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Structures of Dimethyl 9α-Bromo- (I) and Dimethyl 9β-Bromo-10-oxo-8,13-epoxycedrane-12β,15-dioate (II),[*] $C_{17}H_{21}BrO_6$

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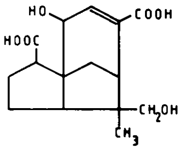
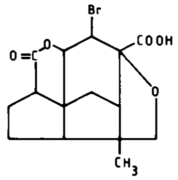
Abstract. (I): $M_r = 401\cdot26$, tetragonal, $P4_12_12$, $a = 11\cdot904\ (2)$, $c = 24\cdot599\ (5)$ Å, $V = 3486\ (1)$ Å^3, $Z = 8$, $D_x = 1\cdot53$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 23\cdot10$ cm^{-1}, $F(000) = 1648$, $T = 294$ K, $R = 0\cdot0276$ for 1899 observed reflections. (II): $M_r = 401\cdot26$, orthorhombic, $P2_12_12_1$, $a = 11\cdot286\ (1)$, $b = 11\cdot558\ (1)$, $c = 12\cdot974\ (1)$ Å, $V = 1692\cdot4\ (2)$ Å^3, $Z = 4$, $D_x = 1\cdot57$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54178$ Å, $\mu = 33\cdot43$ cm^{-1}, $F(000) = 824$, $T = 294$ K, $R = 0\cdot0466$ for 2350 observed reflections. The molecuar framework of both compounds consists of an epoxycedrane skeleton. In (I) and (II) the six-membered ring has a distorted boat conformation, two of the five-membered rings have a distorted half-chair conformation and the third five-membered ring has a distorted envelope conformation. The structural differences of (I) and (II) relate to the configuration of Br, which is α in (I) and β in (II), and the orientation of one of the methoxycarbonyl side chains.

Introduction. In the literature there exists only scarce structural information on the skeleton of cedrane. An important source of derivatives of this strained sesquiterpene is shellac, a resin of insect origin (*Laccifera lacca*). A major component of the acid fraction obtained on basic hydrolysis of shellac is shellolic acid which on chemical evidence (Yates & Field, 1960) was assigned structural formula (1). The results of this study were confirmed by a crystallographic structure analysis (Gabe, 1962) of a bromo-epoxy-shellolic γ-lactone (BSL) (formula 2). The absolute configuration of the cedrane skeleton was independently determined by the analyses of cedryl chromate (CC) (Amirthalingam, Grant & Senol, 1972) and of the α-bromonorketone of (+)-2,5-diepi-β-cedrene (DEC) (Karlsson, Pilotti & Wiehager, 1973). In the course of synthetic studies on shellolic acid derivatives, we came across two different 9-monobromo-dehydro-epoxy-shellolic acids. The present investigation was undertaken to clarify the stereochemistry of these two isomers and also to study the effect of substituting the OH group at C(10) by the more rigid oxo function upon the conformation of the cedrane skeleton.



(1)



(2)

Experimental. Crystals obtained from the Chemistry Department, University of Indore, India. Colourless crystals, 0·5 × 0·3 × 0·3 mm (I), 0·12 × 0·2 × 0·4 mm (II). Enraf–Nonius CAD-4F diffractometer. Zr-filtered Mo $K\alpha$ radiation (I), Ni-filtered Cu $K\alpha$ radiation (II). $\omega/2\theta$ scan with $\omega = (0\cdot40 + 0\cdot35\tan\theta)°$ (I) and $\omega = (0\cdot40 + 0\cdot14\tan\theta)°$ (II). Lattice parameters from 21 reflections for both structures [θ range 5·9 – 13·7° (I), 15·1 – 26·7° (II)]. 2925 intensities measured with $2\theta_{\max} = 46°$ and $0 \le h \le 13$, $0 \le k \le 13$, $0 \le l \le 27$, 1899 reflections with $I > 2\cdot5\sigma(I)$ considered observed (I); 3551 intensities, $2\theta_{\max} = 140°$, hkl and $\bar{h}\bar{k}\bar{l}$ pairs, $0 \le |h| \le 13$, $0 \le |k| \le 14$, $0 \le |l| \le 15$, 2350 intensities with $I > 3\sigma(I)$ for (II). Equivalent reflections were not merged because of the determination of the absolute configurations. Absorption correction (max. = 2·061, min. = 1·399) and isotropic extinction correction ($g = 1\cdot62 \times 10^{-6}$) were applied on (II) only. The structures were solved with Patterson and difference Fourier methods. All H atoms were located from difference syntheses and included in the refinement with fixed, isotropic thermal parameters. Anisotropic, weighted full-matrix least-squares refinement on F gave $R = 0\cdot0276$, wR $(=\sum w^{1/2}||F_o|-|F_c||/\sum w^{1/2}|F_o|) =$

