(6)—C(7)	121.0 (8)
C(9)—O(10)	1.231 (8)	C(5)—N(8)—C(9)	124.9 (6)
C(9)—O(11)	1.326 (9)	C(6)—C(5)—N(8)	114.9 (7)
O(11)—C(12)	1.450 (10)	N(8)—C(9)—O(10)	126.8 (8)
C(12)—C(13)	1.549 (11)	N(8)—C(9)—O(11)	109.8 (6)
C(13)—C(14)	1.434 (13)	C(9)—O(11)—C(12)	115.3 (6)
C(14)—C(15)	1.571 (11)	O(10)—C(9)—O(11)	123.0 (7)
C(15)—O(16)	1.430 (11)	O(11)—C(12)—C(13)	105.2 (6)
		C(12)—C(13)—C(14)	112.1 (8)
		C(13)—C(14)—C(15)	112.8 (9)
		C(14)—C(15)—O(16)	105.2 (8)

Hydrogen-bond lengths and angles

N(8)—H(8)	1.224	N(8)—H(8)···O(16)	157.9
H(8)···O(16)	1.727	C(9)—O(10)···H(16)	151.2
N(8)···O(16)	2.898 (8)	C(9)—O(10)···O(16)	153.7 (6)
O(10)···H(16)	1.472	O(16)—H(16)···O(10)	145.7
H(16)—O(16)	1.436	O(16)—H(16)···C(9)	149.0
O(10)···O(16)	2.778 (7)		

E.s.d.'s in torsion angles are not greater than 1.8°.

C(2')—C(1)—C(2)—C(3)	105.7
C(2')—C(1)—C(2)—C(7)	-74.3
C(4)—C(5)—N(8)—C(9)	-16.1
C(6)—C(5)—N(8)—C(9)	163.9
N(8)—C(9)—O(11)—C(12)	176.9
C(9)—O(11)—C(12)—C(13)	170.7
O(11)—C(12)—C(13)—C(14)	-69.4
C(12)—C(13)—C(14)—C(15)	-175.4
C(13)—C(14)—C(15)—O(16)	170.4

Discussion. The phenyl and urethane groups are planar, and the (CH₂)₄ chain is approximately planar (*i.e.* all *trans*). The conformation is most easily described in terms of the mutual orientation of these planes and the torsion angles at the interconnecting bonds. These data for HO—BMB—OH are given in Table 3, and compared with equivalent data for MeMMeI (Gardner & Blackwell, 1980), MeMMeII (Hocker & Born, 1979), 4,4'-methylenedianiline (Swardstrom, Duvall & Miller, 1972), 4,4'-methylenebis(2,3,5,6-tetramethylphenol) (Chaudhuri & Hargreaves, 1956), and 4,4'-methylenebis(2-chlorophenol) (Whittaker, 1953). All these molecules have twofold symmetry at the central CH₂ except for MeMMeI, which is asymmetrical despite the chemical symmetry. The central C—CH₂—C bridge angle of 105.2° is significantly smaller than those for the other compounds, which lie in the range 112.0–119.2°. The phenyl rings in HO—BMB—OH are mutually inclined at 98.2°; a perpendicular orientation would be expected for an isolated diphenylmethane unit, as reported for MeMMeI and 4,4'-methylenedianiline, but the value for HO—BMB—OH lies within the observed range of deviations. The planes of the urethane groups are inclined at 13.6° to their adjacent phenyls. Finally, the (CH₂)₄ plane is inclined at 69.4° to the adjacent

Table 3. Comparison of plane orientation, bond and torsion angles (°) in analogous compounds

	Central C—CH ₂ —C	Phenyl— phenyl	Phenyl— urethane	
HO—BMB—OH ^a	105.2	98.2	13.6	
MeMMeI ^b	114.5	90.0	10.2 39.4	
MeMMeII ^c	116.2	96.7		
BHDM ^d	119.2	94.0		
DCHDM ^e	119.0	104.0		
DAPM ^f	116.7	90.0		
	C(9')—N(8')	C(7')—C(2')— C(1)—C(2)	C(2')—C(1)— C(2)—C(7)	C(6)—C(5)— N(8)—C(9)
HO—BMB—OH ^a	163.9	-74.3	-74.3	163.9
MeMMeI ^b	-168.5	-35.4	-74.0	-143.4

(a) This paper. (b) Gardner & Blackwell (1980). (c) Hocker & Born (1979). (d) 4,4'-Methylenebis(2,3,5,6-tetramethylphenol) (Chaudhuri & Hargreaves, 1956). (e) 4,4'-Methylenebis(2-chlorophenol) (Whittaker, 1953). (f) 4,4'-Methylenedianiline (Swardstrom *et al.*, 1972).

urethane; the O(11)—C(12)—C(13)—C(14) torsion angle corresponds approximately to the *gauche* conformation. The hydroxyl groups participate in hydrogen bonds as donors to the C=O and acceptors for the N—H groups of urethane moieties on different molecules, leading to chains of hydrogen bonds along the *b* axis. The bond lengths and angles for these hydrogen bonds are given in Table 2.

