is 1·424 (4) Å. The angelate substituent is nonplanar, with a twist of 20·0 (5)° about the central bond. The apparent thermal motion of C(21) is large ($B_{\rm eq}$ = 13·7 Å^2), and may be indicative of unresolved disorder. Molecules are linked in the solid by spiral H-bonded chains along the direction of the *a* axis. The H bond involves hydroxyl group O(4) as donor and epoxide O atom O(1) as acceptor, with O···O separation 2·794 (3) Å and O—H···O angle approximately 150°.

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Acta Cryst. (1986). C**42**, 1063–1066

Structure of *cis,cis,cis,cis*-1,2,3,4,5-Pentakis(methylsulfonyloxymethyl)cyclopentane Methanol Solvate

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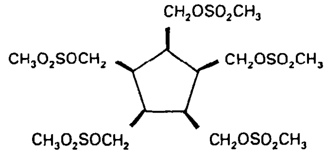
Abstract. $C_{15}H_{30}O_{15}S_5$.0·256 (8) CH_3OH, M_r = 618·9, triclinic, $P\bar{1}$, a = 11·902 (1), b = 12·994 (1), c = 9·786 (1) Å, α = 110·00 (1), β = 109·97 (1), γ = 92·00 (1)°, V = 1316·9 (3) Å^3, Z = 2, D_x = 1·561 g cm^{-3}, Mo $K\alpha$ (graphite monochromator), λ = 0·71073 Å, μ = 4·86 cm^{-1}, $F(000)$ = 650·32, T = 295 (1) K, R = 0·050 for 355 variables and 3159 unique reflections having $I > 3\sigma(I)$. The value of the dihedral angle describing the envelope conformation of the cyclopentane ring is 40·7 (5)°. Most bond lengths and angles fall within normal ranges. The $CH_2OSO_2CH_3$ groups are disposed in such a way that their unexpected resistance to nucleophilic attack is explained.

Introduction. The title compound (Gregory, 1983), hereafter PMMCP, undergoes elimination of methanesulfonic acid rather than nucleophilic displacement upon treatment with strong nucleophiles such as benzylthiolate. Inasmuch as substitution by sulfur constitutes an important component in the elaboration of PMMCP into dodecahedrane and other novel cage compounds (Tolbert, Gregory & Brock, 1985), we determined the crystal structure of PMMCP to evaluate the structural factors inhibiting the desired reaction.



Experimental. Colorless, thin tablet with pointed ends, 0·35 × 0·20 × 0·05 mm grown from methanol and mounted in air, bounding planes $\{100\}$, $\{01\bar{1}\}$, $\{10\bar{1}\}$, $\{1\bar{1}0\}$. Enraf–Nonius CAD-4/*F* diffractometer; 22 reflections having 12·6 ≤ θ ≤ 13·3° used to determine lattice parameters; ω–2θ scans; transmission coefficients for absorption correction (Gaussian integration) 0·90–0·96; $\theta \le 27{\cdot}5°$; hemisphere of data with $0 \le h \le 15$, $-16 \le k \le 16$, $-11 \le l \le 10$. Average intensity loss for three control reflections 4·2% overall (not corrected). 6029 unique reflections measured; 3159 data having $I > 3\sigma(I)$ used for refinement. Structure solved using direct methods; computer programs as described previously (Brock & Webster, 1976). Scattering factors from Cromer & Waber (1974); anomalous terms included for S atoms.