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[*] Dimethyl 5α-bromo-8-methyl-4-oxoperhydro-6,8-epoxymethano-3a,7-methanoazulene-3,6-dicarboxylate and dimethyl 5β-bromo-8-methyl-4-oxoperhydro-6,8-epoxymethano-3a,7-methanoazulene-3,6-dicarboxylate, respectively.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (I) *and* (II) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Molecule (I)				
Br	0·51760 (4)	0·17861 (4)	0·82680 (2)	0·0708 (2)
O(1)	0·5309 (2)	−0·0854 (2)	0·8802 (1)	0·056 (1)
O(2)	0·7854 (2)	0·0881 (2)	0·9221 (1)	0·0508 (9)
O(3)	0·4681 (3)	−0·2796 (3)	0·7948 (1)	0·081 (1)
O(4)	0·4723 (2)	−0·1030 (3)	0·7630 (1)	0·066 (1)
O(5)	0·7108 (3)	0·3088 (2)	0·9164 (1)	0·071 (1)
O(6)	0·7789 (3)	0·3090 (2)	0·8318 (1)	0·061 (1)
C(1)	0·6860 (3)	−0·0759 (3)	0·8181 (2)	0·039 (1)
C(2)	0·6454 (4)	−0·1819 (3)	0·7867 (2)	0·047 (1)
C(3)	0·7091 (5)	−0·2795 (4)	0·8110 (2)	0·068 (2)
C(4)	0·8229 (4)	−0·2282 (3)	0·8248 (2)	0·060 (1)
C(5)	0·7906 (3)	−0·1175 (3)	0·8525 (2)	0·042 (1)
C(6)	0·8747 (3)	−0·0179 (3)	0·8543 (2)	0·042 (1)
C(7)	0·8094 (3)	0·0782 (3)	0·8257 (2)	0·043 (1)
C(8)	0·7411 (3)	0·1312 (3)	0·8723 (2)	0·041 (1)
C(9)	0·6169 (3)	0·0919 (3)	0·8745 (2)	0·044 (1)
C(10)	0·6033 (3)	−0·0305 (3)	0·8588 (1)	0·040 (1)
C(11)	0·7369 (3)	0·0181 (3)	0·7838 (2)	0·042 (1)
C(12)	0·5189 (4)	−0·1965 (4)	0·7833 (2)	0·058 (1)
C(13)	0·8876 (4)	0·0281 (4)	0·9109 (2)	0·053 (1)
C(14)	0·9885 (4)	−0·0438 (4)	0·8287 (2)	0·065 (1)
C(15)	0·7412 (4)	0·2599 (4)	0·8768 (2)	0·049 (1)
C(16)	0·3516 (5)	−0·1002 (7)	0·7608 (3)	0·097 (2)
C(17)	0·7743 (6)	0·4314 (4)	0·8317 (3)	0·086 (2)
Molecule (II)				
Br	0·8155 (1)	0·2993 (1)	0·3557 (1)	0·0501 (2)
O(1)	0·7047 (4)	0·0718 (3)	0·2973 (3)	0·043 (1)
O(2)	0·9967 (3)	0·1929 (3)	0·2081 (3)	0·035 (1)
O(3)	0·4985 (4)	−0·1049 (4)	0·2098 (4)	0·055 (1)
O(4)	0·5007 (3)	0·0756 (3)	0·1475 (4)	0·046 (1)
O(5)	1·0388 (4)	0·4103 (3)	0·1344 (4)	0·049 (1)
O(6)	0·8446 (4)	0·4378 (3)	0·1077 (4)	0·048 (1)
C(1)	0·7514 (5)	0·0551 (5)	0·1177 (4)	0·028 (1)
C(2)	0·6600 (5)	−0·0426 (5)	0·1018 (5)	0·037 (2)
C(3)	0·7285 (6)	−0·1541 (5)	0·1214 (6)	0·041 (2)
C(4)	0·8517 (6)	−0·1290 (5)	0·0768 (6)	0·042 (2)
C(5)	0·8774 (5)	−0·0078 (5)	0·1194 (5)	0·030 (2)
C(6)	0·9663 (5)	0·0746 (5)	0·0639 (4)	0·031 (2)
C(7)	0·8904 (5)	0·1854 (5)	0·0478 (4)	0·030 (2)
C(8)	0·9048 (4)	0·2499 (4)	0·1534 (5)	0·028 (1)
C(9)	0·7899 (5)	0·2401 (5)	0·2173 (4)	0·029 (1)
C(10)	0·7429 (5)	0·1163 (5)	0·2202 (5)	0·031 (2)
C(11)	0·7636 (5)	0·1423 (5)	0·0297 (5)	0·033 (2)
C(12)	0·5462 (5)	−0·0314 (6)	0·1611 (5)	0·039 (2)
C(13)	1·0586 (5)	0·1180 (5)	0·1384 (6)	0·037 (2)
C(14)	1·0175 (6)	0·0275 (6)	−0·0356 (5)	0·043 (2)
C(15)	0·9406 (5)	0·3748 (5)	0·1320 (5)	0·033 (2)
C(16)	0·3939 (7)	0·1009 (8)	0·2023 (8)	0·068 (2)
C(17)	0·8665 (8)	0·5565 (5)	0·0783 (6)	0·053 (2)

