

- HIRSHFELD, F. L. (1963). *J. Chem. Soc.* p. 2126.  
 HIRSHFELD, F. L. & RABINOVICH, D. (1966). *Acta Cryst.* **20**, 146.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 KAY, M. I., OKAYA, Y. & COX, D. E. (1971). *Acta Cryst.* **B27**, 26.  
 McIVER, J. & KOMARNICKI, A. (1971). *Chem. Phys. Letters*. In the press.  
 NORMAN, N. & POST, B. (1961). *Acta Cryst.* **14**, 503.  
 PAWLEY, G. S. (1965). *Acta Cryst.* **18**, 560.  
 ROBERTSON, J. M., SHEARER, H. M. M., SIM, G. A. & WATSON, D. G. (1962). *Acta Cryst.* **15**, 1.  
 SHIMANOUCI, H., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1966). *Bull. Chem. Soc. Japan*. **39**, 2322.  
 WHITTAKER, E. C. & ROBINSON, G. (1944). *The Calculus of Observations*, 4th ed., p. 303 London: Blackie.  
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.

*Acta Cryst.* (1972). **B28**, 1806

## Crystal and Molecular Structure of Racemic 2-*exo*-Norbornanol *p*-Toluenesulfonate: A Case of Enantiomeric Disorder

BY C. ALTONA\* AND M. SUNDARALINGAM†

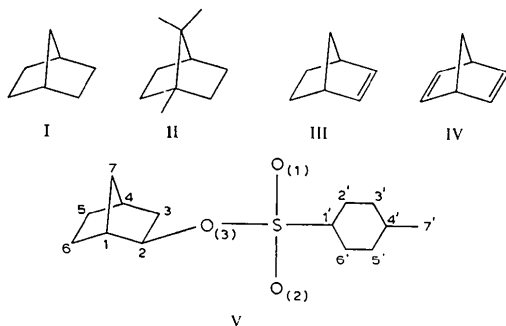
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

(Received 27 August 1971)

The tosyl ester of racemic 2-*exo*-norbornanol (bicyclo[2.2.1]heptane-2-*exo*-ol *p*-toluenesulfonate), m.p. 54.5°, crystallizes in the triclinic system:  $a = 6.181$ ,  $b = 11.092$ ,  $c = 11.060$  Å,  $\alpha = 111.4$ ,  $\beta = 103.6$ ,  $\gamma = 94.8^\circ$ ,  $Z = 2$ . 2189 independent nonzero reflections were measured on a four-circle diffractometer (Cu  $K\alpha$  radiation), utilizing the  $\theta$ - $2\theta$  scan mode. Statistical tests indicate the centric space group  $P\bar{1}$ . The structure was solved by the heavy-atom method. Full-matrix least-squares refinement reduced the  $R$  index to about 8%, and convergence seemed complete. However, a difference synthesis revealed partial disorder of carbon atoms C(1), C(3), C(4), and C(6) of the norbornane moiety. The disordered atoms form a second, enantiomeric cage, sharing the 'non-disordered' atoms C(2), C(5) and C(7) with the original molecule. The crystal packing about the cage atoms appears sufficiently loose to permit a statistical disruption of the regular arrangement of L and D molecules, approximately 24% of L being replaced by D and *vice versa*. Further refinement proceeded to a final  $R$  index of 4.1%. Atomic distances are (uncorrected for thermal libration): (C-C) average aromatic ring =  $1.384(\pm 4)$ , (C-C) average cage =  $1.527(\pm 5)$ , (S=O) average =  $1.425(\pm 2)$ , S-C(1') =  $1.758(\pm 2)$ , S-O(3) =  $1.573(\pm 2)$ , O(3)-C(2) =  $1.473$  Å.

### Introduction

Accurate structural data of a series of carefully selected norbornanes might provide a basis for understanding various factors governing the ground-state energy and geometry of these moderately strained and moderately 'flexible' compounds (Altona & Sundaralingam, 1970).



A survey of the literature shows, surprisingly enough, that the exact geometry of the parent compound (I) and of simple derivatives cannot be regarded as settled. Recent electron-diffraction analyses of norbornane (Morino, Kuchitsu & Yokozeki, 1967; Chiang, Wilcox & Bauer, 1968; Dallinga & Toneman, 1968) and of 1,4-dichloronorbornane (Chiang *et al.*, 1968) yielded contradictory results for all carbon-carbon bond distances as well as for some valency angles. Two X-ray diffraction studies of (2,3-disubstituted) norbornanes have appeared (Fratini, Britts & Karle, 1967; Norment, 1965) and a preliminary report on a neutron-diffraction analysis of a highly hindered norbornanol compound is available (Johnson, 1967).

More is known of substituted camphanes (II) and camphors (Ferguson, Fritchie, Robertson & Sim, 1961; Brueckner, Hamor, Robertson & Sim, 1962; Cesur & Grant, 1965; Allen & Rogers, 1966; Wunderlich, 1967; Alden, Kraut & Traylor, 1968), of derivatives of norbornene (III) (MacDonald & Trotter, 1965*a,b*; Abrahamsson & Nilsson, 1966; Sato, Shiro & Koyama, 1968, 1969; Nilsson, 1968; Destro, Filippini, Gramaccioli & Simonetta, 1969) and of norbornadiene (IV)

\* Present address: Laboratory of Organic Chemistry, The University of Leiden, Netherlands.

† Present address: Department of Biochemistry, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

and its derivatives (Dallinga & Toneman, 1968; Baenzinger, Richards & Doyle, 1965; Soleimani, 1966).

On the other hand, interest in theoretical calculations (full-relaxation molecular mechanics approach) for the *a priori* investigation of molecular geometry is steadily increasing since the advent of large-scale computers and the development of sophisticated programs. The success of this method presently hinges, at least in part, on the quality of the force field used (for a review see Williams, Stang & Schleyer, 1968). Many attempts have been made to define workable force-field equations and to find 'force constants' that are applicable (*i.e.* they yield correct physical parameters within the limits of the method) to as wide a range of organic structure as possible. The calculation of acceptable strain energies and geometries of (substituted) norbornanes can be seen as one of the tests that should be applied to any proposed force field (Gleicher & Schleyer, 1967; Allinger, Hirsch, Miller, Tyminsky & Van Catledge, 1968). Comparison of experimental and calculated structures has been profitable. It was demonstrated that norbornanes and camphanes may adapt their geometry to strain induced by certain substituents by either of two possible modes of twist in which the entire skeleton takes part (Altona & Sundaralingam, 1970).

As part of our experimental program in this interesting field, we started to study simple 2-*exo*-substituted norbornanes. Unfortunately, the alcohol, the fluoride and the chloride failed to yield good X-ray diffraction data; excessive disordering was apparent even at low temperatures. Moreover, the chloride showed several phase changes on cooling which were poorly reproducible (Altona & Sundaralingam, 1968). The tosyl ester (V) appeared more promising, and a three-dimensional analysis was undertaken.