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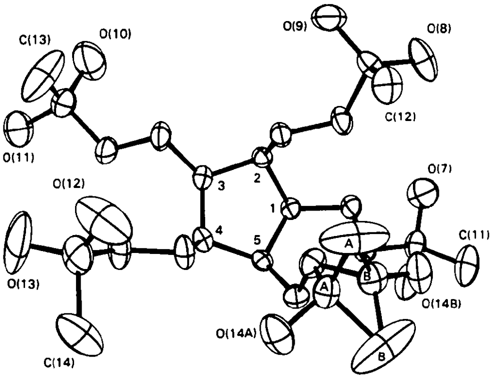

Fig. 1. Perspective drawing of the molecular structure of PMMCP. The numbering system for the cyclopentane ring is shown; the atoms of the side chain attached to C(*n*) are C(*n* + 5), O(*n*), S(*n*), C(*n* + 10), O(2*n* + 4) and O(2*n* + 5). The disordered S(5*A*)/S(5*B*) and *X*(15*A*)/*X*(15*B*) atom pairs are marked. In this and the following drawing the shapes of the ellipsoids correspond to 50% probability contours of atomic displacement, and the H atoms have been omitted for the sake of clarity.

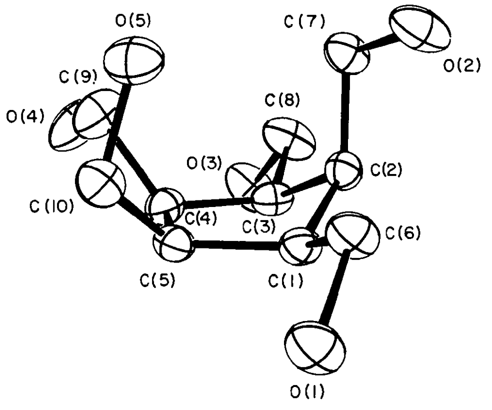

Fig. 2. Perspective view of the central portion of the PMMCP molecule illustrating the envelope conformation of the cyclopentane ring and the orientations of the side chains.

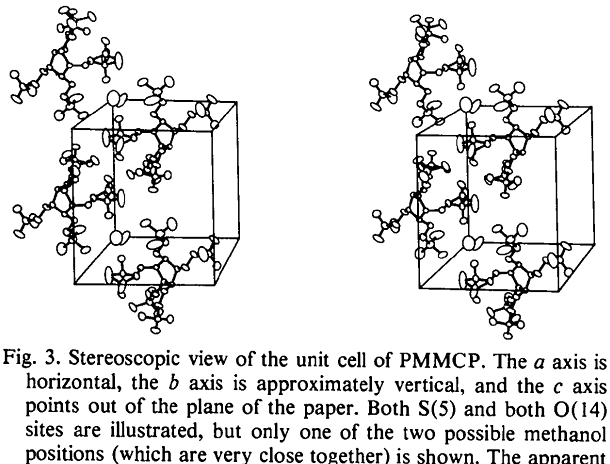

Fig. 3. Stereoscopic view of the unit cell of PMMCP. The *a* axis is horizontal, the *b* axis is approximately vertical, and the *c* axis points out of the plane of the paper. Both S(5) and both O(14) sites are illustrated, but only one of the two possible methanol positions (which are very close together) is shown. The apparent short contacts are avoided if partial ordering of the alternate sites in the chains parallel to the *b* axis is postulated (see text).

One of the methylsulfonyl groups was found to be disordered (see Fig. 1); the occupancy factor refined for atoms S(5*A*) and O(14*A*) is 0·481 (3). The other two terminal atoms attached to S(5*A*) and S(5*B*), a C and an O atom, overlap such that two composite peaks, denoted as *X*(15*A*) and *X*(15*B*), are observed; the fractional O-atom contribution to *X*(15*A*) is 0·757 (24). This occupancy factor together with the S—*X* bond lengths suggests that the atoms of this group that would normally be denoted as C(15) and O(15) are disordered with each other only when attached to S(5*B*). Average S(*n*)—C and S(*n*)—O(terminal) distances, *n* = 1–4, are 1·726 (5) and 1·414 (6) Å, respectively. The two S(5*A*)—*X*(15) distances of 1·688 (6) and 1·464 (5) Å are close to these values, but the two S(5*B*)—*X*(15) distances of 1·575 (5) and 1·518 (7) Å seem to represent averages. The population of the S(5*A*) and S(5*B*) sites is probably not completely random since a somewhat short O···O contact [2·635 (12) Å] results if two O(14*B*) sites related by the inversion center at $0\frac{1}{2}0$ are both occupied. It may be (see also below) that the atoms affected by the 'disorder' do not conform to the inversion symmetry, and that this part of the structure could be better described in the space group *P*1.