0·0289, $w = [\sigma^2(F_o) + 0{\cdot}000406F_o^2]^{-1}$, $S = 1{\cdot}22$ (I) and $R = 0{\cdot}0466$, $wR = 0{\cdot}0459$, $w = [\sigma^2(F_o) + 0{\cdot}000292F_o^2]^{-1}$, $S = 1{\cdot}25$ (II). Max. Δ/σ ratios were 0·012 (I) and 0·039 (II) for non-H atoms and 0·018 (I) and 0·090 (II) for H atoms. Final difference syntheses revealed maximal electron densities of $\pm 0{\cdot}32$ e Å^{-3} (I) and $\pm 0{\cdot}66$ e Å^{-3} (II) at about 0·9 Å from Br. The absolute configurations of (I) and (II) were ascertained by refinement of the inverted models [in $P4_32_12$ for (I)] resulting in $R = 0{\cdot}0557$, $wR = 0{\cdot}0596$ for (I) and $R = 0{\cdot}0541$, $wR = 0{\cdot}0554$ for (II). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Calculations performed with *SHELX*76 (Sheldrick, 1976) and the *EUCLID* package (illustrations and molecular geometry) (Spek, 1982) on the CDC Cyber-175 of the University of Utrecht.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters of (I) and (II) are listed in Table 1,* the molecular geometries in Table 2; a view of the molecules with the atomic numbering is presented in Figs. 1 and 2. The epoxy-cedrane moieties consist of a system of four rings: a six-membered ring *A*, two *cis*-fused five-membered rings *B* and *D* and a five-membered ring *C* containing the O bridge.