### Experimental

The title compound was prepared from commercial 2-*exo*-norbornanol and *p*-toluenesulfonyl chloride, as described by Kwart & Takeshita (1963). Slow evaporation of a solution in pentane yielded colorless triclinic needles, elongated along **a**. A preliminary investigation by means of Weissenberg photographs taken at room temperature and at  $-170^\circ$  revealed no abnormalities. The final unit-cell dimensions were determined from room-temperature measurements of 19 selected reflections on a four-circle Picker diffractometer (Cu  $K\beta$  radiation,  $\lambda = 1.39217 \text{ \AA}$ ). The stated errors are three times the calculated standard deviations from the least-squares procedure (program *PICK*; Corfield, Doedens & Ibers, 1967).

The crystal was mounted in a sealed Lindemann capillary with the needle axis **a** coincident with the  $\phi$  axis of the goniostat. The diffraction intensities of 2349 independent reflections with  $2\theta \leq 136^\circ$ , representing about 80% of the total number in the effective sphere of Cu  $K\alpha$  radiation, were measured on a Picker four-circle diffractometer, applying the automatic  $\theta$ - $2\theta$

scan mode. The crystal cross section measured  $0.12 \times 0.18 \text{ mm}$  (approximately along **b** and **c** respectively). The reflection chosen as primary standard (112) lost less than 3% of its original intensity during the entire period of data collection. Secondary standards ( $1\bar{2}4$ ,  $1\bar{2}4$ ,  $1\bar{2}\bar{2}$ ) chosen in each quadrant also remained virtually constant. Background intensity was measured on the low and high  $2\theta$  side of each reflection. Reflections with measured intensities  $I_o < 1.3\sigma(I)$ , where  $\sigma(I) = (I_{\text{scan}} + I_{\text{bkg}})^{1/2}$ , were considered statistically insignificant and equated to zero. Applying this criterion, 2189 reflexions were observed. The intensities were reduced to structure factor moduli in the usual way. The effect of neglecting absorption corrections is estimated to be less than 2% in  $F^2$ .

Possible space groups are  $P\bar{1}$  and  $P1$ . At the outset of the structure determination,  $P\bar{1}$  was chosen on the basis of the interpretation of the Patterson function. In view of the disorder phenomenon encountered in the final stages of refinement (see below) it was deemed necessary to apply various statistical tests to the observed data set (*International Tables for X-ray Crystallography*, 1967). The intensity distribution agreed very well with the assumption of a centric space group. Crystal data are listed in Table 1.

Table 1. Crystal data for 2-*exo*-norbornanol *p*-toluenesulfonate

$C_{14}H_{18}O_3S$ ; M.W. 266.35; m.p. 54–55°.
Triclinic, space group $P\bar{1}$ .
$a = 6.181 \pm 0.003$ , $b = 11.092 \pm 0.003$ , $c = 11.060 \pm 0.006 \text{ \AA}$ ,
$\alpha = 111.4 \pm 0.1$ , $\beta = 103.6 \pm 0.1$ , $\gamma = 94.8 \pm 0.1^\circ$ .
$V = 674.4 \text{ \AA}^3$ .
$D_m^{20} = 1.309$ , $D_x^{20} = 1.311 \text{ g.cm}^{-3}$ , $Z = 2$ .
$\mu(\text{Cu } K\alpha) = 2.1 \text{ cm}^{-1}$ .

### Structure determination and refinement

The structure was solved by the heavy-atom technique. The unsharpened three-dimensional Patterson function  $P(uvw)$  showed a strong interaction at  $\frac{1}{2}\frac{1}{2}0$ , which was interpreted as the S–S vector. Additional maxima around this peak were consistent with two possible orientations of the  $\text{SO}_3\text{C}(1')$  tetrahedron. Structure factors were calculated for two trial sets, consisting of atoms S, O(2), O(3), C(1'), using 1300 low-angle reflections ( $\sin^2 \theta/\lambda^2 < 0.25$ ). A Fourier synthesis based on the phases of the better of the two trial sets revealed the locations of all remaining carbon atoms and of the missing oxygen atom O(1).

The model obtained seemed to refine successfully. After four cycles of full-matrix least-squares calculations (program *ORFLS*) using the cut-off data set, followed by seven cycles with the full data set, during which stage the hydrogen atoms (except those of the methyl group) were introduced at calculated positions, yielded an  $R$  index of 0.12. Further refinement, including anisotropic temperature factors for all heavy atoms, caused  $R$  to drop to 0.083. At this point convergence seemed to be complete. However, a scrutiny of

the bond distances in the cage moiety and of the  $U_{ii}$  values of some of the carbon atoms revealed several unexpected anomalies. The reason for this behaviour became clear from a study of the three-dimensional difference map, from which the hydrogen contributions had been deleted. Not only were all 18 hydrogen atoms well located with peak densities of  $0.6\text{--}1.2\text{ e.}\text{\AA}^{-3}$  but 4 new peaks showed up ( $1.3\text{--}2.1\text{ e.}\text{\AA}^{-3}$ ) that were interpreted as disordered carbon sites C(1*D*), C(3*D*), C(4*D*), C(6*D*) (Fig. 1).

It appeared that a second norbornane nucleus, enantiomeric with respect to the original molecule, could be constructed out of these four atoms and three original atoms C(2), C(5) and C(7). The plane through C(2), C(5) and C(7) was a quasi mirror plane relating the original atoms C(1), C(3), C(4), and C(6) to their 'disordered' counterparts. Our first task was to determine the occupancy factors for these atomic sites. Full-matrix least-squares calculations were carried out, starting with the best heavy-atom positions combined with the isotropic temperature factors established previously. Hydrogen positions were taken from the above mentioned difference map. The input ratio, C(1)/C(1*D*) *etc.*, was estimated at 85/15. The atomic positions and isotropic temperature factors of the seven original cage carbon atoms and of the four disordered ones, together with eight occupancy factors, were refined. Convergence was obtained in two cycles. It was found that the sums of the occupancies [e.g. C(1)+C(1*D*)] varied from 1.01 to 1.04, and the ratios were similarly constant to within 3%. Therefore, the average ratio (76/24) was taken and used throughout the remainder of this work. The *R* index at this stage was 0.093.

Next, the cage part of the molecule and the tosylate moiety were refined in turn. Anisotropic temperature factors were again introduced for the heavy atoms; all hydrogen atoms were kept fixed at previously determined positions. A difference Fourier synthesis, calculated during an intermediate stage ( $R=0.056$ ), revealed nine low peaks ( $0.2\text{--}0.3\text{ e.}\text{\AA}^{-3}$ ) at or near the positions expected for the disordered ( $\frac{1}{4}$ ) hydrogen atoms; three disordered hydrogen atoms remained missing. It was also found that the three hydrogen atoms attached to C(7') were smeared out over six distinct positions. Apparently, two energetically equivalent methyl rotamers exist in the crystal, separated by a low-energy barrier. The coordinates of some of the 'cage' hydrogen atoms needed slight adjustments. The ordered and disordered hydrogen atoms were included in the final least-squares calculations with their appropriate occupancy factors, but not refined. At this stage, the real part of the anomalous dispersion correction  $\Delta F'$  was applied to the form factor of the sulfur atom, and the previous unitary weights were replaced by a weighting scheme as follows:

$$w = 0.65 + 0.07 F_o \quad (F_o > 5.0)$$

$$w = 1 \quad (F_o \leq 5.0)$$

The quantity minimized was  $w(\Delta F)^2$ .

