

2,5-Dimethylhexane-2,5-diol at 110 K

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Abstract. $C_8H_{18}O_2$, monoclinic, $P2_1/c$; $a=15.590$ (3), $b=9.948$ (4), $c=8.932$ (2) Å, $\beta=91.80$ (2)° at 110 K; $Z=6$, $D_o(293\text{ K})=1.0$, $D_c(110\text{ K})=1.045$ g cm⁻³; $\mu(\text{Mo})=0.79$ cm⁻¹. The structure was solved by the symbolic addition method. Least-squares refinement gave $R=0.085$ and $R_w=0.116$ for 4057 observed reflexions ($I>3\sigma$). Hydrogen bonds connect the molecules into zigzag layers parallel to (100).

Introduction. 2,5-Dimethylhexane-2,5-diol is commercially available (EGA Chemie K.G., Keppler & Reif, BRD). Plate-like crystals along (100) were obtained by cooling a solution in a 1:1 mixture of light petroleum (40–60°) and acetone from *ca* 50 to 4°C. Details of the measurements at 100 K are given in a preliminary communication (Helmholdt, Ruysink, Reynaers & Kemper, 1972). 4057 reflexions with $I>3\sigma(I)$ were collected and used in the refinement.

The structure was solved by the symbolic addition method (Karle & Karle, 1966). There is a set of four molecules (*A*) in general positions and a set of two molecules (*B*) on inversion centres. The structure was refined by the least-squares program of the X-

RAY system (1972). The scale and overall temperature factor were put in one block and the parameters of *A* and *B* in a second and third block respectively. During the final refinement cycles the H atoms were kept fixed with C–H=1.08 and O–H=0.97 Å. For the heavy atoms anisotropic, and for the H atoms isotropic temperature factors were considered. Scattering factors for the heavy atoms were taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965). The weighting scheme was $w=[\sigma_f^2+2.7\times 10^{-4}|F_o|^2]^{-1}$, where σ_f^2 is the variance in $|F_o|$ due to counting statistics. $R=[\sum(F_o-F_c)^2/\sum F_o^2]^{1/2}=0.085$ and $R_w=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}=0.116$ for the 4057 observed reflexions. Atomic parameters are given in Table 1.†

Discussion. A projection of the structure along [001] is given in Fig. 1. Molecules of type *A* lie around the planes $x=0.2$ and $x=0.8$. Fig. 2 gives the projection along [100] of *A* around $x=0.2$ together with the projection of some groups of type O(15)–H belonging to *B*. The figures show that there are chains in the

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‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31749 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

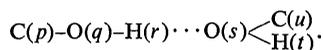
Table 1. *Final atomic coordinates* ($\times 10^5$) and *thermal parameters* ($\times 10^4$)

For numbering of atoms see Figs. 1 and 3. The standard deviations calculated by the least-squares program are in parentheses. The temperature factors are of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{31})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{31}	U_{23}
O(1)	24797 (9)	57148 (15)	29384 (16)	211 (7)	147 (6)	158 (6)	-14 (5)	-38 (5)	-12 (5)
C(2)	28402 (15)	35336 (24)	19562 (27)	257 (11)	225 (11)	259 (11)	81 (8)	-68 (9)	-61 (8)
C(3)	15642 (16)	38399 (24)	35415 (25)	294 (11)	238 (11)	206 (10)	-89 (9)	-35 (8)	47 (8)
C(4)	21145 (13)	44795 (20)	23529 (22)	194 (9)	147 (8)	140 (8)	-7 (7)	-22 (7)	2 (7)
C(5)	15447 (13)	48656 (21)	9949 (21)	148 (8)	218 (10)	119 (8)	-21 (7)	-1 (6)	14 (7)
C(6)	20007 (12)	55763 (21)	-2784 (22)	138 (8)	193 (9)	160 (8)	14 (7)	14 (6)	21 (7)
C(7)	14126 (12)	61078 (20)	-15578 (21)	134 (8)	147 (8)	153 (8)	6 (6)	13 (6)	7 (7)
C(8)	9514 (14)	49727 (22)	-23920 (22)	230 (10)	209 (10)	135 (8)	-48 (8)	-18 (7)	-1 (7)
C(9)	7758 (14)	71521 (22)	-10169 (23)	181 (9)	204 (10)	198 (9)	34 (8)	43 (7)	18 (8)
O(10)	19573 (9)	67241 (15)	-26421 (16)	184 (7)	158 (7)	164 (6)	-10 (5)	64 (5)	3 (5)
C(11)	54856 (12)	50880 (22)	50637 (23)	118 (8)	254 (10)	188 (9)	30 (7)	4 (7)	-63 (8)
C(12)	59882 (12)	43777 (21)	38442 (22)	107 (8)	191 (9)	159 (8)	12 (7)	-4 (6)	-22 (7)
C(13)	58575 (16)	28570 (24)	38810 (29)	258 (11)	203 (11)	381 (13)	-2 (9)	111 (10)	-55 (10)
C(14)	57784 (15)	49395 (27)	22881 (25)	209 (10)	388 (13)	183 (9)	28 (9)	-17 (8)	8 (9)
O(15)	68730 (9)	46784 (16)	42241 (16)	100 (6)	257 (8)	192 (7)	30 (5)	-8 (5)	-53 (6)