In both molecules ring *A* is a heavily distorted boat, as follows from the Cremer & Pople (1975) puckering parameters θ and φ: 77·0 (3), 305·4 (3)° (I) and 81·3 (4), 306·0 (4)° (II). Rings *C* and *D* have a half-chair conformation: $\varphi = 121{\cdot}4$ (7), 275·4 (6)° (I) and 125·2 (9), 271·0 (9)° (II), respectively. Ring *B* is a distorted envelope in (I) [$\varphi = 137{\cdot}8$ (5)°] and intermediate between half-chair and envelope in (II) [$\varphi = 134{\cdot}5$ (8)°].

Comparison with the three other cedrane derivatives mentioned in the *Introduction* (SBL, CC and DEC) shows that when the six-membered ring contains a C(sp^2) atom its conformation is also a distorted boat

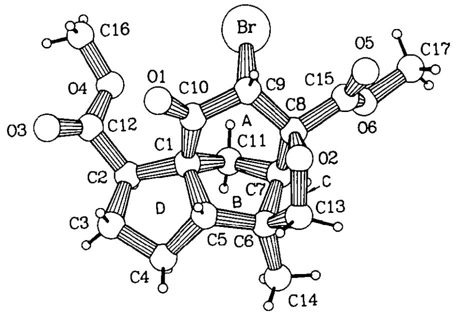

Fig. 1. A perspective view of the molecular conformation of (I) with atom numbering according to IUPAC (1979).

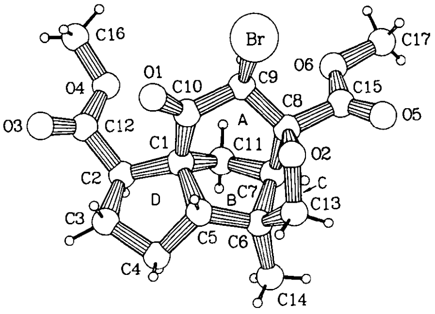

Fig. 2. A perspective view of the molecular conformation of (II) with atom numbering according to IUPAC (1979).

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom coordinates and the complete geometry data of (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39732 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å), *bond angles* (°) *and endocyclic torsion angles* (°) *for* (I) *and* (II)

