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The Twin-Chair Conformation of Bicyclo[3.3.1]nonane: X-ray Diffraction Study of 5-Methyl-1-*p*-toluenesulphonyloxymethylbicyclo[3.3.1]nonan-9-ol

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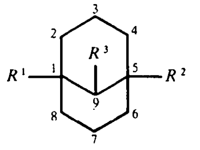
Abstract. $C_{18}H_{26}O_4S$, triclinic, $P\bar{1}$, a = 7·377 (2), b = 11·303 (3), c = 12·132 (2) Å, α = 67·19 (2), β = 71·07 (2), γ = 71·18 (2)°, U = 859 Å^3, Z = 2, D_c = 1·308 Mg m^{-3}, $F(000)$ = 364, μ(Mo $K\alpha$) = 0·21 mm^{-1}. The structure was refined to R = 0·042 for 2224 reflections. The 1,5,9-trisubstituted bicyclo[3.3.1]nonane has a twin-chair conformation with a C(3)···C(7) separation of 3·080 (4) Å. Force-field calculations indicate that the substituents at C(1) and C(5) are responsible for the finding that the 3,7-separation is *ca* 0·03 Å shorter than in the unsubstituted hydrocarbon, bicyclo[3.3.1]nonane.

Introduction. A twin-chair bicyclo[3.3.1]nonane (I) constructed from six-membered rings with tetrahedral angles would feature a C(3)···C(7) separation of 2·52 Å and an H···H 3,7-separation with the physically impossible value of *ca* 0·75 Å. An early X-ray diffraction study of a bicyclo[3.3.1]nonane derivative disclosed a molecule with a modified twin-chair conformation in which the C(3)···C(7) separation is enlarged to 3·06 Å and it was deduced that the H···H 3,7-separation may be *ca* 1·8 Å (Brown, Eglinton, Martin, Parker & Sim, 1964; Brown, Martin & Sim, 1965). Other diffraction investigations have been reported and it appears that the H···H 3,7-separation in bicyclo[3.3.1]nonane is undoubtedly shorter than 2 Å, though the actual value is not yet known with precision (Bovill, Cox, Flitman, Guy, Hardy, McCabe, Macdonald, Sim & White, 1979). Calculations of the geometry of bicyclo[3.3.1]nonane by the method of molecular mechanics yield a range of estimates for the various conformational parameters of the molecule, *e.g.* for the H···H 3,7-separation 2·20 Å (Allinger, Tribble, Miller & Wertz, 1971), 2·12 Å (Peters, Baas, van de Graaf, van der Toorn & van Bekkum, 1978), 2·03 Å (Allinger, 1977; Osawa, Aigami & Inamoto, 1979) and 1·97 Å (White & Bovill, 1976, 1977). It is evident that the geometry of the twin-chair conformation of bicyclo[3.3.1]nonane provides a useful test of the relative merits of the force fields currently employed in conformational calculations and additional diffraction studies of a variety of derivatives are desirable. 5-Methyl-1-*p*-toluenesulphonyloxymethylbicyclo[3.3.1]nonan-9-ol (II) provides an example of a bicyclononane with substituents at positions 1, 5 and 9 and an X-ray study of this material was undertaken.



(I) $R^1 = R^2 = R^3 = H$

(II) $R^1 = CH_3C_6H_4SO_2OCH_2$
$R^2 = CH_3$
$R^3 = OH$

A small crystal was used for intensity measurements with Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer and 2224 independent reflections in the range $\theta < 27°$ satisfied the criterion $I > 3\sigma(I)$. The

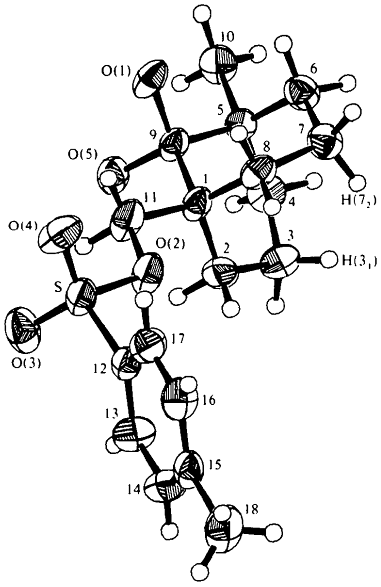


Fig. 1. *ORTEP* diagram (Johnson, 1965) of the molecule. The thermal ellipsoids of the S, O and C atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0·1 Å.

