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THE CRYSTAL STRUCTURE AND CONFORMATION OF CYCLOHEXYLTOSYLATE ($C_{13}H_{18}SO_3$)

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Abstract—The crystal structure of cyclohexyltosylate has been determined by X-ray and neutron diffraction methods, as a basis for studies of strain in substituted cyclohexyltosylates. A slight flattening of the chair is evident in the solid material, which crystallises in the equatorial conformer.

INTRODUCTION

THIS study of cyclohexyltosylate ($C_{13}H_{18}SO_3$) forms part of a program of structure analysis of cyclohexyltosylates being pursued in this laboratory. The aim of this program is to obtain information about the distortion produced in a cyclohexyl ring by the addition of a t-Bu group as compared with the unsubstituted cyclohexyltosylate. NMR studies of a number of fluorocyclohexane compounds using ^{19}F have given anomalous results,[1] and measurements of the conformational free energy for the tosylate group using the kinetics of acetolysis[2] differ considerably from those obtained using the NMR method. These results may in part be explained by a distortion of the cyclohexane ring produced by the introduction of a t-Bu group in the reference compounds. Martin,[3] using NMR results, had predicted a flattening of the cyclohexane chair in 4-t-butylcyclohexyl tosylates, and analyses of these compounds by X-rays and neutrons are almost complete.* For this paper, "flattening" of the chair is described in terms of a standard chair having mean bond angle 109·5°, and mean torsional angle 60°.[4] The present analysis shows that the chair is somewhat flattened even before substitution and that the material crystallises solely as the equatorial conformer, whereas in solution it exists as an equilibrium mixture of both equatorial and axial conformers. A neutron diffraction experiment was carried out concurrently with the X-ray analysis to confirm the H atom positions, in particular the axial hydrogen attached to C_8, which is the carbon atom of the chair bonded to the tosylate group (Fig 1).

Crystal data, $C_{13}H_{18}SO_3$, *cyclohexyltosylate*

Crystal dimensions:		
	0·5 × 0·2 × 0·2 mm	X-rays
	0·1 × 0·25 × 0·3 mm	
	0·7 × 0·6 × 0·3 cm ..	neutrons.

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* Independent determinations of the structures of the *cis* and *trans* compounds have been made using X-rays by Johnson, Cheer and Schaefer (1970).[5] Joint papers on each of these compounds will be submitted for publication shortly. A separate paper on the neutron structure of *trans*-4-t-butycyclohexyltosylate is being prepared by Moore and James (1971).[6]

Monoclinic, space-group $P2_{1/c}$
Absent spectra: 0k0, k = 2n + 1
h0l, l = 2n + 1
a = 5·923 ± 0·003, b = 17·624 ± 0·005, c = 12·870 ± 0·004 Å
$\beta = 93{\cdot}3 \pm 0{\cdot}3°$
Calculated density 1·264 g cm^{-3}
Linear absorption coefficient: $\mu = 18{\cdot}0$ cm^{-1} for, $\lambda = 1{\cdot}5418$ Å (X-rays); $\mu = 2{\cdot}32$ cm^{-1} for, $\lambda = 1{\cdot}187$ Å (neutrons).

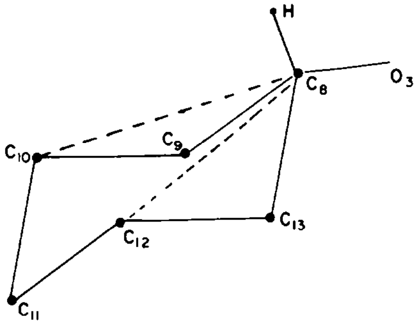

FIG 1

DISCUSSION

Bond lengths and angles. The intramolecular bond lengths and angles involving the non-H atoms are shown diagrammatically in Figs 2 and 3.

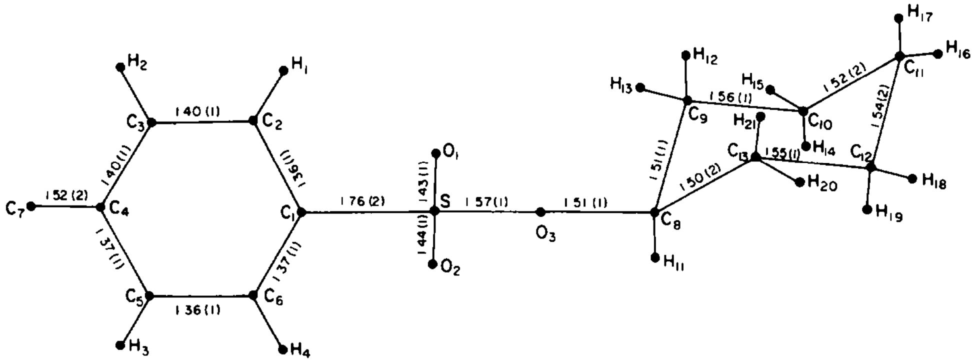

FIG 2. Bond lengths (Å) from X-ray refinement, with standard deviations in parentheses.