After four cycles of calculations, all shifts in the atomic coordinates were less than 10% of the calculated estimated standard deviation, and refinement was terminated. The *R* index had dropped to 0.041, or 0.039 when five intense low-order reflections suffering from extinction were deleted from the list. The final  $\Delta F$  map was essentially featureless (a few scattered maxima of  $0.2\text{--}0.3\text{ e.}\text{\AA}^{-3}$  occurred), except about the sulfur atom where density patches ( $0.3\text{--}0.4\text{ e.}\text{\AA}^{-3}$ ) were found approximately midway between the bonds S-O(2), S-O(3), and S-C(1'). However, the experimental data set is probably not of sufficient accuracy to warrant the conclusion that these peaks represent true localized electron densities.

The scattering curves employed are those of Berg-huis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and carbon, those of Stewart, Davidson & Simpson (1965) for hydrogen, and those of Cromer & Waber (1965) for sulfur. During the final stages, a parallel calculation of two cycles was carried out using Dawson's (1960) scattering factors for sulfur, keeping the norbornane moiety fixed. The only noticeable difference between the two results was a 1% scale-factor change. The final structure factors are shown in Table 2, the positional parameters and the temperature factors of the heavy atoms are listed in Tables 3 and 4, respectively, and the hydrogen atom parameters are given in Table 5.

For the tosylate moiety, carbon atoms C(1') to C(7'), a rigid-body analysis of the thermal parameters was performed using Schomaker & Trueblood's (1968) *TLS* program, and the resulting *T* and  $\omega$  tensors are listed in Table 6(a). The corrections in bond lengths due to rigid-body librations vary between one and three standard deviations; those in bond angles are less than one standard deviation. Addition of the sulphur atom to the rigid body had only a slight effect on the results.

We must now consider the important question of whether or not the atoms C(2), C(5), and C(7), referred to above as forming a 'quasimirror' plane relating the  $\frac{3}{4}$  to the  $\frac{1}{4}$  carbon sites, are to be regarded as being dis-

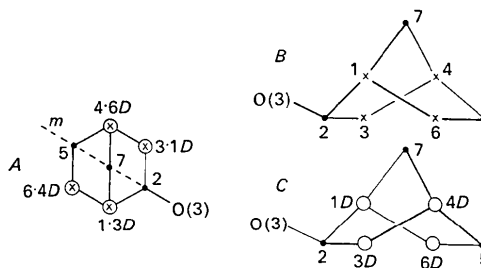


Fig. 1. Relationship between ordered and disordered cage carbon atoms. Dots indicate 'nondisordered atoms', crosses  $\frac{3}{4}$  atoms, circles  $\frac{1}{4}$  carbons, *m* is a quasi mirror plane relating the  $\frac{3}{4}$  cage part to the  $\frac{1}{4}$  part. For clarity, projections *B* and *C* (*m* in the plane of the paper) are drawn separately; in the crystal, the two cages have atoms O(3), C(2), C(5), and C(7) in common (but see text).



Table 3. Positional coordinates of the heavy atoms of racemic 2-*exo*-norbornanol *p*-toluenesulfonateE.s.d.'s are shown in parentheses (each  $\times 10^4$ ).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Occupancy factor
S	2506.1 (0.8)	2523.7 (0.4)	45.9 (0.4)	1.00
O(1)	471 (3)	1569 (1)	-639 (2)	1.00
O(2)	3635 (3)	3041 (2)	-687 (2)	1.00
O(3)	1798 (2)	3679 (1)	1130 (2)	1.00
C(1')	4440 (3)	1922 (2)	1031 (2)	1.00
C(2')	6739 (3)	2441 (2)	1451 (2)	1.00
C(3')	8194 (4)	1992 (2)	2255 (2)	1.00
C(4')	7438 (4)	1017 (2)	2648 (2)	1.00
C(5')	5131 (4)	493 (2)	2186 (2)	1.00
C(6')	3620 (3)	937 (2)	1387 (2)	1.00
C(7')	9055 (5)	533 (3)	3541 (3)	1.00
C(1)	4117 (5)	5259 (3)	3312 (3)	0.76
C(2)	3230 (3)	5002 (2)	1813 (2)	1.00
C(3)	1832 (5)	6028 (3)	1767 (3)	0.76
C(4)	2118 (5)	6840 (3)	3268 (3)	0.76
C(5)	4606 (5)	7630 (2)	3928 (2)	1.00
C(6)	5938 (6)	6506 (4)	3928 (3)	0.76
C(7)	2163 (4)	5814 (2)	3834 (2)	1.00
C(1 <i>D</i> )	1534 (20)	5961 (13)	2439 (18)	0.24
C(3 <i>D</i> )	5233 (31)	5384 (16)	3012 (19)	0.24
C(4 <i>D</i> )	4731 (36)	6442 (19)	4207 (17)	0.24
C(6 <i>D</i> )	2643 (25)	7364 (13)	2732 (16)	0.24

ordered, each electron density consisting of a  $\frac{3}{4}$  and a  $\frac{1}{4}$  carbon atom at unknown, but close distance. Two lines of evidence can be considered.

First, such splitting might reveal itself in the form of 'abnormal' thermal parameters. This is not the case. The magnitudes of the principal axes of the thermal ellipsoids of C(2), C(5), and C(7) are perfectly in line with those of C(1), C(3), C(4), and C(6). Moreover, a rigid-body analysis of the cage moiety [carbon atoms C(1) to C(7)] yielded differences of  $U_{ij}$ , derived from

Table 5. Positional coordinates ( $\times 10^3$ ), isotropic temperature factors ( $\text{Å}^2$ ), and occupancy factors for the hydrogen atomsEndo and *exo* positions are denoted *n* and *x* respectively.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>	Occupancy factor
H(2')	725	308	117	6.35	1.00
H(3')	983	233	254	6.35	1.00
H(5')	450	-17	233	6.35	1.00
H(6')	205	63	115	4.74	1.00
H(71)	819	-22	372	7.07	0.50
H(72)	990	130	448	7.07	0.50
H(73)	1030	14	308	7.07	0.50
H(74)	1073	103	380	7.07	0.50
H(75)	863	68	444	7.07	0.50
H(76)	903	-49	304	7.07	0.50
H(1)	475	450	343	6.35	0.76
H(2 <i>n</i> )	433	504	129	7.07	0.76
H(3 <i>n</i> )	243	669	138	7.07	0.76
H(3 <i>x</i> )	4	550	133	7.07	0.76
H(4)	100	750	354	6.35	0.76
H(5 <i>n</i> )	498	792	333	7.07	0.76
H(5 <i>x</i> )	483	832	497	7.07	0.76
H(6 <i>n</i> )	687	621	313	7.07	0.76
H(6 <i>x</i> )	650	667	492	7.07	0.76
H(7 <i>a</i> )	248	625	487	7.07	0.76
H(7 <i>s</i> )	83	509	341	7.07	0.76
H(1 <i>D</i> )	-21	572	194	6.35	0.24
H(2 <i>nD</i> )	367	519	103	7.07	0.24
H(3 <i>xD</i> )	560	460	328	7.07	0.24
H(4 <i>D</i> )	566	663	520	6.35	0.24
H(5 <i>nD</i> )	614	783	373	7.07	0.24
H(5 <i>xD</i> )	466	843	442	7.07	0.24
H(5 <i>nD</i> )	311	750	193	7.07	0.24
H(5 <i>xD</i> )	146	790	270	7.07	0.24
*H(3 <i>nD</i> )	672	576	286		
*H(7 <i>aD</i> )	130	635	451		
*H(7 <i>sD</i> )	150	488	377		

\* Calculated positions, not used in the structure factor calculations.