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Table 1. *Atomic coordinates* ($\times 10^4$ *for* S, O *and* C; $\times 10^3$ *for* H)

	x	*y*	*z*
S	4932 (1)	9595 (1)	2811 (1)
O(1)	−1190 (5)	7976 (3)	5745 (3)
O(2)	4446 (3)	8310 (2)	3851 (2)
O(3)	5034 (3)	10487 (2)	3338 (2)
O(4)	3595 (3)	10071 (2)	2025 (2)
O(5)	241 (5)	8377 (3)	7138 (3)
C(1)	2291 (3)	7185 (2)	5690 (2)
C(2)	3848 (4)	6663 (3)	6448 (3)
C(3)	3539 (4)	5466 (3)	7580 (3)
C(4)	1402 (4)	5587 (3)	8293 (3)
C(5)	−148 (4)	6146 (2)	7531 (2)
C(6)	−145 (4)	5207 (3)	6898 (3)
C(7)	1694 (4)	4967 (3)	5904 (3)
C(8)	2300 (4)	6242 (3)	5047 (2)
C(9)	241 (3)	7446 (2)	6544 (2)
C(10)	−2183 (4)	6405 (3)	8380 (3)
C(11)	2553 (4)	8516 (3)	4755 (3)
C(12)	7281 (4)	8952 (2)	2041 (2)
C(13)	8888 (4)	8742 (3)	2494 (3)
C(14)	10730 (4)	8307 (3)	1838 (3)
C(15)	11012 (4)	8086 (2)	746 (3)
C(16)	9390 (5)	8318 (3)	316 (3)
C(17)	7521 (5)	8751 (3)	953 (3)
C(18)	13037 (5)	7590 (4)	58 (4)
H(2_1)	502 (4)	655 (3)	598 (2)
H(2_2)	396 (4)	734 (3)	671 (3)
H(3_1)	399 (4)	467 (3)	736 (3)
H(3_2)	432 (5)	545 (3)	814 (3)
H(4_1)	119 (4)	606 (3)	878 (3)
H(4_2)	120 (4)	468 (3)	892 (3)
H(6_1)	−32 (4)	432 (3)	760 (3)
H(6_2)	−131 (4)	559 (3)	654 (2)
H(7_1)	142 (4)	458 (3)	543 (3)
H(7_2)	281 (4)	435 (3)	630 (3)
H(8_1)	350 (4)	609 (3)	453 (3)
H(8_2)	142 (4)	666 (3)	451 (3)
H(10_1)	−221 (4)	698 (3)	876 (3)
H(10_2)	−241 (4)	563 (3)	903 (3)
H(10_3)	−332 (5)	676 (3)	794 (3)
H(11_1)	268 (5)	919 (4)	510 (3)
H(11_2)	156 (5)	891 (3)	431 (3)
H(13)	863 (5)	895 (3)	330 (3)
H(14)	1172 (6)	818 (4)	214 (3)
H(16)	945 (5)	829 (3)	−45 (3)
H(17)	650 (4)	888 (3)	65 (3)
H(18_1)	1390 (7)	800 (4)	3 (4)
H(18_2)	1346 (6)	672 (5)	21 (4)
H(18_3)	1310 (7)	777 (5)	−89 (5)

Table 2. *Bond lengths* (Å) *and angles* (°)