Table 1. *Positional and displacement parameters for the atoms of PMMCP with e.s.d.'s in parentheses*

The equivalent displacement parameter is defined as (4/3)Tr(β.G), where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

	x	*y*	*z*	B_{eq}(Å^2)
S(1)	0·14574 (11)	−0·62722 (9)	−0·45690 (12)	3·2
S(2)	0·39944 (11)	−0·49148 (9)	0·26650 (13)	3·0
S(3)	0·81193 (12)	−0·01792 (11)	0·30060 (16)	4·2
S(4)	0·44507 (14)	0·12531 (10)	0·33123 (16)	4·7
S(5*A*)	0·0882 (2)	−0·2282 (2)	0·1088 (3)	3·1
S(5*B*)	0·0600 (2)	−0·3254 (2)	0·0434 (3)	3·6
O(1)	0·1976 (3)	−0·5017 (2)	−0·3481 (3)	3·0
O(2)	0·3742 (3)	−0·4418 (2)	0·1358 (3)	3·3
O(3)	0·6756 (3)	−0·0585 (2)	0·1929 (3)	3·9
O(4)	0·4453 (3)	0·0261 (2)	0·1858 (4)	4·2
O(5)	0·1741 (3)	−0·2716 (2)	0·0274 (3)	3·2
O(6)	0·1090 (3)	−0·6278 (3)	−0·6112 (3)	5·4
O(7)	0·2309 (3)	−0·6948 (3)	−0·4117 (4)	5·7
O(8)	0·3564 (3)	−0·6078 (2)	0·1778 (4)	5·1
O(9)	0·5218 (3)	−0·4532 (3)	0·3710 (4)	4·7
O(10)	0·8741 (4)	−0·1093 (3)	0·2890 (6)	7·4
O(11)	0·8507 (3)	0·0672 (3)	0·2599 (5)	7·6
O(12)	0·4328 (5)	0·0867 (3)	0·4410 (4)	9·0
O(13)	0·5470 (4)	0·2041 (3)	0·3654 (6)	9·9
O(14*A*)	0·0818 (7)	−0·1186 (5)	0·1169 (8)	4·7
O(14*B*)	0·0243 (6)	−0·4360 (5)	−0·0692 (8)	5·2
C(1)	0·3517 (3)	−0·3639 (3)	−0·1280 (4)	2·1
C(2)	0·4575 (3)	−0·3285 (3)	0·0334 (4)	2·1
C(3)	0·5074 (4)	−0·2115 (3)	0·0506 (4)	2·2
C(4)	0·3954 (4)	−0·1576 (3)	−0·0055 (4)	2·2
C(5)	0·2920 (4)	−0·2593 (3)	−0·1296 (4)	2·1
C(6)	0·2703 (4)	−0·4728 (3)	−0·1797 (4)	2·6
C(7)	0·4291 (4)	−0·3276 (3)	0·1733 (4)	2·5
C(8)	0·6087 (4)	0·1489 (3)	0·2081 (5)	3·3
C(9)	0·3599 (4)	−0·0783 (3)	0·1231 (5)	3·3
C(10)	0·1684 (4)	−0·2619 (3)	−0·1196 (5)	2·8
C(11)	0·0175 (5)	−0·6563 (5)	−0·4201 (7)	5·7
C(12)	0·3048 (4)	−0·4379 (4)	0·3631 (5)	3·9
C(13)	0·8109 (6)	0·0363 (6)	0·4871 (7)	8·9
C(14)	0·3169 (6)	0·1777 (5)	0·2607 (8)	6·8
X(15*A*)	0·1157 (4)	−0·2772 (5)	0·2283 (5)	8·7
X(15*B*)	−0·0579 (5)	−0·2827 (8)	−0·0106 (7)	11·0
O(sol)	−0·046 (3)	−0·033 (3)	−0·131 (4)	15·6
C(sol)	−0·081 (4)	0·001 (3)	−0·022 (5)	10·3

