verständlich, dass in Hexahydropyridazinen, die an den benachbarten $sp^3$-hybridisierten N-Atomen nur H oder organische einfach gebundene Reste tragen, deutlich grössere N—N-Bindungsabstände von 1,450 (3) bis 1,486 (4) Å gefunden wurden (Katritzky, Baker, Camalli, Spagna & Vaciago, 1980, und die dort zitierte Literatur). Die N—N-Abstände in der kürzlich von uns bestimmten Struktur des Bis(hexahydropyridazino)-thiophosphorsäure-*O*-phenylesters von im Mittel 1,437 (4) Å (Engelhardt & Stromburg, 1984) fügen sich gut in dieses Bild, da hier nur jeweils eines der benachbarten Stickstoff-Atome durch Bindungswechselwirkung zum Phosphor $sp^2$-hybridisiert, das andere aber $sp^3$-hybridisiert ist.

Die Packungen der Moleküle in den Elementarzellen von *cis*- und *trans*-Isomerem (Fig. 3 und 4) weisen keine bemerkenswerten Besonderheiten auf. Besonders kurze intermolekulare Kontaktabstände treten in beiden Strukturen nicht auf.

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# Structure and Molecular Conformation of *tert*-Butoxycarbonyl-L-prolyl-D-prolyl-L-prolyl-D-proline, $C_{25}H_{38}N_4O_7$, a Tetraproline Derivative with Alternating Configurations

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**Abstract.** Boc-(LPro-DPro)$_2$OH, $M_r = 506{\cdot}6$, monoclinic, $P2_1$, $a = 14{\cdot}123\ (5)$, $b = 9{\cdot}048\ (2)$, $c = 11{\cdot}900\ (3)$ Å, $\beta = 119{\cdot}58\ (2)°$, $Z = 2$, $V = 1322{\cdot}4\ (7)$ Å$^3$, $D_x = 1{\cdot}27$, $D_m = 1{\cdot}27$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$(Mo $K\alpha$) = 0·1004 mm$^{-1}$, $F(000) = 544$, room temperature, final $R = 0{\cdot}054$ for 2513 observed reflections. The molecular structure is characterized by two conformationally quasi-equivalent dipeptide halves with an overall left-handed screw trend. This structure is practically identical to that predicted by minimization of the conformational energy in terms of the torsional angles, and closely related to the active conformation of the homologous polymer, behaving as a channel conductor across membranes.

**Introduction.** Some naturally occurring peptide and depsipeptide antibiotics are known to induce permeoselective ionic exchange across biological and synthetic membranes. Typical examples are gramicidin A, a pentadecapeptide which makes channels across biological membranes, behaving as a true ion conductor, and valinomycin, a cyclic dodecadepsipeptide which is

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a highly selective shuttle carrier of alkali ions across the lipidic phase. Both classes of molecules have the peculiarity of regular enantiomeric sequences.

Theoretical investigations (De Santis, Morosetti & Rizzo, 1974) have shown that such a singular feature, since the conformational equivalence is assumed, results in the stabilization of cyclic structures with $S_n$ point symmetry ($n = 6, 8, 10 \ldots$) characterized by an ion complexing cavity, or, when the strict equivalence is slightly relaxed, in flat helical structures with inner-channel dimensions suitable for the ion passage. Both channels and carriers are generally characterized by an arrangement of the polar groups in the inner regions whereas the side chains point to the outer regions of the molecule. Thus the necessary condition for their activity is the presence of amino and/or hydroxy acids with hydrophobic character which provide the 'solubility' in the lipid phase.

Ten years ago we predicted (De Santis, Morosetti & Rizzo, 1974) the carrier behaviour of *cyclo*-(L,D-hexaproline) as well as the channel activity of the homologous polyproline with alternating L and D configurations.

Only more recently have we synthetized poly-(L,D-proline) and found that, at a concentration as low as 0·001 p.p.m., it is capable of inducing ion conductance in bilayer membranes with a channel mechanism as indicated by the typical regular conductance fluctuations monitoring the elemental conductance events of single molecules (De Santis, Palleschi, Savino, Scipioni, Sesta & Verdini, 1984). With the aim of providing useful conformational and structural information on this problem, we carried out the crystal structure analysis of the tetraproline derivative Boc-(LPro-DPro)$_2$OH, an intermediate of the polymerization reaction. At the same time, we carried out its conformational analysis by minimization of the conformational energy in terms of the angles of rotation about the skeleton bonds in order to evaluate the thermodynamic stability of the different conformations. The final experimental X-ray and theoretical lowest-energy structures proved to be very similar and convertible into a fragment of the channel structure by changing the central peptide from the *cis* into the *trans* conformation.