	(I)	(II)		(I)	(II)		(I)	(II)
Br–C(9)	1·959 (4)	1·943 (5)	O(6)–C(17)	1·458 (5)	1·445 (7)	C(5)–C(6)	1·552 (5)	1·560 (8)
O(1)–C(10)	1·203 (4)	1·205 (7)	C(1)–C(2)	1·556 (6)	1·543 (8)	C(6)–C(7)	1·552 (5)	1·555 (8)
O(2)–C(8)	1·429 (5)	1·419 (6)	C(1)–C(5)	1·585 (6)	1·597 (8)	C(6)–C(13)	1·504 (7)	1·507 (9)
O(2)–C(13)	1·437 (5)	1·434 (7)	C(1)–C(10)	1·505 (5)	1·509 (8)	C(6)–C(14)	1·525 (6)	1·516 (8)
O(3)–C(12)	1·193 (6)	1·188 (8)	C(1)–C(11)	1·527 (6)	1·529 (8)	C(7)–C(8)	1·541 (6)	1·568 (8)
O(4)–C(12)	1·340 (6)	1·351 (8)	C(2)–C(3)	1·511 (7)	1·524 (8)	C(7)–C(11)	1·523 (6)	1·533 (8)
O(4)–C(16)	1·438 (6)	1·430 (10)	C(2)–C(12)	1·518 (7)	1·503 (8)	C(8)–C(9)	1·552 (5)	1·543 (8)
O(5)–C(15)	1·191 (5)	1·182 (7)	C(3)–C(4)	1·524 (7)	1·534 (10)	C(8)–C(15)	1·536 (6)	1·525 (7)
O(6)–C(15)	1·330 (5)	1·343 (7)	C(4)–C(5)	1·533 (5)	1·534 (8)	C(9)–C(10)	1·516 (5)	1·527 (8)
C(8)–O(2)–C(13)	109·1 (3)	108·7 (5)	C(1)–C(5)–C(6)	106·5 (3)	106·8 (5)	C(7)–C(8)–C(15)	117·5 (4)	108·6 (5)
C(12)–O(4)–C(16)	116·5 (4)	116·3 (5)	C(4)–C(5)–C(6)	120·5 (3)	120·9 (5)	C(9)–C(8)–C(15)	107·4 (3)	113·0 (4)
C(15)–O(6)–C(17)	115·3 (4)	116·0 (5)	C(5)–C(6)–C(7)	103·1 (3)	102·2 (4)	Br–C(9)–C(8)	113·3 (3)	110·2 (4)
C(2)–C(1)–C(5)	104·8 (3)	105·3 (5)	C(5)–C(6)–C(13)	111·7 (4)	110·6 (5)	Br–C(9)–C(10)	106·8 (3)	111·0 (4)
C(2)–C(1)–C(10)	114·7 (3)	114·7 (5)	C(5)–C(6)–C(14)	114·0 (3)	114·8 (5)	C(8)–C(9)–C(10)	112·5 (3)	112·0 (5)
C(2)–C(1)–C(11)	116·3 (4)	116·3 (5)	C(7)–C(6)–C(13)	101·7 (3)	101·1 (4)	O(1)–C(10)–C(1)	124·4 (3)	123·7 (5)
C(5)–C(1)–C(10)	105·7 (4)	104·9 (5)	C(7)–C(6)–C(14)	114·0 (4)	113·1 (5)	O(1)–C(10)–C(9)	119·2 (3)	123·0 (5)
C(5)–C(1)–C(11)	102·3 (3)	103·3 (4)	C(13)–C(6)–C(14)	111·4 (4)	113·7 (5)	C(1)–C(10)–C(9)	116·4 (3)	113·3 (5)
C(10)–C(1)–C(11)	111·4 (3)	110·8 (5)	C(6)–C(7)–C(8)	103·2 (4)	102·5 (4)	C(1)–C(11)–C(7)	101·3 (4)	100·6 (5)
C(1)–C(2)–C(3)	105·7 (4)	104·9 (5)	C(6)–C(7)–C(11)	104·2 (3)	105·5 (5)	O(3)–C(12)–O(4)	124·5 (4)	123·5 (5)
C(1)–C(2)–C(12)	115·4 (4)	116·1 (5)	C(8)–C(7)–C(11)	113·4 (3)	112·6 (4)	O(3)–C(12)–C(2)	125·8 (4)	126·7 (6)
C(3)–C(2)–C(12)	115·6 (4)	114·9 (5)	O(2)–C(8)–C(7)	107·2 (3)	107·0 (4)	O(4)–C(12)–C(2)	109·6 (4)	109·7 (5)
C(2)–C(3)–C(4)	103·1 (4)	103·7 (5)	O(2)–C(8)–C(9)	102·3 (3)	108·2 (5)	O(2)–C(13)–C(6)	105·8 (3)	105·6 (4)
C(3)–C(4)–C(5)	102·7 (4)	102·0 (5)	O(2)–C(8)–C(15)	107·2 (3)	109·7 (4)	O(5)–C(15)–O(6)	124·7 (4)	125·1 (5)
C(1)–C(5)–C(4)	103·2 (4)	104·0 (5)	C(7)–C(8)–C(9)	113·9 (3)	110·3 (4)	O(5)–C(15)–C(8)	123·1 (4)	124·9 (5)
						O(6)–C(15)–C(8)	112·3 (4)	110·0 (4)
C(5)–C(1)–C(2)–C(3)	10·4 (5)	13·4 (6)	C(1)–C(11)–C(7)–C(6)	47·7 (4)	47·3 (5)	C(8)–C(9)–C(10)–C(1)	−31·1 (5)	−41·3 (6)
C(1)–C(2)–C(3)–C(4)	−34·5 (5)	−36·5 (7)	C(11)–C(7)–C(6)–C(5)	−32·2 (4)	−33·6 (5)	C(9)–C(10)–C(1)–C(11)	−23·0 (5)	−19·8 (7)
C(2)–C(3)–C(4)–C(5)	45·9 (5)	45·5 (7)	C(7)–C(6)–C(5)–C(1)	5·1 (5)	7·5 (5)	C(6)–C(7)–C(8)–O(2)	13·0 (4)	11·2 (5)
C(3)–C(4)–C(5)–C(1)	−38·6 (4)	−36·1 (6)	C(10)–C(1)–C(11)–C(7)	69·5 (4)	71·4 (5)	C(7)–C(8)–O(2)–C(13)	9·9 (4)	13·3 (5)
C(4)–C(5)–C(1)–C(2)	17·4 (4)	14·3 (6)	C(1)–C(11)–C(7)–C(8)	−63·8 (4)	−63·8 (5)	C(8)–O(2)–C(13)–C(6)	−29·8 (4)	−33·8 (5)
C(6)–C(5)–C(1)–C(11)	23·4 (4)	20·7 (6)	C(11)–C(7)–C(8)–C(9)	12·6 (5)	6·7 (6)	O(2)–C(13)–C(6)–C(7)	36·4 (4)	39·2 (5)
C(5)–C(1)–C(11)–C(7)	−43·0 (4)	−40·5 (5)	C(7)–C(8)–C(9)–C(10)	36·2 (5)	47·3 (6)	C(13)–C(6)–C(7)–C(8)	−29·4 (4)	−29·7 (5)