The e.s.d's given are those calculated from the least squares matrix and do not include additional errors for inadequate absorption and thermal motion corrections. The mean C—C bond for the benzene ring is 1·375 ± 0·018 which differs by less than one standard deviation from that obtained for crystalline benzene.[9] The average C-C distance for the chair structure of 1·530 ± 0·016 agrees with that obtained for cyclohexane.[10] The range of values here is similar to that obtained by Hanson and Ahmed[11] for the toluene-*p*-sulphonate ion of d-methadone hydrobromide. The $S - O_1$, $S - O_2$, $S - C_1$, $C_4 - C_7$ distances also agree with those obtained for this substance.

The S – C_1 distance of 1·76 (2) Å is much shorter than the value calculated by Abrahams[12] and Pauling,[13] though it agrees with the experimental values obtained for β-sulphanilamide.[14] The bonds linking sulphur with O_1 and O_2 are also very short. Chemically the shortness of these bonds suggest that there must be considerable π-bonding with the dπ orbitals of sulphur of the type described by Cruickshank[15] and the values are in excellent agreement with those given in this paper. The shortness of the bonds C_8–C_9 and C_8–C_{13} could be the result of the sp hybrid bonding with oxygen when this is considered together with the dπ bonding of the sulphur. The arrangement of the atoms around the sulphur is approximately tetrahedral. The large deviation of the angle O_1–S–O_2 (120·6(8)) from the ideal tetrahedral value is similar to that obtained in β-sulphanilamide.[14] This distortion would tend to produce minimum hindrance similar to that of the type of non-bonded interactions described by Bartell.[16]

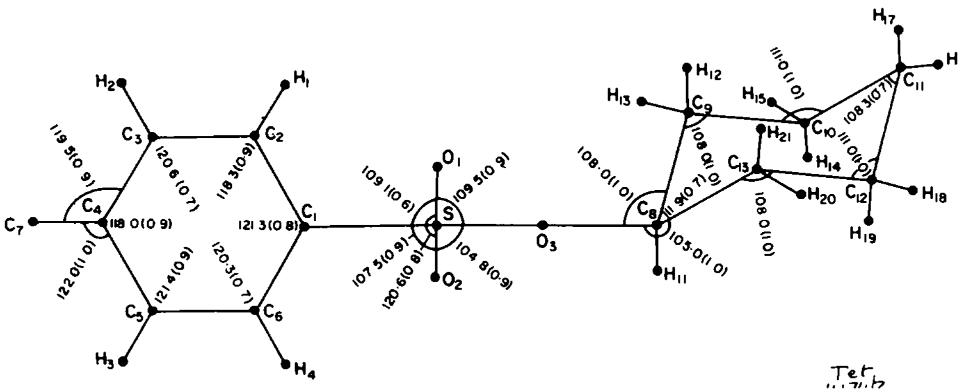

FIG 3. Bond angles (degrees) from X-ray refinement, with standard deviations in parentheses.

A calculation of the least squares plane through the atoms of the benzene ring showed that the ring is planar within the limits of precision. The Me carbon, the sulphur and hydrogens are all displaced from the plane in the same direction, a result found also for β-sulphanilamide.[14]

The shortest intermolecular distance is that between O_1 and C_9 (3·74(3)) closely followed by that between O_1 and C_{11} (3·89(4)).

One of the objects of this structure determination was to establish a basis for the study of conformational changes caused by the t-Bu substitution. Although the mean bond angle in the chair is 109·7°, the mean torsional angle is 57·5°, with the smallest 56·5° and the largest 59·7°. This indicates a slight flattening even before the t-Bu substitution. It is also noticeable that the internal bond angle at C_8 (attached to the tosylate group) is 112°, significantly larger than the 108° angle at atom C_{11}. Another measure of flattening is afforded by the angle made by the axial hydrogen attached to C_8, with the plane defined by $C_8C_{10}C_{12}$ (Fig 1). In an unstrained chair this angle is approximately 90°, whereas here it was found to be 99° (e.s.d. 2°). This is in accord with the results of Davis and Hassel[17] from an electron diffraction study.

Electron density distribution. The final difference synthesis produced a generally flat topography with background fluctuations rarely exceeding $\pm 0{\cdot}2\,e\text{Å}^{-3}$. A peak of $-0{\cdot}6\,e\text{Å}^{-3}$ occurs however near the S atom site. Similar peaks are mentioned in bis(dimethydithiophosphato) nickel (II),[18] and in β-Sulphanilamide[14] and is most probably caused by discrepancies arising from errors in the isolated atom scattering curve of sulphur when applied to a bonded atom.