**Experimental.** Prismatic colourless crystals from *n*-hexane–ethyl acetate mixed solvent. Crystal 0·5 × 0·5 × 0·25 mm. Cell parameters refined by least squares from the angular positions of 15 reflections ($2\theta$ range 11–26°). Automatic four-circle Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Relevant data-collection details are given in Table 1. In the estimation of $\sigma(I)$ the formula $\sigma(I) = (T+p^2I^2)^{1/2}$ (McCandlish, Stout & Andrews, 1975) was used, with $p = 0{\cdot}015$ ($T$ = total counts, $I$ = net counts). Lorentz and polarization corrections applied to the values of $I$ and $\sigma(I)$. Anomalous

Table 1. *Data-collection details*

| | | | |
|---|---|---|---|
| Radiation | Graphite-monochromatized Mo $K_\alpha$ | Check reflections | Three every 100 reflections: no decay |
| Data range ($2\theta$)(°) | 3·0–60 | Reflections measured | 4310 |
| Range of indices | $h$ 0.18; $k$ 0.12: $l$ −15.14 | Unique reflections | 4032 |
| Scan mode | $\theta/2\theta$ | $R_{int}$ (%), from merging equivalent reflections | 2·50 |
| Scan speed (°mm$^{-1}$) | 1·2–29·3 | Observed reflections $\|I > 3\sigma(I)\|$ | 2513 |
| Scan range (°) | ±1·2 | | |
| Background counts | Half the scan time | | |

diffraction effects were evaluated by changing the sign of all coordinates, but no appreciable improvements in agreement were obtained.

Structure solved by direct methods with *MULTAN*80 (Main *et al.*, 1980). The $E$ map computed with the phases from the set with the highest figure of merit showed the positions of 23 of the 36 non-H atoms. The remaining atoms were located by iterated Fourier syntheses. Block-diagonal least-squares refinement; $\sum w(|F_o|-|F_c|)^2$ minimized, $w = \sin\theta/\lambda$. Isotropic refinement converged at $R = 0{\cdot}14$. At this stage all the H atoms, except those linked to the O atoms, were positioned geometrically and readjusted after each cycle. Refinement was continued allowing all the non-H atoms to vibrate anisotropically; H atoms were assigned the thermal parameters obtained in the final isotropic refinement of the atoms to which they are bonded. During the refinement difference-Fourier maps, calculated only with the contributions of the non-H atoms, revealed successively the positions of some H atoms. These contributions were included in the subsequent cycles, replacing the corresponding geometrically positioned H atoms. Convergence was reached at $R = 0{\cdot}054$, $R_w = 0{\cdot}064$ and $S = 2{\cdot}37$, when 17 H atoms were located from Fourier maps. $(\Delta/\sigma)_{max} = 0{\cdot}5$ in the final refinement cycle. The final difference-Fourier map, with a root-mean-square deviation of electron density of 0·06, showed values not exceeding 0·2 e Å$^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used were *MULTAN*80 on the Univac 1110 computer of the University of Rome and *CAOS* (Cerrini & Spagna, 1977) on the HP 21MX minicomputer of the CNR Computing Centre in Montelibretti.

**Discussion.** The final fractional coordinates with e.s.d.'s are listed in Table 2;* Fig. 1 gives a projection of the structure and the numbering of the atoms.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39725 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Conformational analysis*

It is a peculiar feature of the proline residue in a peptide chain that it is conformationally constrained by the presence of the pyrrolidine ring which allows only a limited dispersion of the torsional angle $\varphi$ around the $C_\alpha$—N bond in connection with the different ring puckers, and severely limits the sterically allowed conformations of the adjacent residue.

In fact, only two types of local conformations are sterically allowed for a proline residue when followed by another proline residue; they are characterized by the *cis* or *trans* conformations of the peptide bond where the pair of torsional angles $\varphi$ and $\psi$ around the $C_\alpha$—N and $C_\alpha$—C bonds is restricted about −70 and 150° respectively for the L stereoisomer (70 and −150° for the D stereoisomer), according to both X-ray crystal structure analyses of proline-containing oligopeptides (Benedetti *et al.*, 1983) and conformational-energy calculations (Ascoli, De Santis, Palleschi & Rizzo, 1975).

In order to test the reliability of the theoretical conformational analysis which we have recently tried on the homologous poly(L,D-proline), a synthetic polypeptide behaving as a channel conductor across bilayer membranes, we have carried out conformational-energy calculations of the possible most stable conformers of Boc-(LPro-DPro)$_2$OH.