After refinement of this model for the disorder, H atoms could be located in difference Fourier maps [except around *X*(15*A*) and *X*(15*B*)], and were included as fixed contributions after idealization ($r_{C-H} = 1{\cdot}04$ Å, *B* 1·0 Å^2 larger than B_{eq} of attached C atom). The subsequent refinement converged with agreement factors *R* and *wR* of 0·056 and 0·068, and appeared satisfactory in most respects. An analysis, however, of $\sum(w|F_o| - |F_c|)^2$ [where $w = 4F_o^2/\sigma^2(F_o^2)$] as a function of $|F_o|$, $\sin\theta/\lambda$, and the Miller indices showed the agreement at low scattering angles to be worse than expected for reflections in all intensity ranges, with F_o generally larger than F_c. Examination of the crystal packing (see Fig. 3) indicated there might be space for a solvent molecule very near the origin. The two largest peaks in a difference Fourier map (0·83, 0·74 e Å^{-3}) were 1·63 Å apart and were located in this area.

Table 2. *Selected distances* (Å), *angles* (°) *and conformation angles* (°) *for PMMCP, with e.s.d.'s in parentheses*

C(1)	C(2)	1·548 (5)	C(2)	C(3)	1·545 (5)
C(3)	C(4)	1·549 (6)	C(4)	C(5)	1·583 (5)
C(5)	C(1)	1·558 (5)			
C(1)	C(6)	1·509 (5)	C(2)	C(7)	1·514 (5)
C(3)	C(8)	1·515 (5)	C(4)	C(9)	1·527 (6)
C(5)	C(10)	1·508 (6)			
C(6)	O(1)	1·478 (4)	C(7)	O(2)	1·469 (4)
C(8)	O(3)	1·474 (4)	C(9)	O(4)	1·469 (5)
C(10)	O(5)	1·466 (5)			
S(1)	O(1)	1·571 (3)	S(2)	O(2)	1·568 (3)
S(3)	O(3)	1·554 (3)	S(4)	O(4)	1·561 (3)
S(5*A*)	O(5)	1·512 (4)	S(5*B*)	O(5)	1·584 (3)
S(1)	O(6)	1·418 (3)	S(1)	O(7)	1·420 (4)
S(2)	O(8)	1·430 (3)	S(2)	O(9)	1·414 (3)
S(3)	O(10)	1·413 (4)	S(3)	O(11)	1·410 (3)
S(4)	O(12)	1·378 (4)	S(4)	O(13)	1·427 (4)
S(5*A*)	O(14*A*)	1·405 (7)	S(5*B*)	O(14*B*)	1·419 (7)
S(1)	C(11)	1·741 (5)	S(2)	C(12)	1·726 (5)
S(3)	C(13)	1·722 (6)	S(4)	C(14)	1·715 (6)
S(5*A*)	*X*(15*A*)	1·464 (5)	S(5*A*)	*X*(15*B*)	1·688 (6)
S(5*B*)	*X*(15*A*)	1·575 (5)	S(5*B*)	*X*(15*B*)	1·518 (7)
O(sol)	C(sol)	1·22 (4)			
O(sol)	O(14*A*)	2·98 (3)	O(sol)	O(11)′	2·98 (4)
C(sol)	O(14*A*)	2·80 (4)			