Table 4. Anisotropic thermal parameters of the heavy atoms ( $\times 10^5$ )

$$T = \exp [ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) ]$$

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	2822 (18)	815 (5)	923 (6)	268 (9)	430 (9)	347 (5)
O(1)	3282 (45)	993 (13)	1233 (14)	14 (22)	18 (22)	311 (14)
O(2)	4345 (47)	1336 (16)	1249 (16)	617 (23)	966 (24)	717 (12)
O(3)	2855 (39)	779 (10)	1350 (12)	253 (18)	767 (18)	368 (10)
C(1')	2659 (50)	686 (17)	874 (18)	249 (22)	479 (23)	241 (15)
C(2')	2704 (54)	918 (17)	1226 (19)	125 (23)	663 (25)	458 (16)
C(3')	2583 (62)	1012 (24)	1225 (26)	192 (39)	426 (31)	331 (23)
C(4')	3395 (65)	865 (21)	836 (21)	480 (28)	381 (29)	193 (20)
C(5')	3594 (68)	842 (21)	1171 (22)	186 (28)	561 (30)	461 (20)
C(6')	2676 (58)	758 (18)	1138 (19)	-126 (25)	394 (25)	345 (17)
C(7')	4766 (112)	1367 (45)	1166 (44)	908 (51)	224 (55)	453 (34)
C(1)	3500 (88)	1170 (30)	1175 (30)	309 (41)	60 (41)	596 (26)
C(2)	2776 (53)	796 (17)	1011 (19)	162 (23)	478 (26)	369 (15)
C(3)	4367 (102)	1033 (28)	1155 (30)	669 (32)	459 (44)	519 (25)
C(4)	3853 (96)	1008 (28)	1366 (34)	544 (42)	737 (47)	260 (25)
C(5)	4858 (94)	1058 (25)	1416 (29)	-20 (37)	471 (42)	228 (22)
C(6)	4114 (114)	1569 (42)	1322 (38)	97 (55)	-47 (53)	244 (33)
C(7)	4613 (84)	1491 (29)	1085 (24)	97 (39)	869 (36)	455 (22)
C(1 <i>D</i> )	2256 (370)	850 (125)	987 (161)	546 (173)	305 (190)	257 (119)
C(3 <i>D</i> )	2902 (515)	782 (164)	1615 (172)	45 (208)	-191 (220)	440 (151)
C(4 <i>D</i> )	4889 (662)	1312 (201)	915 (187)	978 (331)	49 (326)	448 (198)
C(6 <i>D</i> )	3916 (485)	732 (133)	1395 (146)	644 (203)	661 (206)	312 (127)

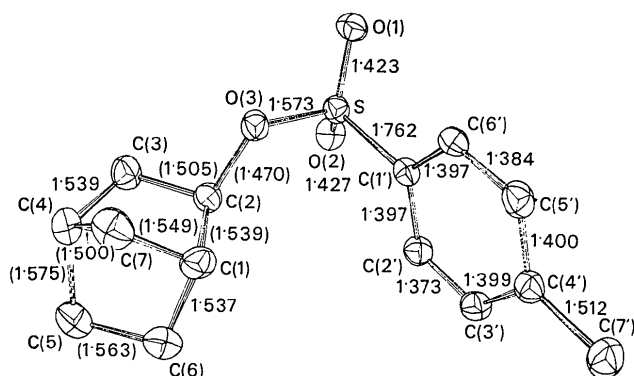


Fig. 2. ORTEP plot (Johnson, 1967) of 2-exo-norbornanol *p*-toluenesulfonate, showing the molecule in perspective and the bond distances, corrected for rigid-body librations. Values in parentheses are suspect because of the possibility of hidden disorder (see text).

input  $B_{ij}$  and from calculated rigid-body parameters that were of the order of one standard deviation (root-mean-square  $\Delta U_{ij} = 0.0034 \text{ \AA}^2$ ); again, the three carbon atoms in question behaved perfectly normally.

On the other hand, geometrical criteria can be applied. If the plane ( $m$ ) through C(2)–C(5)–C(7) represents a true mirror plane, then it should coincide with a plane ( $M$ ) through the midpoints of the four vectors C(1)–C(1D), C(3)–C(3D), etc. However, the perpendicular distances of the three carbon atoms to the least-squares  $M$  plane (r.m.s. deviations of the latter plane:  $0.005 \text{ \AA}$ ) are quite large:  $-0.050$ ,  $0.027$ , and  $-0.038$  for C(2), C(5), and C(7) respectively, *i.e.* more than 10 times the calculated standard deviations in the atomic positions. Conversely, the distances of each pair of  $\frac{1}{2}$ ,  $\frac{1}{2}$  carbon atoms to  $m$  were checked. In two cases [C(1)/C(1D), C(3)/C(3D)], the differences amounted to over four and three times the standard deviations

Table 6.  $T$  and  $\omega$  tensors, their eigenvalues and eigenvectors for (a) carbon atoms C(1')–C(7') of the *p*-tolyl moiety (b) for carbon atoms C(1)–C(7) of the norbornyl moiety

E.s.d.'s are given in parentheses. The data are given relative to an orthogonal axial system ( $\text{\AA}$ ), base vector  $l$  parallel to  $a$ , base vector 2 parallel to  $c^* \times a$  (see Fig. 5)

(a) *p*-Tolyl moiety

	11	22	33	12	13	23
$T(\text{\AA}^2)$	0.054 (0.002)	0.052 (0.002)	0.039 (0.002)	0.002 (0.002)	-0.003 (0.002)	-0.018 (0.002)
$\omega(\text{deg}^2)$	26.0 (5.3)	26.4 (5.8)	19.6 (5.2)	-14.7 (2.8)	12.2 (3.9)	-9.8 (4.0)

Principal values and direction cosines of eigenvectors

$T:$		$l$	$m$	$n$
	0.256 $\text{\AA}$	-0.248	-0.787	0.565
	0.232	-0.967	0.231	-0.103
	0.163	-0.049	-0.572	-0.819
$\omega:$		$l$	$m$	$n$
	7.0°	-0.636	0.614	-0.467
	3.6	-0.258	-0.740	-0.621
	3.1	-0.727	-0.274	0.629

R.m.s. deviation  $\Delta U_{ij} = 0.0024 \text{ \AA}^2$ .