The conformational energy was evaluated using our best set of semi-empirical van der Waals potential functions and torsional contributions adopted with success in the conformational analysis of synthetic polymers (De Santis, Giglio, Liquori & Ripamonti, 1963), polypeptides (De Santis, Giglio, Liquori & Ripamonti, 1965) and polynucleotides (Calascibetta, De Santis, Dentini & Morosetti, 1975; De Santis, Morosetti, Palleschi & Savino, 1981) and in predicting the structures of complex peptides such as gramicidin S (De Santis & Liquori, 1971) and actinomycin (De Santis, Rizzo & Ughetto, 1972).

Table 2. *Fractional coordinates and equivalent isotropic thermal factors of the non-hydrogen atoms, with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | *x* | *y* | *z* | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 0·3909 (3) | −0·0186 (5) | 0·6487 (4) | 5·7 (2) |
| O(2) | 0·3120 (4) | −0·0655 (5) | 0·7688 (4) | 6·2 (2) |
| O(3) | 0·3867 (4) | 0·2650 (6) | 0·8166 (5) | 4·5 (2) |
| O(4) | 0·4417 (4) | 0·3048 (5) | 1·2071 (4) | 5·2 (2) |
| O(5) | 0·1460 (5) | 0·3246 | 1·0518 (6) | 4·8 (3) |
| O(6) | 0·0839 (5) | 0·5411 (12) | 1·2973 (7) | 6·5 (4) |
| O(7) | 0·2306 (4) | 0·3894 (8) | 1·3601 (6) | 4·5 (2) |
| N(1) | 0·2096 (3) | 0·2168 (5) | 0·6863 (3) | 3·9 (1) |
| N(2) | 0·3480 (3) | 0·3882 (5) | 1·0028 (4) | 3·5 (1) |
| N(3) | 0·2504 (2) | 0·1237 (4) | 1·1337 (3) | 3·2 (1) |
| N(4) | 0·0662 (3) | 0·3100 (5) | 1·2205 (4) | 3·0 (1) |
| C(1) | 0·3172 (5) | 0·0019 (6) | 0·6847 (6) | 4·4 (2) |
| C(2) | 0·2334 (6) | 0·1194 (7) | 0·6047 (7) | 3·9 (3) |
| C(3) | 0·1217 (5) | 0·0503 (5) | 0·5148 (5) | 6·3 (2) |
| C(4) | 0·0425 (3) | 0·1616 (4) | 0·5094 (3) | 8·8 (1) |
| C(5) | 0·0930 (3) | 0·2272 (5) | 0·6415 (4) | 5·9 (1) |
| C(6) | 0·2927 (3) | 0·2821 (5) | 0·7900 (3) | 3·4 (1) |
| C(7) | 0·2601 (4) | 0·3828 (5) | 0·8690 (4) | 3·7 (1) |
| C(8) | 0·2506 (6) | 0·5426 (6) | 0·8240 (8) | 5·4 (3) |
| C(9) | 0·3613 (7) | 0·6044 (9) | 0·9029 (8) | 6·6 (3) |
| C(10) | 0·4106 (4) | 0·5270 (6) | 1·0343 (5) | 4·7 (2) |
| C(11) | 0·3685 (3) | 0·2878 (4) | 1·0933 (3) | 3·5 (1) |
| C(12) | 0·3038 (3) | 0·1450 (5) | 1·0554 (4) | 3·8 (1) |
| C(13) | 0·3800 (3) | 0·0114 (4) | 1·0930 (3) | 6·9 (1) |
| C(14) | 0·3475 (3) | −0·0934 (5) | 1·1585 (4) | 7·9 (1) |
| C(15) | 0·2897 (4) | −0·0111 (7) | 1·2136 (5) | 4·5 (2) |
| C(16) | 0·1727 (4) | 0·2182 (8) | 1·1230 (5) | 3·4 (2) |
| C(17) | 0·1146 (3) | 0·1797 (7) | 1·1993 (5) | 3·6 (2) |
| C(18) | 0·0159 (3) | 0·0809 (5) | 1·1203 (4) | 5·2 (1) |
| C(19) | −0·0733 (4) | 0·1922 (6) | 1·0387 (5) | 5·7 (2) |
| C(20) | −0·0516 (3) | 0·3203 (5) | 1·1308 (5) | 4·9 (2) |
| C(21) | 0·1237 (2) | 0·4257 (4) | 1·2923 (3) | 4·2 (1) |
| C(22) | 0·3156 (4) | 0·5003 (7) | 1·4296 (5) | 5·1 (2) |
| C(23) | 0·4174 (5) | 0·4055 (11) | 1·4798 (6) | 7·6 (3) |
| C(24) | 0·3096 (6) | 0·6137 (10) | 1·3355 (7) | 8·4 (4) |
| C(25) | 0·3032 (7) | 0·5632 (9) | 1·5402 (7) | 7·9 (3) |