Table 2. *Geometry of the hydrogen bonds*

Distances in (Å) and angles in (°). The numbering is as follows:



L = angle between line $q-s$ and plane s, t, u . If both lone pairs of $O(s)$ take part in the bond $L=0$ and if one lone pair is involved $L=55^\circ$.

q	s	$q-s$	$r-s$	$q-r-s$	$p-q-r$	$p-q-s$	$t-s-u$	$q-s-t$	$q-s-u$	L
O(1)	O(15')	2.727	1.76	176	108	110.2	112	107	120.8	43
O(10')	O(1)	2.720	1.76	169	110	116.7	108	115	118.0	27
O(15')	O(10)	2.726	1.77	169	112	115.0	110	118	123.2	29

c direction in which A , A'' and groups of the type $O(15)-H$ are linked by hydrogen bonds. As is seen from Fig. 1, chains in the c direction at $x \approx 0.2$ are linked to chains at $x \approx 0.8$ by B . This gives layers, with zigzag structure, parallel to (100). Neighbouring layers are linked by van der Waals interaction only, which explains the easy cleavage of the crystals along (100). Data concerning the geometry of the hydrogen bonds are given in Table 2. Within experimental error the length of the three independent hydrogen bonds is equal to the average value 2.724 Å; deviations from linearity up to 11° are observed. The angles L of Table 2 show that, especially for $O(1)-H \cdots O(15')$, predominantly one of the O lone pairs is involved in the hydrogen-bonding.

Table 3. *Bond lengths and angles*

Standard deviations, calculated from those in Table 1 ($\times 1.5$), are 0.005 Å and 0.3°, respectively.

C(4)—C(5)	1.530 Å	O(1)—C(4)—C(2)	108.8°
C(5)—C(6)	1.533	O(1)—C(4)—C(3)	109.1
C(6)—C(7)	1.536	O(1)—C(4)—C(5)	106.6
C(11)—C(11')	1.525	O(10)—C(7)—C(6)	107.2
C(11)—C(12)	1.534	O(10)—C(7)—C(8)	105.4
C(4)—C(2)	1.522	O(10)—C(7)—C(9)	109.0
C(4)—C(3)	1.525	O(15)—C(12)—C(11)	104.1
C(7)—C(8)	1.521	O(15)—C(12)—C(13)	109.1
C(7)—C(9)	1.526	O(15)—C(12)—C(14)	108.4
C(12)—C(13)	1.527	C(2)—C(4)—C(3)	110.0
C(12)—C(14)	1.524	C(2)—C(4)—C(5)	112.8
C(4)—O(1)	1.445	C(3)—C(4)—C(5)	109.4
C(7)—O(10)	1.445	C(6)—C(7)—C(8)	111.8
C(12)—O(15)	1.442	C(6)—C(7)—C(9)	112.2
		C(8)—C(7)—C(9)	111.0
		C(11)—C(12)—C(13)	111.7
		C(11)—C(12)—C(14)	112.3
		C(13)—C(12)—C(14)	111.0
		C(4)—C(5)—C(6)	115.6
		C(5)—C(6)—C(7)	115.5
		C(11')—C(11)—C(12)	115.0

The molecules are depicted in Fig. 3. Analysis of the thermal parameters (Cruickshank, 1956) has shown that the molecules cannot be considered as rigid bodies. Therefore the bond lengths and angles given in Tables 2 and 3 are not corrected for libration. Due to the repulsion between the central C atoms and the atoms of the $-C(CH_3)_2OH$ groups the angles of type $C(4)-$

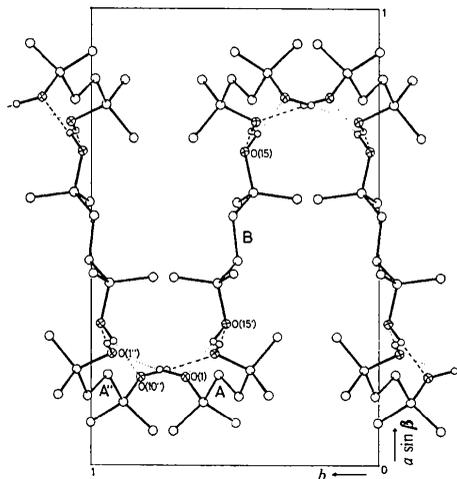


Fig. 1. Projection along [001] onto the plane perpendicular to [001]. $\circ = C$, $\oplus = O$, $\circ = H$. Molecules at general positions are given by A (coordinates in Table 1), A' (related to A by inversion) and A'' (related to A by c glide plane). Molecules at special positions are indicated by B ; $O(15)$ is from Table 1 and $O(15')$ related to it by inversion. H atoms of CH_3 groups are not given. Hydrogen bonds are indicated by ---, but by --- and \cdots if one oxygen atom forms hydrogen bonds with two successive molecules in the c direction.