C(5)	C(1)	C(2)	106·5 (3)	C(1)	C(2)	C(3)	99·6 (3)
C(2)	C(3)	C(4)	106·3 (3)	C(3)	C(4)	C(5)	104·4 (3)
C(4)	C(5)	C(1)	104·6 (3)				
C(6)	C(1)	C(2)	115·6 (3)	C(6)	C(1)	C(5)	118·3 (3)
C(7)	C(2)	C(3)	112·8 (3)	C(7)	C(2)	C(1)	118·5 (3)
C(8)	C(3)	C(4)	119·7 (3)	C(8)	C(3)	C(2)	112·7 (3)
C(9)	C(4)	C(5)	114·3 (3)	C(9)	C(4)	C(3)	116·0 (3)
C(10)	C(5)	C(1)	116·2 (3)	C(10)	C(5)	C(4)	118·2 (3)
O(1)	C(6)	C(1)	105·4 (3)	O(2)	C(7)	C(2)	106·8 (3)
O(3)	C(8)	C(3)	107·7 (3)	O(4)	C(9)	C(4)	104·9 (3)
O(5)	C(10)	C(5)	110·7 (3)				
S(1)	O(1)	C(6)	119·0 (2)	S(2)	O(2)	C(7)	120·9 (2)
S(3)	O(3)	C(8)	117·9 (3)	S(4)	O(4)	C(9)	120·1 (3)
S(5*A*)	O(5)	C(10)	124·0 (3)	S(5*B*)	O(5)	C(10)	122·0 (3)

C(5)	C(1)	C(2)	C(3)	−40·2 (3)	C(6)	C(1)	C(2)	C(7)	−51·3 (5)
C(1)	C(2)	C(3)	C(4)	42·2 (3)	C(7)	C(2)	C(3)	C(8)	48·6 (5)
C(2)	C(3)	C(4)	C(5)	28·5 (3)	C(8)	C(3)	C(4)	C(9)	−30·7 (5)
C(3)	C(4)	C(5)	C(1)	2·8 (3)	C(9)	C(4)	C(5)	C(10)	6·1 (5)
C(4)	C(5)	C(1)	C(2)	23·6 (4)	C(10)	C(5)	C(1)	C(6)	23·6 (5)

Final cycles included C and O atoms of a methanol molecule disordered about the origin with a total occupancy factor of 0·256 (8) CH_3OH per PMMCP molecule. The presence of the methanol was confirmed by high-resolution ^{1}H NMR experiments; peak integrations gave an occupancy very similar to that found crystallographically. Identities of the O and C atoms were assigned on the basis of peak heights in the difference map and distance criteria. If methanol is present at a given site, then steric considerations preclude occupancy of both of the two closest O(14*A*) sites, which are related to each other by an inversion center. Fig. 3 shows that all the 'disorder' in this structure occurs in a region close to the *b* axis. It seems likely that the methylsulfonyl groups connected to C(5) and the included molecules of the methanol solvent interact through H bonding, and that they form clusters that are at least partially ordered.

Final refinement on *F* magnitudes; *R*, *wR* = 0·050, 0·053; e.s.d. in an observation of unit weight = 2·33; $w = 4I/[\sigma^2(I)]$, where $[\sigma^2(I)]$ includes a term $(0{\cdot}02I)^2$; maximum Δ/σ in last cycle 0·02; features in final difference Fourier synthesis have heights 0·58 to −1·37 e Å^{-3} and are associated with the S(5*A*)/S(5*B*), S(4) and S(3) methylsulfonyl groups. The latter two groups have higher than average displacement parameters, and the possibility of their being slightly disordered cannot be excluded.

Discussion. The molecular structure and the atom numbering scheme are shown in Fig. 1, a view of the central part of the PMMCP molecule is given in Fig. 2, and the crystal packing is displayed in Fig. 3. Atomic coordinates are listed in Table 1, and some bond lengths, bond angles, and conformation angles are given in Table 2.*

As can be seen in Fig. 2, the cyclopentane ring of the PMMCP molecule adopts an envelope conformation. The angle between the planes [C(1), C(2), C(3)] and [C(1), C(3), C(4), C(5)] is 40·7 (5)°; the maximum deviation from the latter plane is 0·018 (4) Å. This asymmetry is also reflected in the conformation angles C(*n*)—C(*n* + 1)—C(*n* + 2)—C(*n* + 3) and C(*n* + 5)—C(*n*)—C(*n* + 1)—C(*n* + 6), where *n* = 1–5 (see Table 2). The side chains attached to C(4) and C(5) are almost eclipsed. The rather long [1·583 (5) Å] C(4)—C(5) bond indicates that the eclipsed geometry causes considerable strain. Since the C(9)—O(4) and C(10)—O(5) vectors are pointed in quite different directions, the SO_2CH_3 groups, although bulky, probably do not

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* Lists of the refined atomic displacement parameters, the H-atom parameters, and the observed and calculated structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42860 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contribute substantially to this crowding (see also Fig. 3).