(b) Norbornyl moiety

	11	22	33	12	13	23
$T(\text{\AA}^2)$	0.068 (0.003)	0.063 (0.003)	0.052 (0.003)	-0.001 (0.002)	-0.008 (0.002)	-0.011 (0.002)
$\omega(\text{deg}^2)$	18.5 (6.7)	22.7 (6.5)	37.2 (7.8)	3.8 (4.5)	1.7 (4.7)	20.7 (4.5)

Principal values and direction cosines of eigenvectors

$T:$		$l$	$m$	$n$
	0.271 $\text{\AA}$	-0.678	0.510	0.530
	0.257	-0.673	0.720	-0.168
	0.207	-0.296	-0.470	-0.831
$\omega:$		$l$	$m$	$n$
	7.2°	-0.107	-0.579	-0.808
	4.3	-0.975	-0.099	0.200
	2.8	-0.196	0.809	-0.554

R.m.s. deviation  $\Delta U_{ij} = 0.0035 \text{ \AA}^2$

in the  $\frac{1}{4}$  carbon atoms. Calculation of all possible least-squares planes through the midpoints and through one, two, or three of the *m* atoms also showed that C(2) fits badly, and that C(5) fits best, but considering the standard deviations involved, not quite well enough.

Note that the geometrical arguments are based on the assumption that the 'ordered' ( $\frac{3}{4}$ ) and the 'disordered' ( $\frac{1}{4}$ ) norbornyl moieties have exactly the same geometry. Since they differ only in being optical antipodes in very similar and loose packing environments (see below), this assumption seems justified. For the sake of completeness, the **T** and  **$\omega$**  tensors are listed in Table 6(b).

From the above analysis, the sad conclusion must be drawn that C(2), C(5) and C(7) must be regarded as

being disordered, and that their atomic positions, given in Table 3, represent only averages, perhaps differing from the true ones by a few hundredths of an ångström. Even atom O(3) might fall in this category. Attempts

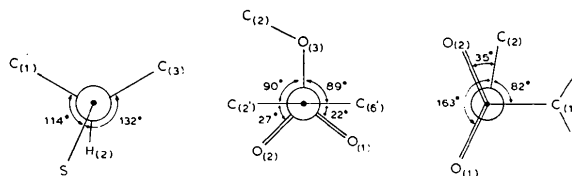


Fig. 3. Torsion angles showing the folding of the sulphonate ester bridge. (a) Projection along O(3)-C(2); (b) projection along C(1')-S; (c) projection along S-O(3).

Table 7. Bond distances and angles in the tosylate

The two values relate to uncorrected and corrected values respectively for thermal motion. Values in parentheses are unreliable due to possible disordering of atoms C(2), C(5), and C(7) (see text).

S—O(1)	1.423 (2) Å	C(1)—C(7)	(1.537) Å	(1.549) Å
S—O(2)	1.427 (2)	C(2)—C(3)	(1.492)	(1.505)
S—O(3)	1.573 (2)	C(3)—C(4)	1.531 (4)	1.539
S—C(1')	1.758 (2)	C(4)—C(5)	(1.565)	(1.575)
C(1')—C(2')	1.388 (3)	C(4)—C(7)	(1.486)	(1.500)
C(2')—C(3')	1.368 (4)	C(5)—C(6)	(1.550)	(1.563)
C(3')—C(4')	1.389 (4)	C(1D)—C(2)	(1.64)	
C(4')—C(5')	1.391 (3)	C(1D)—C(6D)	1.53 (3)	
C(5')—C(6')	1.379 (3)	C(1D)—C(7)	(1.57)	
C(1')—C(6')	1.386 (3)	C(2)—C(3D)	(1.48)	
C(4')—C(7')	1.508 (4)	C(3D)—C(4D)	1.53 (3)	
O(3)—C(2)	(1.473)	C(4D)—C(5)	(1.46)	
C(1)—C(2)	(1.528)	C(4D)—C(7)	(1.57)	
C(1)—C(6)	1.529 (5)	C(5)—C(6D)	(1.49)	
C(2')—H(2')	0.94	C(1)—H(1)	0.99	
C(3')—H(3')	0.98	C(2)—H(2 <sub>n</sub> )	1.00	
C(5')—H(5')	0.89	C(3)—H(3 <sub>n</sub> )	1.05	
C(6')—H(6')	0.94	C(3)—H(3 <sub>x</sub> )	1.12	
C(7')—H(7 <sub>1</sub> )	1.06	C(4)—H(4)	1.06	
C(7')—H(7 <sub>2</sub> )	1.05	C(5)—H(5 <sub>n</sub> )	0.90	
C(7')—H(7 <sub>3</sub> )	1.05	C(5)—H(5 <sub>x</sub> )	1.09	
C(7')—H(7 <sub>4</sub> )	1.05	C(6)—H(6 <sub>n</sub> )	1.14	
C(7')—H(7 <sub>5</sub> )	1.05	C(6)—H(6 <sub>x</sub> )	1.01	
C(7')—H(7 <sub>6</sub> )	1.06	C(7)—H(7 <sub>s</sub> )	0.99	
		C(7)—H(7 <sub>a</sub> )	1.03	
O(1)—S—O(2)	119.8 (1)°	S—O(3)—C(2)	(121.0)°	
O(1)—S—O(3)	103.8 (1)	O(3)—C(2)—C(1)	(107.1)	
O(2)—S—O(3)	109.3 (1)	O(3)—C(2)—C(3)	(110.4)	
O(1)—S—C(1')	109.3 (1)	C(2)—C(1)—C(6)	(105.3)	
O(2)—S—C(1')	109.2 (1)	C(2)—C(1)—C(7)	(100.7)	
O(3)—S—C(1')	104.3 (1)	C(6)—C(1)—C(7)	(100.7)	
S—C(1')—C(2')	120.4 (2)	C(1)—C(2)—C(3)	(105.4)	
S—C(1')—C(6')	118.8 (2)	C(2)—C(3)—C(4)	(102.7)	
C(6')—C(1')—C(2')	120.9 (2)	C(3)—C(4)—C(5)	(108.1)	
C(1')—C(2')—C(3')	119.1 (2)	C(3)—C(4)—C(7)	(102.2)	
C(2')—C(3')—C(4')	121.8 (2)	C(5)—C(4)—C(7)	(102.0)	
C(3')—C(4')—C(5')	117.8 (2)	C(4)—C(5)—C(6)	(101.0)	
C(4')—C(5')—C(6')	121.6 (2)	C(5)—C(6)—C(1)	(104.6)	
C(5')—C(6')—C(1')	118.7 (2)	C(1)—C(7)—C(4)	(95.4)	
C(3')—C(4')—C(7')	121.4 (2)			
C(5')—C(4')—C(7')	120.8 (2)			
Some short intramolecular contacts				
S—H(2 <sub>n</sub> )	2.63 Å	O(1)—H(6')	2.59 Å	
S—H(2')	2.82	O(2)—H(2 <sub>n</sub> )	2.40	
S—H(6')	2.80	O(3)—H(1)	2.55	

to split these atoms for structure factor calculations were soon abandoned, as no single solution could be found.

### Discussion

The geometry and the thermal vibration ellipsoids of the molecule are shown in Fig. 2. The bond distances and angles are shown in Table 7. Distance values, both uncorrected and corrected for thermal motion, are given. Our data for the tosylate part of the molecule seem rather accurate. Unfortunately, all but two of the carbon-carbon distances and all valency angles in the norbornyl part must be regarded with suspicion, because of the uncertainty in the positional and thermal parameters of C(2), C(5) and C(7).