S–O(2)	1·565 (2)	C(16)–C(17)	1·380 (5)
S–O(3)	1·418 (2)	C(2)–H(2_1)	0·87 (3)
S–O(4)	1·429 (2)	C(2)–H(2_2)	0·97 (3)
S–C(12)	1·751 (3)	C(3)–H(3_1)	0·97 (3)
O(1)–C(9)	1·489 (4)	C(3)–H(3_2)	1·02 (3)
O(2)–C(11)	1·484 (4)	C(4)–H(4_1)	0·90 (3)
O(5)–C(9)	1·489 (4)	C(4)–H(4_2)	1·04 (3)
C(1)–C(2)	1·530 (3)	C(6)–H(6_1)	1·05 (3)
C(1)–C(8)	1·543 (3)	C(6)–H(6_2)	0·99 (3)
C(1)–C(9)	1·543 (3)	C(7)–H(7_1)	0·95 (2)
C(1)–C(11)	1·520 (4)	C(7)–H(7_2)	1·01 (3)
C(2)–C(3)	1·524 (4)	C(8)–H(8_1)	0·91 (3)
C(3)–C(4)	1·523 (4)	C(8)–H(8_2)	0·95 (3)
C(4)–C(5)	1·526 (3)	C(10)–H(10_1)	0·93 (3)
C(5)–C(6)	1·531 (3)	C(10)–H(10_2)	0·94 (3)
C(5)–C(9)	1·536 (3)	C(10)–H(10_3)	1·03 (3)
C(5)–C(10)	1·532 (4)	C(11)–H(11_1)	1·04 (3)
C(6)–C(7)	1·524 (4)	C(11)–H(11_2)	0·94 (3)
C(7)–C(8)	1·520 (4)	C(13)–H(13)	1·03 (3)
C(12)–C(13)	1·379 (3)	C(14)–H(14)	0·87 (3)
C(12)–C(17)	1·371 (4)	C(16)–H(16)	0·93 (3)
C(13)–C(14)	1·375 (4)	C(17)–H(17)	0·89 (3)
C(14)–C(15)	1·379 (4)	C(18)–H(18_1)	0·89 (4)
C(15)–C(16)	1·368 (4)	C(18)–H(18_2)	0·89 (5)
C(15)–C(18)	1·502 (5)	C(18)–H(18_3)	1·08 (5)

O(2)–S–O(3)	109·7 (1)	C(9)–C(5)–C(10)	109·6 (2)
O(2)–S–O(4)	108·9 (1)	C(5)–C(6)–C(7)	115·1 (2)
O(3)–S–O(4)	116·8 (1)	C(6)–C(7)–C(8)	111·9 (2)
O(2)–S–C(12)	100·2 (1)	C(7)–C(8)–C(1)	115·1 (2)
O(3)–S–C(12)	110·3 (1)	C(1)–C(9)–C(5)	109·5 (2)
O(4)–S–C(12)	109·6 (1)	C(1)–C(9)–O(1)	105·8 (2)
C(11)–O(2)–S	114·7 (2)	C(1)–C(9)–O(5)	107·6 (2)
C(2)–C(1)–C(8)	114·2 (2)	C(5)–C(9)–O(1)	110·0 (2)
C(2)–C(1)–C(9)	108·7 (2)	C(5)–C(9)–O(5)	109·6 (2)
C(2)–C(1)–C(11)	109·0 (2)	O(1)–C(9)–O(5)	114·0 (2)
C(8)–C(1)–C(9)	108·2 (2)	C(1)–C(11)–O(2)	108·2 (2)
C(8)–C(1)–C(11)	110·5 (2)	C(13)–C(12)–S	119·3 (2)
C(9)–C(1)–C(11)	105·9 (2)	C(17)–C(12)–S	119·8 (2)
C(1)–C(2)–C(3)	115·1 (2)	C(13)–C(12)–C(17)	120·7 (2)
C(2)–C(3)–C(4)	112·6 (2)	C(12)–C(13)–C(14)	118·4 (3)
C(3)–C(4)–C(5)	116·3 (2)	C(13)–C(14)–C(15)	122·1 (3)
C(4)–C(5)–C(6)	112·8 (2)	C(14)–C(15)–C(16)	118·0 (2)
C(4)–C(5)–C(9)	109·0 (2)	C(14)–C(15)–C(18)	121·1 (3)
C(4)–C(5)–C(10)	108·7 (2)	C(16)–C(15)–C(18)	120·9 (3)
C(6)–C(5)–C(9)	108·7 (2)	C(15)–C(16)–C(17)	121·3 (3)
C(6)–C(5)–C(10)	108·1 (2)	C(16)–C(17)–C(12)	119·5 (3)