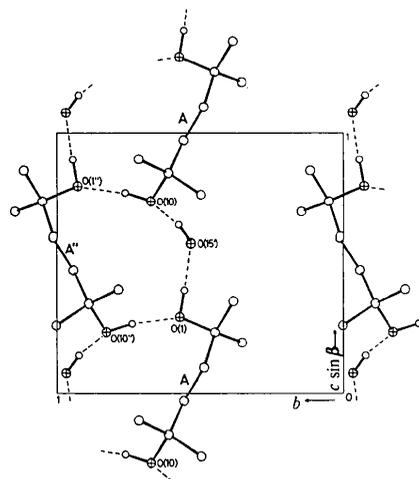


Fig. 2. Projection of molecules A around $x \approx 0.2$ and of groups of type $O(15)-H$ along $[100]$ onto the plane perpendicular to $[100]$.

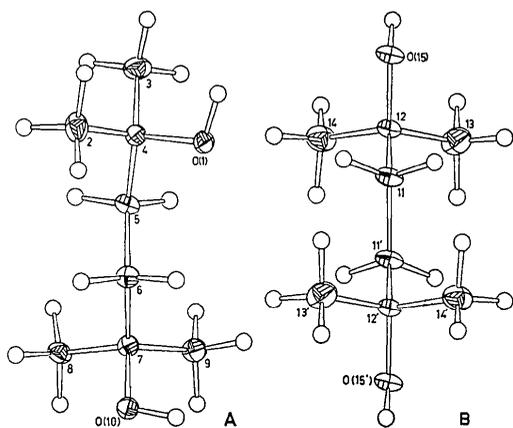


Fig. 3. Molecules of 2,5-dimethylhexane-2,5-diol. *A* is at a general position, *B* at an inversion centre.

C(5)–C(6) (mean 115.4°) are *ca* 3° larger than the value of about 112° found in aliphatic hydrocarbons (Bodor, Bednowitz & Post, 1967). As observed in other glycols (Jeffrey & Shen, 1972), in the groups $-\text{C}(\text{CH}_3)_2\text{OH}$ the angles C–C–O are generally smaller than the angles C–C–C. Due to the repulsions mentioned above the bonds of type C(4)–C(5) and C(5)–C(6) (mean 1.532 \AA) have a tendency to be longer than the bonds of type C–CH₃ (mean 1.528 \AA). A similar trend has been observed by Jeffrey & Shen (1972) for 2,5-dimethylhexane-2,5-diol tetrahydrate.

The C–O lengths can be compared with the values observed by Ruysink & Vos (1974) for the C–O bonds in *trans* (1.436 and 1.452 \AA) and *cis* (1.432 and 1.440 \AA) 2,5-dimethyl-3-hexene-2,5-diol and with the value of 1.459 \AA reported by Jeffrey & Shen (1972). No explanation has yet been found for the variation in C–O lengths.

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5-Mesylamino-2*H*-1,2,3-triazole-4-carbonitrile Monohydrate

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Abstract. $\text{C}_4\text{H}_5\text{N}_5\text{O}_2\text{S} \cdot \text{H}_2\text{O}$, triclinic $P\bar{1}$; $a=5.846$ (1), $b=5.222$ (1), $c=13.700$ (2) \AA , $\alpha=88.87$ (3), $\beta=94.41$ (4), $\gamma=84.10$ (2) $^\circ$, $V=414.62 \text{ \AA}^3$; $Z=2$, $D_x=1.643$, $D_m=1.645 \text{ g cm}^{-3}$; $\mu(\text{Mo } K\alpha, \lambda=0.7107 \text{ \AA})=3.19 \text{ cm}^{-1}$. The structure was solved by the heavy-atom and Fourier techniques. An R of 0.035 was obtained for 1633 observed reflexions after least-squares refinement. The endocyclic H atom is linked to N(2).

Introduction. Intensities of 1825 independent reflexions were collected on a Syntex $P2_1$ computer-controlled four-circle diffractometer with Mo $K\alpha$ radiation from a graphite monochromator. After data reduction 192 reflexions with $|F| - 5\sigma(F) < 0$ were taken as unobserved. The position of the S atom was located in a Patterson map ($R=0.52$). Structure factor and Fourier calculations gave the positions of all non-hydrogen