Of the various ester groups that can be used in X-ray studies of cycloaliphatic alcohols (bromoacetates, *p*-bromobenzoates, *p*-bromobenzenesulfonates, tosylates), the tosylate group has the advantage of carrying only one relatively heavy atom (sulfur), and hence greater accuracy can be expected in the final results. It is surprising, therefore, that to date no accurate X-ray analysis of a tosyl ester appears to have been reported. Fruitful comparisons can be made with a recent accurate determination of the structure of the tosylate anion (Huber, 1969; Arora & Sundaralingam, 1971) and with the results of an X-ray study of the tosylate ester of *cis-trans*-2,5-di-*t*-butylcyclohexanol (Faber & Altona, 1971). For the *p*-tolyl moiety, the agreement between the four determinations is excellent (Table 8) and requires little special comment. A shortening of the bonds C(2')-C(3') and C(5')-C(6'), parallel

to the long axis of the *p*-tolyl group in the anion, was noted and discussed by Huber (1969) and by Arora & Sundaralingam (1971).

Table 8. Comparison of bond distances of the *p*-tolyl moiety in two esters and in two tosylate anions

All except bond distances of Arora & Sundaralingam (1971) are corrected for thermal motion.

	Faber & Altona		Arora & Sundaralingam	
	This work	(1971)	Huber (1969)	(1971)
S—C(1')	1.762 Å	1.753 Å	1.780 Å	1.753 Å
C(1')—C(2')	1.397	1.396	1.395	1.382
C(1')—C(6')	1.397	1.399	1.385	1.385
C(3')—C(4')	1.399	1.400	1.394	1.384
C(4')—C(5')	1.400	1.396	1.396	1.376
C(2')—C(3')	1.373	1.376	1.371	1.376
C(5')—C(6')	1.384	1.382	1.378	1.378
C(4')—C(7')	1.512	1.501	1.513	1.510
$\sigma$ (C—C)	0.004	0.004	0.006	0.003

A similar shortening is apparent in both tosyl esters, the difference between the averages of eight 'long' bonds ( $1.398 \pm 0.001$  Å) and four 'short' bonds ( $1.379 \pm 0.002$  Å) being of the same order of magnitude as seen in the anion ( $1.392 \pm 0.003$  Å and  $1.375 \pm 0.004$  Å respectively).

The benzene ring shows small but significant distortions from planarity and has a 'twist-boat' shape. C(1') and C(4') each deviate by  $-0.008$  Å from the least-squares plane through the six benzene carbon atoms, and C(2') and C(5') by  $+0.008$  Å, whereas C(3') and C(6') lie in the plane. The (S) atom and the

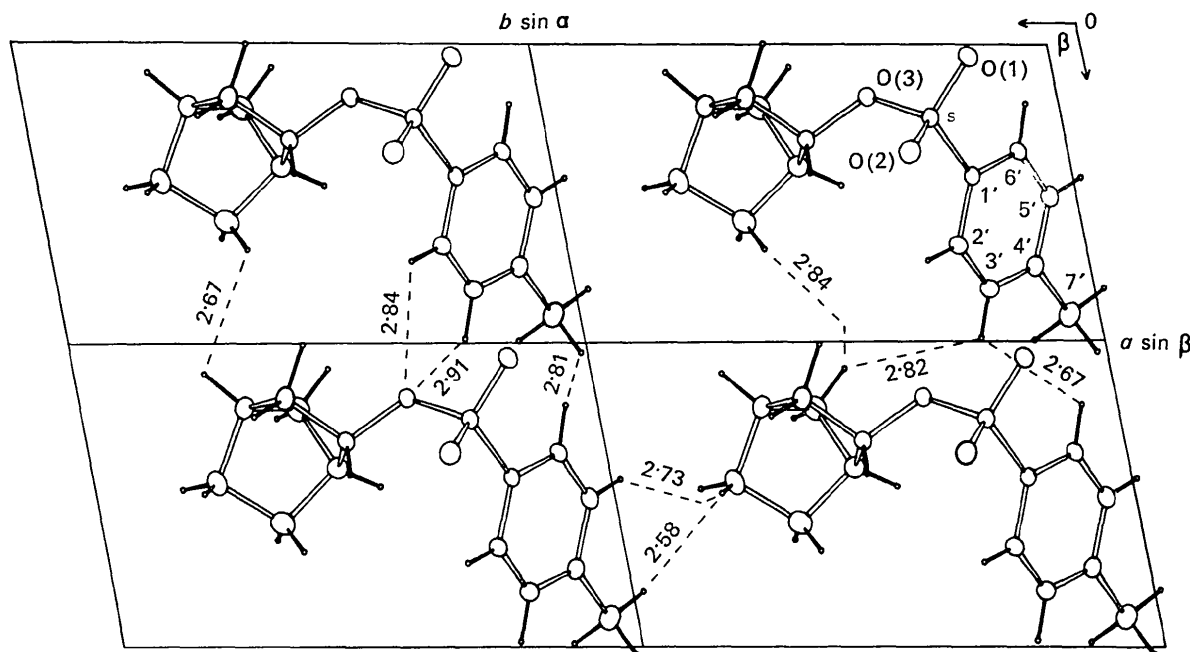


Fig. 4. Projection of the structure down the *c* axis (ORTEP, Johnson, 1967), showing some selected short hydrogen-oxygen and hydrogen-hydrogen contacts.



methyl carbon atom deviate out of plane by 0.068 and -0.024 Å respectively.

The bond distances and angles in the -SO<sub>3</sub> group were not corrected for the thermal effects because inspection of observed and calculated  $U_{ij}$ 's of the oxygen atoms indicated that these atoms are involved in some additional vibration and/or rotation, more or less independent of the thermal motions of the adjoining tolyl and norbornyl parts. Moreover, the S-O bonds of the -SO<sub>3</sub> 'bridge' may carry out nonrigid rotational oscillations (Huber, 1969) and corrections seem of doubtful physical significance. The agreement of the S-O (uncorrected) and S-C (corrected) bond lengths found in this analysis with corresponding values in the di-*t*-butylcyclohexanol derivative (Faber & Altona, 1971) is reasonable; the values are respectively: S-C, 1.762 ± 0.002 and 1.753 ± 0.002 Å; S=O (average), 1.430 ± 0.002 and 1.424 ± 0.002 Å; S-O, 1.573 ± 0.002 and 1.567 ± 0.002 Å. The S-C and S=O bonds seem shorter in these esters than in the tosylate anion for which (corrected) distances of 1.780 and 1.457 Å have been reported (Huber, 1969).

The well-known 'flattening' of the -SO<sub>3</sub> group ap-

pears even more marked in both tosylate esters than in the anion. In the present ester the O=S=O angle (119.8°) is significantly larger than the corresponding value in the anion (average 113.1°). The O=S-C bond angles are tetrahedral (109.3°, compare in the anion: 105.5°) but the 'single-bonded' O-S-C angle is significantly smaller (104.3°).