structure was solved with a version of *MULTAN* (Germain, Main & Woolfson, 1971) adapted for the Glasgow University ICL 2976 computer by Dr C. J. Gilmore. The O atom of the hydroxyl group at C(9) appeared in an electron-density distribution as two distinct and equal peaks, one on either side of the plane through C atoms 1, 5, 9, 10 and 11, and both peaks were included in subsequent calculations as O(1) and O(5), with site-occupation parameters of 0·5. The coordinates and isotropic temperature factors of the S, C and O atoms were adjusted by full-matrix least squares with unit weights ($R = 0{\cdot}13$) after which the H atoms, apart from the half-weight disordered ones at C(9), O(1) and O(5), were located in a difference map. When the H atoms were included at ideal positions and the S, C and O atoms assigned anisotropic thermal parameters, R fell to 0·050. Finally, the positional and isotropic thermal parameters of the H atoms were included as variables and the weighting scheme was altered to $w = 2{\cdot}447/[\sigma^2(|F|) + 0{\cdot}000184|F|^2]$; these calculations converged at $R = 0{\cdot}042$, $R_w = 0{\cdot}045$. The Fourier and least-squares calculations were performed with *SHELX* (Sheldrick, 1976).*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34604 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The molecular structure is shown in Fig. 1. The atomic coordinates are listed in Table 1, bond lengths and angles in Table 2, torsion angles in Table 3 and intermolecular separations in Table 4.

The $C(sp^3)$–$C(sp^3)$ lengths in the bicyclo[3.3.1]-nonane moiety are 1·520–1·543 Å, mean 1·530 Å. The C–H lengths in the methylene groups at C(2), C(3), C(4), C(6), C(7) and C(8) are 0·87–1·05 Å, mean 0·98 Å. The C–C–C angles at C(2), C(4), C(6) and C(8) are 115·1–116·3°, mean 115·4°, and those at C(3) and C(7) are 112·6 and 111·9°, mean 112·3°. The angles C(2)–C(1)–C(8) and C(4)–C(5)–C(6) are 114·2 and 112·8°. On the other hand, C(9)–C(1)–C(2), C(9)–C(1)–C(8), C(9)–C(5)–C(4) and C(9)–C(5)–C(6) are distinctly smaller than tetrahedral, 108·2–109·0°, mean 108·7°.

Within the cyclohexane rings the torsion angles about bonds 2–3, 3–4, 6–7 and 7–8 are 42·1–45·7°, mean 44·2°, those about 1–2, 4–5, 1–8 and 5–6 are 51·4–54·3°, mean 53·5°, and those about 1–9 and 5–9 are 61·1–62·6°, mean 62·0°. The range spanned by these angles demonstrates the pronounced deviations of the rings from ideal cyclohexane geometry.

Table 3. *Torsion angles* (°)

C(12)–S–O(2)–C(11)	175·9 (2)	C(11)–C(1)–C(9)–O(5)	−60·5 (3)
O(3)–S–O(2)–C(11)	59·9 (2)	C(2)–C(1)–C(11)–O(2)	67·3 (3)
O(4)–S–O(2)–C(11)	−69·1 (2)	C(8)–C(1)–C(11)–O(2)	−58·9 (3)
O(2)–S–C(12)–C(13)	−81·7 (2)	C(9)–C(1)–C(11)–O(2)	−175·9 (2)
O(2)–S–C(12)–C(17)	102·8 (2)	C(1)–C(2)–C(3)–C(4)	−43·2 (3)
O(3)–S–C(12)–C(13)	33·9 (2)	C(2)–C(3)–C(4)–C(5)	42·1 (3)
O(3)–S–C(12)–C(17)	−141·6 (2)	C(3)–C(4)–C(5)–C(6)	69·4 (3)
O(4)–S–C(12)–C(13)	163·9 (2)	C(3)–C(4)–C(5)–C(9)	−51·4 (3)
O(4)–S–C(12)–C(17)	−11·5 (2)	C(3)–C(4)–C(5)–C(10)	−170·8 (2)
S–O(2)–C(11)–C(1)	179·5 (2)	C(4)–C(5)–C(6)–C(7)	−66·6 (3)
C(8)–C(1)–C(2)–C(3)	−67·1 (3)	C(9)–C(5)–C(6)–C(7)	54·3 (3)
C(9)–C(1)–C(2)–C(3)	53·9 (3)	C(10)–C(5)–C(6)–C(7)	173·2 (2)
C(11)–C(1)–C(2)–C(3)	168·9 (2)	C(4)–C(5)–C(9)–C(1)	61·1 (2)
C(2)–C(1)–C(8)–C(7)	67·0 (3)	C(4)–C(5)–C(9)–O(1)	177·1 (2)
C(9)–C(1)–C(8)–C(7)	−54·2 (3)	C(4)–C(5)–C(9)–O(5)	−56·8 (3)
C(11)–C(1)–C(8)–C(7)	−169·7 (2)	C(6)–C(5)–C(9)–C(1)	−62·2 (2)
C(2)–C(1)–C(9)–C(5)	−62·6 (2)	C(6)–C(5)–C(9)–O(1)	53·7 (3)
C(2)–C(1)–C(9)–O(1)	178·8 (2)	C(6)–C(5)–C(9)–O(5)	180·0 (2)
C(2)–C(1)–C(9)–O(5)	56·5 (3)	C(10)–C(5)–C(9)–C(1)	180·0 (2)
C(8)–C(1)–C(9)–C(5)	61·9 (2)	C(10)–C(5)–C(9)–O(1)	−64·2 (3)
C(8)–C(1)–C(9)–O(1)	−56·6 (2)	C(10)–C(5)–C(9)–O(5)	62·0 (3)
C(8)–C(1)–C(9)–O(5)	−178·9 (2)	C(5)–C(6)–C(7)–C(8)	−45·7 (3)
C(11)–C(1)–C(9)–C(5)	−179·6 (2)	C(6)–C(7)–C(8)–C(1)	45·7 (3)
C(11)–C(1)–C(9)–O(1)	61·8 (2)		