Most bond lengths and angles (except those involving the disordered atoms) fall within normal ranges. The C(1)—C(2)—C(3) angle at 99·6 (3)° is somewhat compressed relative to the other four C—C—C angles in the cyclopentane ring, which average 105·5 (6)°.

Nucleophilic displacement of a methylsulfonate group requires that the incoming nucleophile approach from the back side of the CH_2 group, *i.e.* at 180° from the breaking C—O bond. In each case save one (assuming that the crystal structure represents a locus of solution conformations), this requires that the trajectory of the nucleophile take it directly past an adjacent $CH_2OSO_2CH_3$ group. The steric crowding introduced in this manner greatly decreases the rate of nucleophilic attack, and abstraction of a ring proton competes successfully.

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Structure of 2-Amino-2,6-dideoxy-α-D-glucopyranose-6-sulfonic Acid

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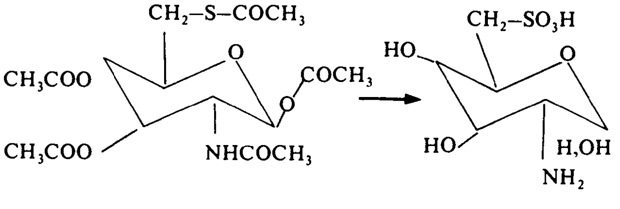
Abstract. $C_6H_{13}NO_7S$, $M_r = 243{\cdot}2$, monoclinic, $P2_1$, $a = 10{\cdot}818\ (2)$, $b = 5{\cdot}015\ (3)$, $c = 8{\cdot}838\ (2)$ Å, $\beta = 106{\cdot}77\ (2)$°, $V = 459{\cdot}1\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}76$, $D_m = 1{\cdot}74$ Mg m^{-3}, graphite-monochromated Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}35$ mm^{-1}, $F(000) = 256$, final $R = 0{\cdot}045$ for 1338 independent observed reflections (measured at 293 K). The conformation of the glucopyranose ring is a distorted chair. The N(1), O(21), O(31) and C(11) substituents are equatorial while the C(5)—O(51) bond is axial. The packing of the molecules is governed by van der Waals contacts and one H bond. The sulfonic ion is H-bonded to the amino group [N···O = 2·881 (6) Å].

Introduction. The crystal structure of 2-amino-2,6-dideoxy-α-D-glucopyranose-6-sulfonic acid has been determined as part of an investigation on conformational properties of sulfoaminosugars, which are of great interest because of their biological activity. Studies by chemical techniques have been very limited to date.

Aminosugar-sulfonic acids have been identified in hydrolysates of sulfite-treated glycoproteins and as a constituent of the cell-wall hydrolysates of *Halococcus* bacterium (Weber & Winzler, 1970; Reistad, 1977), although their structures have not been completely established. No other studies on these sulfoaminosugar derivatives have been published so far.

The compound (II) has been obtained by oxidation of 1,3,4-tri-*O*-acetyl-6-*S*-acetyl-*N*-acetyl-6-thio-*β*-D-glucosamine (I) with hydrogen peroxide (30%) in acetic acid and posterior deacetylation with Amberlite IR-120 (H^+) resin.



(I) (II)

A previous ¹H NMR study showed that in solution the α and *β* anomers appear to be in equilibrium, although the α anomer is dominant. The α anomer, which was synthesized in the Chemistry Department of

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