(DEC), whereas with only C(sp^3) atoms the conformation is a distorted chair (SBL and CC). The five-membered rings display a great conformational variety. Rings *B* and *D* adopt envelopes in SBL, a strongly distorted envelope and half-chair in CC and a distorted half-chair and a half-chair in DEC respectively.

In DEC the fusion of rings *B* and *D* is *trans,* in all other compounds the fusion is *cis*. Ring *C*, present only in SBL, is intermediate between an envelope and a half-chair.

The angles between the least-squares planes of the four rings of (I) and (II) are 87·2 (2) and 87·9 (3)° for rings *A* and *B*, 86·2 (2) and 84·8 (3)° for rings *A* and *C*, 82·3 (2) and 84·3 (3)° for rings *B* and *C*, and 37·3 (3) and 35·1 (4)° for rings *B* and *D*.

The C—C bond lengths within the ring system are in the ranges 1·504 (7)–1·585 (6) Å (I) and 1·507 (9)–1·597 (8) Å (II); the shorter C—C bond in both structures is C(6)—C(13), the longer bond is that shared by the *cis*-fused rings *B* and *D*. C—C bonds involving sp^2 C(10) are relatively short: 1·516 (5), 1·505 (5) Å (I) and 1·527 (8), 1·509 (8) Å (II). The averages of the remaining C—C bonds within the rings are 1·537 (16) and 1·542 (14) Å respectively. All methoxycarbonyl groups of (I) and (II) are planar within 0·04 Å with the exception of the C(2) side chain in (I) in which C(16) deviates 0·14 Å from the least-squares plane.

The chief difference between the two cedrane derivatives is the configuration of Br, α in (I) and *β* in (II). The orientation of the C(2) side chain relative to ring *D* is nearly identical in (I) and (II), as follows from the mean difference of 4·5 (7)° of the corresponding torsion angles with respect to C(2)—C(12). However, the mean difference of the side-chain orientation at C(8) is 70 (4)°, which presumably is a consequence of the different disposition of Br in (I) and (II) (Figs. 1, 2).

The maximal differences of corresponding bond lengths and angles of (I) and (II) are 0·027 (7) Å and 8·9 (5)° for C(7)—C(8) and C(7)—C(8)—C(15) respectively. These discrepancies between (I) and (II) both involve C(8) which is bonded to the methoxycarbonyl group with the large difference of orientation. Comparison of the molecular geometry of (I) and (II) with the cedrane derivatives mentioned before reveals several discrepancies of about 0·05 Å and 6°, which are probably due to differences of conformation, ring fusion and substituents. Differences of the same order of magnitude are also present between the three referenced compounds, indicating that the geometry of the cedrane skeleton is very sensitive to structural differences.