For the purposes of analogy with the polymer structure, this structure and those of MeMMeI and MeMMeII yield information concerning the modes of stacking of the diphenylmethanes and the hydrogen bonding of the urethanes. The diphenylmethane is V-shaped, and stacking of these groups in HO—BMB—OH is facilitated by turning the urethanes so they are nearly perpendicular to the stack. As a result, hydrogen bonding within the stack is not possible. A similar situation pertains in MeMMeII, but in MeMMeI the asymmetry of the molecule permits hydrogen bonding of one of the urethanes along the stacking direction, leading to a two-dimensional array of hydrogen bonds. The range of values observed for the urethane—phenyl orientation is indicative of the conformational freedom which enables the urethanes to optimize the hydrogen-bonding network. We are currently working on the structure of propanol-capped MDI (PMP) and will report on this in due course.

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Structure of 3,4-Bis(trimethylsilyl)bicyclo[4.2.0]octa-1,3,5-triene

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Abstract. $C_{14}H_{24}Si_2$, $M_r = 248.5$, orthorhombic, $Pna2_1$, $a = 23.296$ (5), $b = 9.447$ (2), $c = 7.227$ (2) Å, $V = 1590.5$ Å³, $F(000) = 544$, $\rho_{calc} = 1.04$ Mg m⁻³ ($Z = 4$), $\mu(Cu K\alpha) = 1.75$ mm⁻¹. Final $R = 0.065$ for 1595 reflections. Systematic absences for $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$, establish the space group as either $Pna2_1$ or $Pnma$. The former was shown to be correct in the structure determination.

Introduction. The title compound (Hillard & Vollhardt, 1977), which was of interest as a precursor in our investigation of substituted *o*-xylylene compounds, was recrystallized from ether–methanol at 253 K as colorless crystals, m.p. 317 K. The purpose of determining the structure was threefold: first, the title compound is a unique example of a strained aromatic in which the strain is due to the small fused ring as well as to the bulky *ortho* substituents; second, the structure constitutes the first crystal structure report of an *ortho*-bis(trimethylsilyl)benzene; third, it permits comparison of the steric effect of *ortho-tert*-butyl groups with that of *ortho*-trimethylsilyl groups.

The cell constants were obtained by a least-squares fit to the automatically centered settings for 15 reflections on a Syntex $P2_1$ automated diffractometer equipped with a graphite monochromator (Cu $K\alpha$, $\lambda = 1.54178$ Å). Data collection was started on a crystal of approximate dimensions $0.75 \times 0.45 \times 0.35$ mm using the θ - 2θ scan mode for the h,k,l octant out to 2θ of 142° . The variable scan option was used at 4 – 29.3°

min⁻¹. The background scan time/total scan time was set at 0.5. Three standard reflections were monitored every 57 reflections. After 1128 reflections had been collected, the standards had dropped by about 33%. A second crystal ($0.70 \times 0.45 \times 0.30$ mm) was mounted and data collection was resumed using the same data-collection parameters, except that the variable scan rate was increased to 8 – 29.3° min⁻¹. Roughly 500 reflections were retaken with the second crystal to average in the first crystal. The standards of the second crystal had deteriorated about 13% at the end of the data collection. After the data were corrected for crystal decay and Lorentz and polarization effects, the data were averaged. Of the 1644 unique reflections, 1595 were considered observed at the $1.96\sigma(I)$ level and were used in the data refinement.

The structure was solved by the *MULTAN* program (Germain, Main & Woolfson, 1971). The E statistics indicated that the space group might be noncentrosymmetric. The molecule was not expected to exhibit symmetry in the crystal because of the variety of relative orientations available to the six methyl groups about the Si–CH₃ bonds. Successful refinement in the noncentrosymmetric case gave $Pna2_1$ for the space group. Most of the H atom positions were located in difference maps, allowing all H positions to be calculated using standard techniques. Full-matrix least-squares refinements on the positions and anisotropic thermal parameters of the non-hydrogen atoms and the isotropic thermal parameters of the ring H atoms converged to the agreement factors: $R = 0.065$, $R_w = 0.080$, and $[\sum w(|F_{obs}| - |F_{calc}|)^2 / (m - n)]^{1/2}$, where m is the number of observations and n is the number of

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