The crystal packing of the molecules is stabilized by two hydrogen bonds between the O atoms O(1) and O(4) bridging the pair of molecules related by a screw axis, as illustrated in Fig. 3 where the projection on the *ac* plane of the unit cell is shown. It is noteworthy that the C(11)—O(4) [1·243 (5) Å] carbonyl bond is significantly stretched with respect to the others [C(6)—O(3) 1·213 (7), C(16)—O(5) 1·213 (8), C(21)—O(6) 1·201 (11) Å], suggesting a higher basic character of the hydrogen-bonded O atom. Finally, in connection with the property of ion transport across membranes, Fig. 4 illustrates the conformational transformation from the structure of the tetraproline residue as found in this crystal structure analysis to the corresponding fragment of the poly(L,D-proline) channel structure (De Santis, Palleschi, Savino, Scipioni, Sesta & Verdini, 1984) (Fig. 4*b*) by rotating around the central peptide bond N(2)—C(11) by 180°, corresponding to the transformation of the *cis* to the *trans* conformation. At present we are trying to prepare ion complexes of the homologous compound Boc-(LPro-DPro)$_2$OCH$_3$, which should be stabilized in a conformation similar to that shown in Fig. 4(*b*) corresponding to a fragment of a helical turn of the ion-conducting structure.

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The Conformations and Relative Configurations of the *cis*- and *trans*-Fused Isomers of Perhydro-1,8a-epoxy-2-naphthyl Methanesulfonate, $C_{11}H_{18}O_4S$

By E. O. Schlemper and Glenn R. Clark

Department of Chemistry, University of Missouri, Columbia, MO 65211, *USA*

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Abstract. *cis* (1): $M_r = 246{\cdot}3$, $P2_1/n$, $a = 12{\cdot}289$ (2), $b = 5{\cdot}741$ (2), $c = 17{\cdot}293$ (3) Å, $\beta = 93{\cdot}83$ (2)°, $V = 1217{\cdot}3$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}344$ (2) g cm^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), $\mu = 2{\cdot}51$ cm^{-1}, $F(000) = 528$, $T = 295$ (1) K, $R = 0{\cdot}051$, 1243 reflections [$F_o{}^2 > 2\sigma(F_o{}^2)$]. *trans* (2): $M_r = 246{\cdot}3$, $P2_1/c$, $a = 6{\cdot}283$ (3), $b = 21{\cdot}429$ (7), $c = 9{\cdot}080$ (6) Å, $\beta = 108{\cdot}30$ (2)°, $V = 1160{\cdot}7$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}410$ (2) g cm^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), $\mu = 2{\cdot}63$ cm^{-1}, $F(000) = 528$, $T = 145$ (5) K, $R = 0{\cdot}040$, 1166 reflections [$F_o{}^2 > 2\sigma(F_o{}^2)$]. The above structures define the conformations of the *cis*- and *trans*-fused isomers. The methanesulfonate is viewed as a precursor of a carbocation in which the axis of the *p* orbital is collinear with the C(2)—O(2) bond of the methanesulfonate. The conformation of the epoxymethanesulfonate unit is then described using the convention employed for cyclopropylcarbinyl carbocations. Following this convention, the relationship

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between the epoxide and methanesulfonate units in the *cis*-fused (1) is 'bisected' while in the *trans*-fused (2) the relationship is 'perpendicular'.

Introduction. The stabilization of an adjacent carbocation by a cyclopropane (a cyclopropylcarbinyl carbocation) is strongly dependent on geometry. Calculations (Danen, 1972) correspond to rates of solvolysis of rigid cyclopropylcarbinyl halides or cyclopropylcarbinyl sulfonates in indicating that the bisected geometry ($\varphi = 0°$ following the usage of de Meijere) is stabilized with respect to the perpendicular geometry ($\varphi = 90°$) by more than 84 kJ mol^{-1} (de Meijere, 1979). A similar dependence has been predicted for the stabilization of an adjacent carbocation by an oxirane (Danen, 1972). However, experimental attempts to verify the effect have been restricted to solvolyses of flexible substrates (Whalen, 1970; Cooper, Vitullo & Whalen, 1971; Whalen & Cooper, 1978; Whalen, Brown, Ross & Russell, 1978; Santelli, 1974; Santelli & Viala, 1978; Peters, 1978). Therefore, we wished to determine the conformations of these rigid epoxymethanesulfonates so that their solvolytic behavior could be correlated with geometry.