In (I) there are two short intermolecular contacts $< 3{\cdot}3$ Å, C(2)···O(2) $(\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z)$ 3·151 (5) Å and C(12)···O(2) $(\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z)$ 3·046 (5) Å; in (II) such short contacts are not present.

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Structure of Arcaine Sulphate, $C_6H_{18}N_6^{2+}.SO_4^{2-}$

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Abstract. $M_r = 270 \cdot 3$, monoclinic, $P2_1/n$, $a = 7 \cdot 263\ (2)$, $b = 35 \cdot 140\ (9)$, $c = 15 \cdot 424\ (4)$ Å, $\beta = 101 \cdot 70\ (3)°$, $V = 3854 \cdot 8$ Å^3, $Z = 12$, $D_x = 1 \cdot 397$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1 \cdot 54178$ Å, $\mu = 2 \cdot 29$ mm^{-1}, $T = 296$ K, $F(000) = 1728$, final $R(F) = 0 \cdot 104$ for 2649 reflections. There are three amine sulphate molecules per asymmetric unit leading to interesting amine–sulphate interactions through an extensive N—H···O-type hydrogen-bond network. The molecules are in the all-*trans* configuration, except for one of the two guanidyl groups in each molecule.

Introduction. Polyamines are low-molecular-weight aliphatic, nitrogenous bases. Polyamines produced from amino acids by bacteria have pharmacological activities in animals. Studies on polyamines have thrown light on the mode of binding of polyamines to DNA (Pattabhi & Chandrasekhar, 1983; Liquori *et al.*, 1967; Woo, Seeman & Rich, 1979; Tsuboi, 1964).

In view of their importance in biological processes, the crystal structure analysis of arcaine sulphate was undertaken as part of the project on studies of polyamines and their interactions.

Experimental. Crystal $0 \cdot 3 \times 0 \cdot 2 \times 0 \cdot 2$ mm, $\theta/2\theta$ scan with line profile analysis (Grant & Gabe, 1978); Picker four-circle automatic diffractometer, graphite-monochromatized Cu $K\alpha$; 5720 independent reflections with $\theta < 60°$ giving the range of h, k and l as -8 to 7, 0 to 39 and 0 to 17 respectively; 2649 with $I_{\mathrm{net}} > 2\sigma(I_{\mathrm{net}})$; three standard reflections measured after every 100 regular reflections, no significant fluctuations observed; data corrected for direct-beam polarization (Le Page, Gabe & Calvert, 1979) and Lorentz effects; no absorption correction; unit-cell parameters determined from least-squares refinement of angle values for 42 reflections with $30 < \theta < 40°$; structure solution by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); anisotropic full-matrix refinement using F_o; 45 out of 54 H atoms (from ΔF synthesis and geometry) included only in structure factor calculations; final $R(F) = 0 \cdot 104$, $R_w(F) = 0 \cdot 062$; $w = 1/\sigma^2(F_o)$ based on counting statistics; goodness of fit $= 3 \cdot 86$; $R(\mathrm{all}) = 0 \cdot 204$, $R_w(\mathrm{all}) = 0 \cdot 064$; final difference map had no peaks $> 0 \cdot 58$ e Å^{-3}; $(\Delta/\sigma)_{\max} = 1 \cdot 0$, $(\Delta/\sigma)_{\mathrm{mean}} = 0 \cdot 2$. Repeated attempts at crystallization under various conditions failed and the determination was carried out with the available crystals, though the poor quality of these crystals restricted the accuracy of the structure. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed using the NRC-PDP-8e system of programs (Larson & Gabe, 1978) adapted for the VAX computer.

Discussion. Atomic positions and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1.‡ A stereoview of the molecule is shown in Fig. 1. Interatomic distances and angles are given in

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* DCB contribution No. 645.

† NRC contribution No. 23727.

‡ Lists of structure factors, anisotropic thermal parameters and torsion angles and details of the hydrogen-bond geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39723 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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