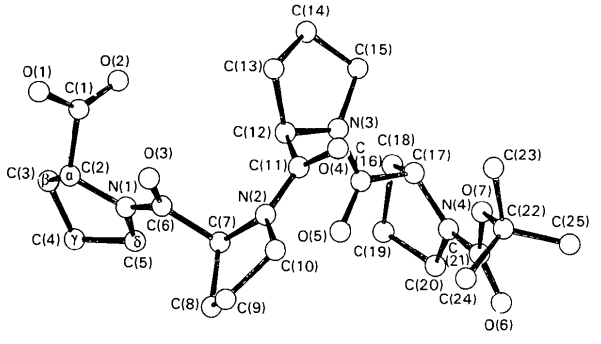


Fig. 1. Molecular structure of Boc-(LPro-DPro)$_2$OH and numbering of the atoms.

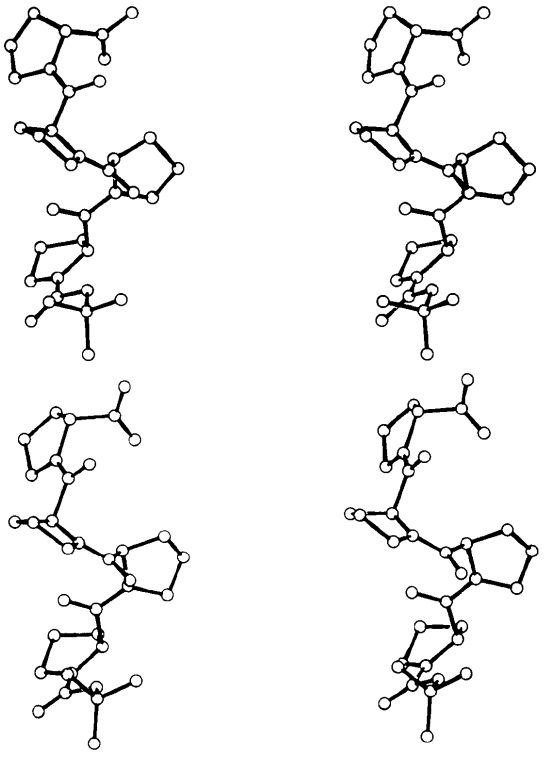

Fig. 2. Stereoviews of the X-ray (experimental, bottom) and the most stable (theoretical, top) conformations of Boc-(LPro-DPro)$_2$OH.

Table 3. *Geometrical backbone parameters*

| | Bond length (Å) | Bond angle (°) | Torsional angle (°) [theoretical] |
|---|---|---|---|
| O(1) | | | |
| C(1) | 1·320 (7) | 112·9 (6) | −137·5 (4) [−131·3] |
| C(2) | 1·525 (8) | 111·5 (7) | 51·9 (6) [61·3] |
| N(1) | 1·468 (8) | 119·2 (6) | 179·6 (4) [178·8] |
| C(6) | 1·349 (8) | 115·6 (4) | 152·7 (4) [165·8] |
| C(7) | 1·534 (6) | 109·8 (5) | −80·9 (7) [−61·5] |
| N(2) | 1·458 (5) | 126·2 (5) | 6·6 (8) [−15·2] |
| C(11) | 1·327 (6) | 118·9 (5) | −124·2 (5) [−123·0] |
| C(12) | 1·518 (6) | 110·2 (4) | 64·9 (4) [61·1] |
| N(3) | 1·471 (5) | 120·3 (5) | 174·8 (3) [179·6] |
| C(16) | 1·348 (8) | 116·7 (6) | 158·1 (3) [161·5] |
| C(17) | 1·535 (7) | 110·8 (5) | −64·8 (6) [−62·6] |
| N(4) | 1·445 (7) | 123·9 (5) | −11·9 (8) [−8·7] |
| C(21) | 1·342 (7) | 109·7 (5) | |
| O(7) | 1·355 (9) | | |

Thus, the eight possible starting conformations of Boc-(LPro-DPro)$_2$OH were generated (the conformation of the terminal *tert*-butoxycarbonyl group was fixed as generally found in all the homologous compounds). These conformations were optimized using an energy-steepest-descent program which also takes into account the electrostatic contributions to the conformational energy.