Experimental. The compounds were prepared as described (Clark, 1984) and crystals obtained by recrystallization from benzene–hexane. D_m not determined. Enraf–Nonius CAD-4 diffractometer. 25 reflections ($15° < 2\theta < 30°$) for cell dimensions. Scattering factors including f' and f'' from *International Tables for X-ray Crystallography* (1974). Computations on PDP 11/34 computer using Enraf–Nonius *SDP* programs. Both structures from *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier methods. (1): crystal ~0·15 × 0·20 × 0·30 mm; no absorption correction (ψ scans indicated less than 5% range); max. $\sin\theta/\lambda = 0{\cdot}538$ Å^{-1}; hkl and $hk\bar{l}$ for $2\theta = 2$–$45°$, $h\bar{k}l$ and $h\bar{k}\bar{l}$ for $2\theta = 2$–$30°$; three intensity standards after every 7200 s of X-ray exposure, ~40% decrease in intensity (correction applied); $R_{\rm int} = 0{\cdot}055$; 1586 reflections independent [343 with $F_o^2 < 2\sigma(F_o^2)$ considered unobserved]; function minimized $\sum w(|F_o| - |F_c|)^2$; H atoms from difference Fourier and chemical reasonability (not refined); 145 variables (including x,y,z, 6 β's for nonhydrogen atoms); $R = 0{\cdot}051$, $R_w = 0{\cdot}083$, $S = 2{\cdot}43$; $w^{-1} = [\sigma^2_{\rm counting} + (0{\cdot}050F_o^2)^2]/4F_o^2$; full matrix; max. $\Delta/\sigma = 0{\cdot}01$; max. $\Delta\rho$ on final difference Fourier synthesis 0·5 e Å^{-3}. (2): crystal ~0·20 × 0·20 × 0·25 mm; no absorption correction (ψ scans indicated less than 5% range); max. $\sin\theta/\lambda = 0{\cdot}538$ Å^{-1}; hkl and $hk\bar{l}$ for $2\theta = 2$–$45°$, $\bar{h}kl$ and $\bar{h}k\bar{l}$ for $2\theta = 2$–$15°$; three intensity standards after every 7200 s of X-ray exposure, ~10% decrease in intensity (correction applied); $R_{\rm int} = 0{\cdot}051$; 1502 independent reflections [336 with $F_o^2 < 2\sigma(F_o^2)$ considered unobserved]; $\sum w(|F_o| - |F_c|)^2$ minimized in full-matrix refinement; H atoms from difference Fourier and chemical reasonability (refined); 217 variables (x,y,z, 6 β's nonhydrogen; x,y,z, B for H); $R = 0{\cdot}040$, $R_w = 0{\cdot}050$, $S = 1{\cdot}48$; $w^{-1} = [\sigma^2_{\rm counting} + (0{\cdot}050F_o^2)^2]/4F_o^2$; max. $\Delta/\sigma = 0{\cdot}04$; max. $\Delta\rho$ on final difference Fourier synthesis 0·4 e Å^{-3}.

Table 1. *Positional parameters, equivalent isotropic thermal parameters and their estimated standard deviations for compound* (1)

$B_{\rm eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	$B_{\rm eq}$(Å^2)
S	0·08114 (9)	0·0238 (2)	0·18985 (5)	4·00 (2)
O(1)	0·0794 (3)	0·1535 (7)	0·2586 (1)	6·35 (8)
O(2)	0·1812 (2)	0·1191 (6)	0·1495 (1)	4·56 (6)
O(3)	−0·0120 (3)	0·0214 (7)	0·1368 (2)	6·03 (9)
O(4)	0·1732 (3)	0·4838 (5)	0·0446 (1)	4·84 (7)
C(1)	0·1479 (3)	0·2512 (8)	0·0185 (2)	3·77 (8)
C(2)	0·1976 (4)	0·0617 (8)	0·0678 (2)	4·19 (9)
C(3)	0·3175 (4)	0·0262 (9)	0·0623 (2)	5·0 (1)
C(4)	0·3777 (3)	0·251 (1)	0·0535 (2)	4·9 (1)
C(5)	0·3387 (4)	0·3830 (8)	−0·0204 (2)	4·38 (9)
C(6)	0·3788 (4)	0·276 (1)	−0·0949 (2)	5·9 (1)
C(7)	0·3315 (4)	0·401 (1)	−0·1662 (2)	7·2 (1)
C(8)	0·2109 (5)	0·416 (1)	−0·1693 (2)	6·8 (1)
C(9)	0·1669 (5)	0·526 (1)	−0·0978 (3)	6·3 (1)
C(10)	0·2169 (3)	0·4066 (8)	−0·0260 (2)	3·95 (9)
C(11)	0·1174 (4)	−0·2604 (9)	0·2128 (2)	4·9 (1)