Table 4. *Intermolecular separations* ≤3·7 Å

$O(4)\cdots O(5^{I})$	2·90 (1)	$O(5)\cdots C(16^{V})$	3·68 (1)
$O(1)\cdots O(3^{I})$	2·93 (1)	$C(15)\cdots C(17^{VI})$	3·68 (1)
$O(4)\cdots C(14^{II})$	3·45 (1)	$O(1)\cdots C(13^{II})$	3·68 (1)
$C(10)\cdots C(18^{III})$	3·56 (1)	$C(14)\cdots C(16^{VI})$	3·69 (1)
$O(4)\cdots C(17^{IV})$	3·61 (1)	$O(3)\cdots C(2^{VII})$	3·69 (1)
$O(1)\cdots C(11^{I})$	3·61 (1)	$C(15)\cdots C(16^{VI})$	3·70 (1)
$O(4)\cdots C(10^{I})$	3·65 (1)	$O(4)\cdots C(16^{IV})$	3·70 (1)
$O(3)\cdots C(10^{I})$	3·68 (1)		

The superscripts refer to the following transformations of the atomic coordinates:

(I)	$-x$,	$2-y$,	$1-z$	(V)	$-1+x$,	y,	$1+z$
(II)	$-1+x$,	y,	z	(VI)	$2-x$,	$2-y$,	$-z$
(III)	$-2+x$,	y,	$1+z$	(VII)	$1-x$,	$2-y$,	$1-z$.
(IV)	$1-x$,	$2-y$,	$-z$				

The $C(3)\cdots C(7)$ and $H(3_1)\cdots H(7_2)$ separations are 3·080 (4) and 1·95 (3) Å. The $C(3)$–$H(3_1)$ and $C(7)$–$H(7_2)$ lengths (0·97 and 1·01 Å) are shorter than the normal spectroscopic value for $C(sp^3)$–H bonds, but this appears to be a well known artifact of the X-ray diffraction method, and when $H(3_1)$ and $H(7_2)$ are displaced along the C–H vectors to make these C–H distances 1·10 Å the $H\cdots H$ transannular distance is 1·82 Å.

In order to relate these results to the parent hydrocarbon, it is necessary to assess the steric effect of substituents at C(1), C(5) and C(9). Accordingly, molecular-mechanics calculations were carried out for bicyclo[3.3.1]nonane, 1,5-dimethylbicyclo[3.3.1]-nonane and 1,5,9-trimethylbicyclo[3.3.1]nonane with the hydrocarbon force field developed by White & Bovill (1976, 1977). The steric effect of an OH group at C(9) should be smaller than that of a CH_3 group. The calculations indicate that the $C(3)\cdots C(7)$ and $H(3_1)\cdots H(7_2)$ separations are influenced by substituents at C(1) and C(5), the separations in bicyclo-[3.3.1]nonane being *ca* 0·03 Å longer than in the di- and trisubstituted derivatives. From the results it can be concluded that the $C(3)\cdots C(7)$ separation of 3·08 Å in (II) is consistent with a $C(3)\cdots C(7)$ separation in bicyclo[3.3.1]nonane of *ca* 3·11 Å. This is in agreement with the electron diffraction result of 3·10 Å (Osina, Mastryukov, Vilkov & Belikova, 1976). The $H\cdots H$ transannular separation in bicyclo[3.3.1]-nonane should be *ca* 1·85 Å (*i.e.* 1·82 + 0·03 Å), in good accord with a previous estimate of 1·86 Å (Bovill *et al.*, 1979). Molecular-mechanics calculations that estimate the $H\cdots H$ separation to be in excess of 2 Å clearly exaggerate the transannular repulsion and cannot be relied on to give accurate conformational energies. The force field developed by White & Bovill (1976, 1977) provides the most acceptable results at present.