Interestingly, the two O=S-O bond angles are *not* equal; the one in the approximately *S-cis* fragment O(2)-S-O(3)-C(2), torsion angle 34.7°, is tetrahedral (109.3°); the other in the *S-trans* arrangement O(1)-S-O(3)-C(2), torsion angle 163.5°, is significantly smaller (103.8°). The S-O(3)-C(2) bond angle is fairly large (121.0°).

The conformation of the C(1')-SO<sub>2</sub>-O(3)-C(2) bridge is of some interest. The tosyl group is folded in a way that might well be characteristic of this type of sidechain. In fact, the results of this analysis aided in solving the structure of the di-*t*-butyl derivative mentioned above (Faber & Altona, 1971). The relevant torsion angles are shown in Fig. 3. The benzene ring has a symmetrical position with respect to the SO<sub>3</sub> group, but all remaining bonds are neither staggered,

Table 9. *Experimental and theoretical bond lengths and valency angles of norbornane and of some derivatives*

Theoretical structures are based on a valence forcefield including interactions between atoms bound to a common atom (Urey-Bradley field). Capitalized abbreviations in the first column are authors' initials, which are explained in the footnotes.

	C(1)-C(2)	C(1)-C(7)	C(2)-C(3)	(C-C)average
Unsubstituted:				
DT (electron diffraction)	1.534 (14) Å	1.535 (35) Å	1.578 (18) Å	1.544 Å
MKY (electron diffraction)	1.539 (15)	1.568 (16)	1.539 (25)	1.547
CWB (electron diffraction)	1.551 (12)	1.559 (15)	1.556 (15)	1.555
Substituted:				
CWB (electron diffraction)	1.553 (15)	1.539 (15)	1.556 (15)	1.550
FBK (X-ray)	1.535 (4)	1.537 (6)	1.558 (6)	1.542
This work	1.538 (3)*			
Theoretical calculation of norbornane:				
GS	1.543	1.531	1.547	1.541
This work†	1.540	1.540	1.547	1.542
This work‡	1.547	1.546	1.553	1.548
	C(2)-C(1)-C(6)	C(2)-C(1)-C(7)	C(1)-C(7)-C(4)	C(1)-C(2)-C(3)
Unsubstituted:				
DT (electron diffraction)	107.1 (1.8)°	101.8 (0.6)°	95.3 (1.6)°	103.0 (0.5)°
MKY (electron diffraction)	107.2 (-)	-	93.2 (1.5)	105.1 (-)
CWB (electron diffraction)	103.5 (-)	101.4 (-)	96.0 (1.0)	104.3 (-)
Substituted:				
CWB (electron diffraction)	104.4 (-)	103.8 (-)	92.8 (1.0)	102.5 (-)
FBK (X-ray)	109.8 (0.5)	101.5 (0.5)	93.5 (0.5)	102.7 (0.5)
Theoretical calculation of norbornane:				
GS	106.1	102.6	93.9	103.0
This work†	109.8	101.1	93.9	103.2
This work‡	108.9	101.9	93.1	103.0

DT: Dallinga & Toneman, 1968; MKY: Morino, Kuchitsu & Yokozeki, 1967; CWB: Chiang, Wilcox & Bauer, 1968; FBK: Fratini, Britts & Karle, 1967; GS: Gleicher & Schleyer, 1967.

\* Mean of C(3)-C(4) and C(1)-C(6) distances; the remaining distances and angles are unreliable because of the disorder

† Force field described by Altona & Sundaralingam, 1970;

‡ Force field described by Lifson & Warshel, 1968.

nor eclipsed, although the S–O(3) bond comes fairly close to eclipsing the C(2)–H(2*n*) bond (Sundaralingam, 1969).

Neither the exact geometry of the bicyclic moiety in simple norbornyl derivatives nor that of the parent compound can be regarded as settled. Relevant experimental data from the literature, both electron-diffraction and X-ray work, are collected in Table 9. A comparison is also made with the results of valence force-field calculations (automatic energy minimization) by Gleicher & Schleyer (1967) and by the present authors.

In this study the C(1)–C(6) and C(3)–C(4) bond lengths (present numbering; in the following discussion as well as in Table 9, the *chemical* numbering is used) are determined with good accuracy (average value  $1.538 \pm 0.003$  Å), and they agree (within the limits of the quoted standard deviations) with those reported by Fratini *et al.* (1967) and with the theoretical results (first column, Table 9). The remaining bond distances and the bond angles of the present work are uncertain. The calculations, as well as the X-ray study of Fratini *et al.* (1967), suggest that the C(1)–C(2) and the C(1)–C(7) bond lengths are of comparable magnitude but that C(2)–C(3) might be significantly longer. On the other hand, the average C(1)–C(2) bond distance reported by Norment (1965) appears extremely long (1.567 Å).

Comparison of the published bond angles show reasonable agreement, except for angle C(2)–C(1)–C(6) for which experimental values ranging from  $103.5^\circ$  (electron diffraction) to  $109.8^\circ$  (X-ray) have been reported. Further work seems necessary to clarify this point. The torsion angles and the ‘twisting’ of the norbornyl fragment caused by steric effects of the sub-

stituents have been discussed elsewhere (Altona & Sundaralingam, 1970) and are not treated here.

#### Packing arrangement

A projection of the ‘ordered’ part of the structure down the *c* axis is shown in Fig. 4; a view of the packing and an outline of the chosen unit cell are shown in Fig. 5. Note that the –SO<sub>3</sub> groups tend to stay away from each other as far as possible, each oxygen atom being in close contact with several hydrogen atoms. Atoms O(1) and O(3) are surrounded mainly with aromatic hydrogen atoms, while atom O(2) is wedged underneath the *endo* hydrogen atoms of a neighboring norbornyl moiety. Furthermore, several short contact distances are observed between hydrogen atoms (Table 10).

Table 10. Distribution of short H–H interatomic distances in the ordered structure, and in a structure in which the reference molecule was replaced by its disordered ( $\frac{1}{2}$ ) counterpart

Contact range (Å)	2.3–2.5	2.5–2.7	2.7–2.9	2.9–3.1
Ordered structure	3	4	8	7
Disordered structure	5	2	3	7

The ‘disordered’ or alternative ( $\frac{1}{2}$ ) norbornyl cage is easily accommodated in the same volume of space as the predominant ( $\frac{2}{3}$ ) moiety. Interestingly, of the 12, presumably attractive, short ( $< 3.1$  Å) oxygen–hydrogen contact distances in the predominant structure only 6 remain on replacing the cage by its enantiomer and a few more short (repulsive) hydrogen–hydrogen contacts appear (Table 10). The shortest carbon–oxygen distance in the predominant structure is 3.30 Å and the shortest one in the alternative structure is 3.28 Å; all distances involving carbon or oxygen and sulfur are greater than 3.5 Å.

The disordering phenomenon encountered in the present work might be called nonconformational enantiomeric disorder, because in this case the enantiomers cannot interconvert by torsional rotations around single bonds. As far as the authors are aware, no other such cases have been reported in the literature, although the possibility exists that some went by undetected. The disorder was discovered because four of the atoms were well resolved and had appreciable electron density. Even with our accurate counter data a much smaller degree of disorder would perhaps have escaped attention, giving rise to concealed errors in the molecular geometry and thermal motion. It is clear that trouble of this kind can be avoided by using an optically pure enantiomer. In cases of possible conformational enantiomeric disorder, there seems to exist no easy remedy except a watchful eye. Rotational disorder was discussed by Hanson (1965).