The final most stable conformation is compared with the X-ray structure in Fig. 2 which gives stereoviews on the plane of the largest principal axes of the second moments of the atom distributions: the structures are quite similar, and the corresponding torsional angles of the peptide chain are reported in Table 3.

Incidentally, it is of some interest that the largest principal axis practically coincides with the crystal axis *c*, suggesting a simple model of crystal packing corresponding to the close packing of the ellipsoids representative of the second moment of the atom distribution.

The molecular structure of Boc-(LPro-DPro)$_2$OH is characterized by quasi-equivalent alternating *cis* and *trans* conformations as can be deduced from Table 3 where the geometrical parameters of the backbone are listed. As a consequence, this induces a conformational splitting of the torsional angles around the C(2)—N(1) and C(7)—N(2) bonds [51·9 (6) and −80·9 (7)° respectively] which assume the same absolute value of 64·9 (5)° in the case of the other two proline residues. In fact, in the former cases this situation seems to arise from the need to avoid competitive closer contacts between the H atom H(C7) and those bonded to C(5) and C(12) [2·24 (7) and 1·95 (7) Å respectively].

Such a competition is absent for the equivalent H atom H(C15) which forms a good contact with H(C17) [2·42 (5) Å] lacking the $C_\alpha$—H atom equivalent to H(C12). It is noteworthy that conformational calculations carried out on the homologous polymer under the condition of conformational equivalence between all the diprolyl repeating units give similar values of conformational splitting (De Santis *et al.*, to be published).

The regular alternation of *cis* and *trans* conformations influences the puckering of the pyrrolidine rings which is characterized by alternating conformations of $C_\gamma$-*exo* and $C_\beta$-*exo* types. In fact, atoms C(4), C(8), C(14) and C(18) are out of the best plane of the other four atoms, for each pyrrolidine ring, by 0·508 (6), 0·478 (7), 0·348 (9) and 0·583 (7) Å respectively, against an average distance for the other atoms of 0·02 (2) Å. The conformational quasi-equivalence of the diprolyl units results in a helical structure characterized by a left-handed screw which indicates an asymmetric influence from the termini, probably from the *tert*-butoxycarbonyl end which in all the homologous compounds was found adjacent to a *cis* peptide bond. How far such a conformational effect is transmitted is an interesting question. In fact, both right and left-handed helices are expected when the peptide chain length increases.

The regular alternation of *cis* and *trans* conformations for the peptide bonds justifies the presence in the NMR proton spectrum of the polymer of two equivalent signals assignable to the $C_\alpha$H protons adjacent to the *cis* and *trans* conformations of the peptide bond (P. De Santis *et al.*, to be published).

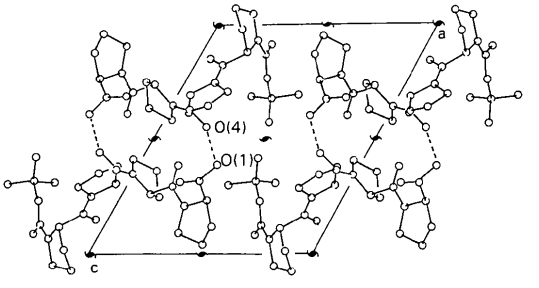


Fig. 3. Crystal packing of Boc-(LPro-DPro)$_2$OH.

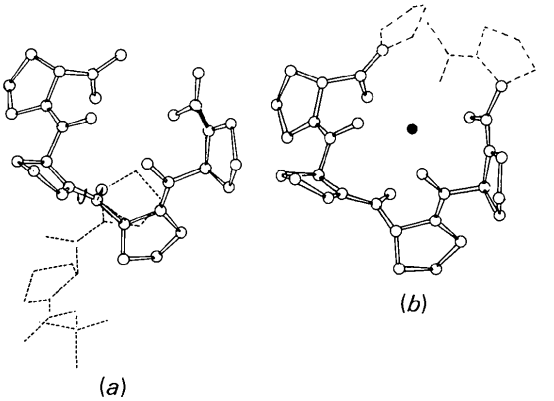


Fig. 4. (*a*) X-ray structure of the tetraprolyl fragment of Boc-(LPro-DPro)$_2$OH after the *cis*→*trans* conformation change of the central peptide bond, compared with (*b*) the channel conformation of poly(L,D-proline).

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, $C_{11}H_{18}O_4S$


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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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