Table 2. *Positional parameters, equivalent isotropic thermal parameters and their estimated standard deviations for compound* (2)

$B_{\rm eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	$B_{\rm eq}$(Å^2)
S	0·1836 (1)	0·1464 (4)	0·73987 (9)	1·58 (2)
O(1)	0·2499 (4)	0·1910 (1)	0·8610 (2)	2·00 (5)
O(2)	0·3208 (3)	0·0857 (1)	0·8101 (2)	1·74 (5)
O(3)	−0·0471 (3)	0·1308 (1)	0·6756 (2)	1·99 (5)
O(4)	0·0034 (3)	−0·0595 (1)	0·6748 (2)	1·51 (4)
C(1)	0·1263 (5)	−0·0132 (1)	0·7819 (4)	1·49 (7)
C(2)	0·2703 (5)	0·0278 (1)	0·7176 (3)	1·45 (7)
C(3)	0·4928 (5)	−0·0013 (2)	0·7265 (4)	1·66 (7)
C(4)	0·4603 (5)	−0·0693 (2)	0·6736 (3)	1·53 (7)
C(5)	0·3786 (5)	−0·1083 (2)	0·7854 (3)	1·46 (7)
C(6)	0·3261 (5)	−0·1757 (2)	0·7318 (4)	1·72 (7)
C(7)	0·2425 (5)	−0·2133 (2)	0·8450 (4)	2·24 (8)
C(8)	0·0418 (5)	−0·1823 (2)	0·8746 (4)	2·13 (7)
C(9)	0·0897 (5)	−0·1149 (2)	0·9270 (4)	1·96 (7)
C(10)	0·1780 (5)	−0·0794 (1)	0·8157 (3)	1·41 (7)
C(11)	0·2933 (6)	0·1668 (2)	0·5917 (4)	2·25 (8)

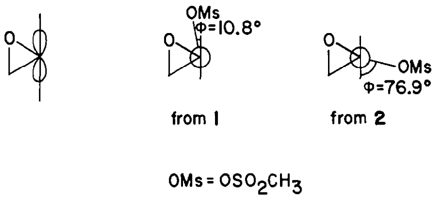

Fig. 1. Definition of φ and magnitude of φ in compounds (1) and (2).

Table 3. *Bond distances* (Å) *and angles* (°) *in compounds* (1) *and* (2) *with e.s.d.'s in parentheses*

	(1)	(2)		(1)	(2)		(1)	(2)		(1)	(2)
S–O(1)	1·404 (2)	1·417 (2)	O(4)–C(10)	1·437 (3)	1·463 (3)	C(9)–C(8)	1·521 (5)	1·521 (4)	C(5)–C(4)	1·536 (4)	1·523 (4)
S–O(2)	1·553 (2)	1·581 (2)	O(4)–C(1)	1·437 (4)	1·433 (3)	C(8)–C(7)	1·482 (6)	1·522 (4)	C(4)–C(3)	1·498 (5)	1·528 (4)
S–O(3)	1·418 (2)	1·422 (2)	C(10)–C(9)	1·512 (5)	1·504 (4)	C(7)–C(6)	1·511 (6)	1·523 (4)	C(3)–C(2)	1·497 (5)	1·510 (4)
S–C(11)	1·731 (4)	1·749 (3)	C(10)–C(5)	1·500 (4)	1·505 (4)	C(6)–C(5)	1·537 (4)	1·527 (4)	C(2)–C(1)	1·488 (4)	1·505 (4)
O(2)–C(2)	1·478 (3)	1·476 (3)	C(10)–C(1)	1·481 (4)	1·465 (4)						