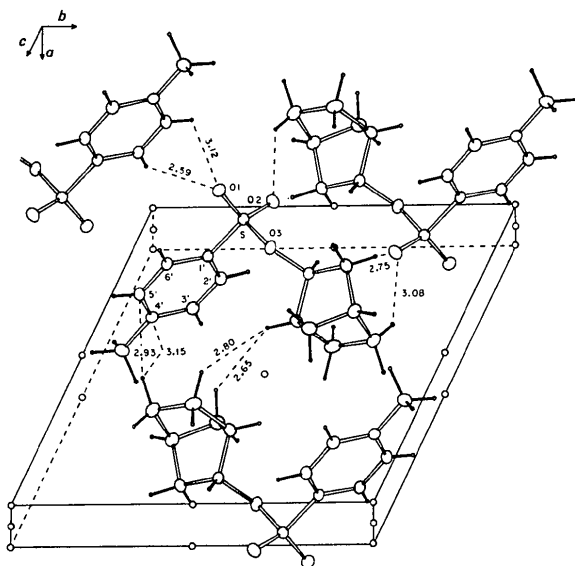


Fig. 5. View of the structure (ORTEP, Johnson, 1967), showing the outlines of the chosen unit cell.

This investigation was supported by grant GP-15977 of the National Science Foundation and by

Grant GM-14828 from the National Institutes of Health of the U.S. Public Health Service. A Fulbright-Hays Travel Grant from the U.S. Educational Foundation in The Netherlands is gratefully acknowledged by one of us (CA). We are indebted to Dr S. T. Rao and Dr D. H. Rohrer for the use of some of their computer programs.

### References

- ABRAHAMSSON, S. & NILSSON, B. (1966). *J. Org. Chem.* **31**, 3631.
- ALDEN, R. A., KRAUT, J. & TRAYLOR, T. G. (1968). *J. Amer. Chem. Soc.* **90**, 74.
- ALLEN, F. H. & ROGERS, D. (1966). *Chem. Comm.* 837.
- ALLINGER, N. L., HIRSCH, J. A., MILLER, M. A., TYMINSKY, I. & VAN CATLEDGE, F. A. (1968). *J. Amer. Soc.* **90**, 1199.
- ALTONA, C. & SUNDARALINGAM, M. (1968). Unpublished observations.
- ALTONA, C. & SUNDARALINGAM, M. (1970). *J. Amer. Chem. Soc.* **92**, 1995.
- ARORA, S. & SUNDARALINGAM, M. (1971). *Acta Cryst.* **B27**, 1293.
- BAENZINGER, N. C., RICHARDS, G. F. & DOYLE, J. R. (1965). *Acta Cryst.* **18**, 924.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BRUECKNER, D. A., HAMOR, R. A., ROBERTSON, J. M. & SIM, G. A. (1962). *J. Chem. Soc.* p. 799.
- CESUR, A. F. & GRANT, D. F. (1965). *Acta Cryst.* **18**, 55.
- CHIANG, J. F., WILCOX, C. F. & BAUER, S. H. (1968). *J. Amer. Chem. Soc.* **90**, 3149.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *J. Inorg. Chem.* **6**, 197.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
- DALLINGA, G. & TONEMAN, L. H. (1968). *Rec. Trav. chim. Pay-Bas*, **87**, 795.
- DAWSON, B. (1960). *Acta Cryst.* **13**, 403.
- DESTRO, R., FILIPPINI, G., GRAMACCIOLI, C. M. & SIMONETTA, M. (1969). *Acta Cryst.* **B25**, 2465.
- FABER, D. H. & ALTONA, C. (1971). *Chem. Commun.* p. 1210.
- FERGUSON, G., FRITCHIE, C. J., ROBERTSON, J. M. & SIM, G. A. (1961). *J. Chem. Soc.* p. 1976.
- FRATINI, A. V., BRITTS, K. & KARLE, I. L. (1967). *J. Phys. Chem.* **71**, 2482.
- GLEICHER, G. J. & SCHLEYER, P. VON R. (1967). *J. Amer. Chem. Soc.* **89**, 582.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 19.
- HUBER, C. S. (1969). *Acta Cryst.* **B25**, 1140.
- International Tables for X-ray Crystallography* (1967). Vol. II. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1967). Chem. Div. Ann. Progr. Rept. 4164, p. 116. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KWART, H. & TAKESHITA, T. (1963). *J. Org. Chem.* **28**, 670.
- LIFSON, S. & WARSHEL, A. (1968). *J. Chem. Phys.* **49**, 5116.
- MACDONALD, A. C. & TROTTER, J. (1965a). *Acta Cryst.* **18**, 243.
- MACDONALD, A. C. & TROTTER, J. (1965b). *Acta Cryst.* **19**, 456.
- MORINO, Y., KUCHITSU, K. & YOKOZEKI, A. (1967). *Bull. Soc. Chim. Japan*, **40**, 1552.
- NILSSON, B. (1968). *Acta Chem. Scand.* **22**, 518.
- NORMENT, H. G. (1965). *Acta Cryst.* **18**, 627.
- SATO, T., SHIRO, M. & KOYAMA, H. (1968). *J. Chem. Soc. (B)*, 935.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.
- SOLEIMANI, E. (1966). *Diss. Abstr.* **B27**, 1866.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- SUNDARALINGAM, M. (1969). *Biopolymers*, **7**, 821.
- WILLIAMS, J. E., STANG, P. J. & SCHLEYER, P. VON R. (1968). *Ann. Rev. Phys. Chem.* **10**, 531.
- WUNDERLICH, J. A. (1967). *Acta Cryst.* **23**, 846.

*Acta Cryst.* (1972). **B28**, 1816

## The Crystal Structure of Triuranium Pentaselenide

BY P. T. MOSELEY

*Applied Chemistry Division, A.E.R.E., Harwell, Berkshire, England*

AND D. BROWN AND B. WHITTAKER

*Chemistry Division, A.E.R.E., Harwell, Berkshire, England*

(Received 10 January 1972)

Triuranium pentaselenide,  $U_3Se_5$ , crystallizes with an orthorhombic unit cell;  $a_o = 12.43$  (2),  $b_o = 8.48$  (1) and  $c_o = 7.77$  (1) Å,  $Z = 4$ , space group probably  $Pnma$ . Two environmentally distinct types of uranium atom and two environmentally distinct types of selenium atom are found in the structure. Uranium-selenium interatomic distances range from 2.80 to 3.18 Å, varying with the coordination numbers of the atoms involved. The final  $R$  value for 615 reflexions, observed by the equi-inclination Weissenberg method, is 0.114.

### Introduction

During recent years considerable attention has been devoted to the chalcogenides of uranium, largely as a

result of the complex structural and bonding problems posed by these apparently simple binary compounds. The crystal chemistry of actinide chalcogenides has been surveyed (Dell & Bridger, 1971) and these com-