The molecular-mechanics calculations for 1,5,9-trimethylbicyclo[3.3.1]nonane indicate that the ring carrying the 9-CH_3 group in the axial position is flattened to a greater extent than the ring with the 9-H atom axial, the torsion angles in the former ring being smaller by 1–3°. Because of the packing disorder, the experimental results for (II) correspond to a superposition of rings with axial and equatorial 9-OH substituents and no distinction is apparent between appropriate torsion angles. An X-ray study of 9-aminobicyclo[3.3.1]nonane-9-carboxylic acid hydrobromide was reported recently (Bhattacharjee, Chacko & Zand, 1979) and in that compound the cyclohexane ring with CO_2H axial and NH_3^+ equatorial is flattened to a greater extent than the ring with CO_2H equatorial and NH_3^+ axial. The $C(3)\cdots C(7)$ separation is 3·12 Å.

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Refinement of Pentaerythritol*

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Abstract. $C_5H_{12}O_4$, tetragonal, $I\bar{4}$, $a = 6{\cdot}087$ (1), $c = 8{\cdot}757$ (2) Å, $Z = 2$, $D_c = 1{\cdot}393$, $D_m = 1{\cdot}363$ Mg m^{-3} (in carbon tetrachloride and xylene). The final R was 0·023 for 274 reflections and a model in which the H-atom thermal parameters were varied isotropically. There is one unique O—H···O hydrogen bond, with distances of 0·75 (2), 1·98 (2), and 2·710 (2) Å for O—H, H···O, and O···O respectively. A rigid-body analysis revealed large root-mean-square amplitudes of libration, a condition not uncommon to plastic-crystal precursors.

Introduction. A series of poly(hydroxymethyl) compounds which undergo phase transitions between the ordered and orientationally disordered (plastic) states are currently under investigation in this laboratory (*e.g.* Rudman, Eilerman & LaPlaca, 1978). Nitta (1926) and Nitta & Watanabé (1937, 1938) reported that pentaerythritol transforms from an ordered body-centered tetragonal phase to a plastic face-centered cubic phase at 452·7 K. The crystal structure was redetermined and refined several times (Llewellyn, Cox & Goodwin, 1937; Shiono, Cruickshank & Cox, 1958), most recently by Hvoslef (1958) who located the H atoms on the basis of $hk0$ and $00l$ neutron diffraction data. However, the published H atom coordinates were incorrect (Smith, 1969).

Pentaerythritol is a model compound for the other members of this series and, as such, it has been the subject of several other studies including calorimetry (Westrum, 1961), NMR (Smith, 1969), infrared spectroscopy (Marzocchi & Castellucci, 1971), and X-ray diffuse scattering (Terauchi, Okamoto, Tasaka & Watanabé, 1971; Bärnighausen, 1978). It has also been used as a model for hydrogen bonding in polyhydric molecules in the computation of the conformational energy of peptides (Némethy & Scheraga, 1977).

Inasmuch as the proper interpretation of these data requires an accurate model and the structure has not been determined to the precision and accuracy that modern methods allow (*cf.* van der Lugt, Smit & Perdok, 1968; Smith, 1969) the crystal structure of the ordered tetragonal phase of pentaerythritol was redetermined.

Single crystals were grown from a saturated aqueous solution. The crystal used for data collection was a square pyramid, approximately 0·24 mm along each side of the base and 0·30 mm in height. The observed reflections and systematic absences ($h + k + l \neq 2n$) were in agreement with the previously reported body-

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* Polymorphism of Crystalline Poly(hydroxymethyl) Compounds. I.

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