	(1)	(2)		(1)	(2)		(1)	(2)
O(1)–S–O(2)	104·5 (1)	104·6 (1)	O(4)–C(10)–C(1)	59·0 (2)	58·6 (2)	C(6)–C(5)–C(4)	113·6 (3)	113·0 (2)
O(1)–S–O(3)	119·7 (2)	119·4 (1)	C(9)–C(10)–C(5)	116·3 (3)	114·9 (2)	C(5)–C(4)–C(3)	112·4 (3)	110·7 (2)
O(1)–S–C(11)	108·9 (1)	109·8 (2)	C(9)–C(10)–C(1)	118·9 (3)	121·7 (2)	C(4)–C(3)–C(2)	112·6 (3)	110·3 (3)
O(2)–S–O(3)	110·0 (1)	109·1 (1)	C(5)–C(10)–C(1)	121·0 (3)	120·3 (2)	O(2)–C(2)–C(3)	106·8 (2)	106·7 (2)
O(2)–S–C(11)	103·6 (1)	102·7 (1)	C(10)–C(9)–C(8)	109·4 (3)	110·4 (3)	O(2)–C(2)–C(1)	107·9 (2)	108·5 (2)
O(3)–S–C(11)	108·9 (2)	109·9 (2)	C(9)–C(8)–C(7)	113·8 (3)	112·1 (3)	C(3)–C(2)–C(1)	115·6 (2)	113·4 (3)
S–O(2)–C(2)	120·9 (2)	118·0 (2)	C(8)–C(7)–C(6)	112·7 (3)	111·7 (3)	O(4)–C(1)–C(10)	59·0 (2)	60·6 (2)
C(10)–O(4)–C(1)	62·0 (2)	60·8 (2)	C(7)–C(6)–C(5)	111·5 (4)	111·7 (3)	O(4)–C(1)–C(2)	115·3 (2)	113·7 (2)
O(4)–C(10)–C(9)	113·8 (3)	113·7 (2)	C(10)–C(5)–C(6)	110·9 (2)	109·8 (2)	C(10)–C(1)–C(2)	120·7 (3)	121·7 (2)
O(4)–C(10)–C(5)	113·6 (2)	113·6 (2)	C(10)–C(5)–C(4)	110·6 (2)	111·9 (2)			

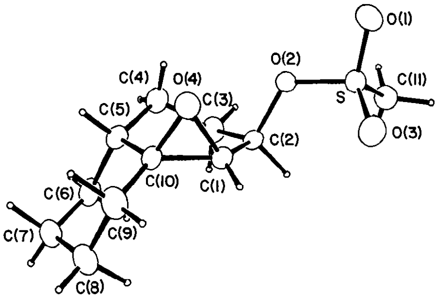

Fig. 2. Perspective view and atom labeling for compound (1).

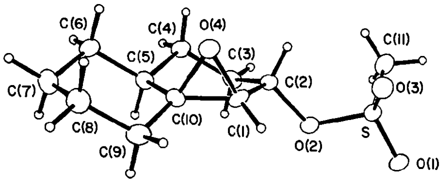

Fig. 3. Perspective view and atom labeling for compound (2).

Discussion. The final atomic parameters are given in Tables 1 and 2.*

The structure of (1) is shown in Fig. 2. The important bond distances and angles are given in Table 3. The saturated six-membered ring is in the chair conformation, while the epoxide-containing ring is a half-chair. The bond distances and angles are normal. The dihedral angle between the plane containing the midpoint between C(10) and O(4), C(1), and C(2), and the plane containing C(1), C(2), and O(2) is 79·2°. The axis of the oxirane Walsh *p* orbital at C(1) (Fig. 1) is perpendicular to the line containing C(1) and bisecting the C(10)–O(4) bond, so $\varphi = 90° - 79{\cdot}2° = 10{\cdot}8°$. Therefore, (1) will lead to an approximately 'bisected' ($\varphi = 0°$) carbocation upon S_N1-type ionization if the axis of the resulting carbocation *p* orbital is collinear with the C(2)–O(2) bond in (1).

The structure of (2) is shown in Fig. 3. The important bond distances and angles are given in Table 3. The saturated six-membered ring is in a chair conformation, while the expoxide-containing ring is a half-chair. The bond distances and angles are normal. The methanesulfonate units in (1) and (2) are in identical conformations if one takes into account that the compounds have the opposite configuration at C(2). The dihedral angle between the plane containing the midpoint between C(10) and O(4), C(1), and C(2), and the plane containing C(1), C(2), and O(2), is −166·9°. The axis of the oxirane Walsh *p* orbital at C(1) is perpendicular to the line containing C(1) and bisecting the C(10)–O(4) bond, so $\varphi = 166{\cdot}9° - 90° = 76{\cdot}9°$. Therefore, (2) will lead to an approximately 'perpendicular' ($\varphi = 90°$) carbocation upon S_N1-type ionization if the axis of the resulting carbocation *p* orbital is collinear with the C(2)–O(2) bond in (2).

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* Lists of structure factors, H-atom parameters, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39668 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.