TABLE 1. ATOMIC COORDINATES FROM X-RAY REFINEMENT, WITH STANDARD DEVIATION IN PARENTHESES

	x/a	y/b	z/c
S	0·5730 (2)	0·3300 (1)	0·1973 (1)
O_1	0·4489 (7)	0·2649 (2)	0·2290 (3)
O_2	0·8163 (7)	0·3295 (3)	0·2056 (4)
O_3	0·5079 (60)	0·3477 (2)	0·0801 (3)
C_1	0·4811 (9)	0·4114 (3)	0·2630 (4)
C_2	0·2868 (10)	0·4072 (4)	0·3137 (4)
C_3	0·2185 (10)	0·4721 (4)	0·3667 (5)
C_4	0·3448 (11)	0·5383 (4)	0·3690 (5)
C_5	0·5348 (11)	0·5399 (4)	0·3141 (5)
C_6	0·6063 (11)	0·4779 (4)	0·2633 (5)
C_7	0·2641 (21)	0·6076 (6)	0·4277 (8)
C_8	0·2642 (9)	0·3456 (3)	0·0396 (4)
C_9	0·2191 (11)	0·2685 (4)	−0·0098 (5)
C_{10}	−0·0247 (11)	0·2678 (4)	−0·0616 (5)
C_{11}	−0·0596 (14)	0·3308 (4)	−0·1403 (5)
C_{12}	−0·0052 (13)	0·4078 (4)	−0·0884 (7)
C_{13}	−0·2390 (11)	0·4090 (4)	−0·0377 (6)
H_1	0·2230 (160)	0·3590 (70)	−0·3260 (80)
H_2	0·0690 (200)	0·4760 (70)	0·4250 (80)
H_3	0·6090 (180)	0·5870 (60)	0·3250 (90)
H_4	0·7700 (190)	0·4780 (60)	0·2510 (100)
H_5	0·7420 (540)	0·1000 (160)	0·0840 (230)
H_6	0·5500 (440)	0·1209 (170)	0·0200 (200)
H_7	0·1660 (340)	0·6340 (110)	0·3970 (150)
H_8	0·7050 (390)	0·1650 (140)	0·1100 (220)
H_9	0·1000 (580)	0·5560 (170)	0·4550 (180)
H_{10}	0·8790 (530)	0·1130 (170)	0·0230 (210)
H_{11}	0·1490 (150)	0·3430 (50)	0·1000 (80)
H_{12}	0·2720 (170)	0·2180 (70)	0·4090 (120)
H_{13}	0·2290 (180)	0·2630 (70)	0·0420 (90)
H_{14}	−0·1290 (200)	0·2920 (80)	−0·0140 (120)
H_{15}	−0·0250 (160)	0·2120 (160)	−0·0770 (70)
H_{16}	0·0590 (220)	0·3270 (60)	−0·2150 (90)
H_{17}	−0·2460 (200)	0·3320 (60)	−0·1690 (80)
H_{18}	−0·0200 (230)	0·4180 (70)	−0·0280 (100)
H_{19}	0·0420 (220)	0·4450 (70)	−0·1390 (110)
H_{20}	0·3420 (170)	0·0840 (80)	0·4040 (110)
H_{21}	0·2760 (220)	0·4570 (70)	−0·0170 (110)

TABLE 2. THERMAL PARAMETERS FROM X-RAY REFINEMENT, WITH STANDARD DEVIATIONS IN PARENTHESES

The thermal parameters are coefficients in the expression $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Hydrogen thermal parameters were not refined.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	0·0361 (5)	0·0050 (1)	0·0071 (1)	0·0009 (1)	−0·0004 (1)	0·0007 (1)
O_1	0·0566 (18)	0·0041 (1)	0·0096 (3)	−0·0007 (4)	0·0007 (6)	0·0015 (2)
O_2	0·0379 (15)	0·0078 (2)	0·0099 (3)	0·0025 (4)	−0·0022 (5)	0·0008 (2)
O_3	0·0340 (13)	0·0057 (1)	0·0071 (2)	0·0003 (3)	0·0019 (4)	0·0003 (1)
C_1	0·0359 (17)	0·0043 (2)	0·0066 (3)	−0·0023 (5)	−0·0013 (6)	0·0002 (2)
C_2	0·0361 (20)	0·0049 (2)	0·0076 (4)	−0·0026 (5)	0·0017 (7)	−0·0002 (2)
C_3	0·0480 (23)	0·0051 (3)	0·0083 (4)	−0·0002 (6)	0·0028 (7)	0·0004 (2)
C_4	0·0525 (26)	0·0051 (2)	0·0074 (3)	−0·0027 (6)	−0·0005 (8)	0·0002 (2)
C_5	0·0449 (23)	0·0048 (2)	0·0111 (4)	−0·0040 (6)	0·0017 (9)	0·0004 (2)
C_6	0·0413 (22)	0·0053 (2)	0·0701 (4)	−0·0032 (6)	0·0045 (8)	0·0007 (2)
C_7	0·0885 (44)	0·0052 (3)	0·0117 (7)	−0·0005 (11)	0·0035 (14)	−0·0009 (4)
C_8	0·0319 (16)	0·0042 (2)	0·0072 (3)	−0·0002 (4)	−0·0000 (5)	−0·0002 (2)
C_9	0·0485 (23)	0·0045 (2)	0·0086 (4)	0·0014 (6)	−0·0001 (8)	−0·0008 (2)
C_{10}	0·0441 (22)	0·0041 (2)	0·0102 (4)	0·0002 (6)	−0·0028 (8)	−0·0010 (2)
C_{11}	0·0521 (28)	0·0070 (3)	0·0089 (4)	−0·0020 (7)	−0·0031 (9)	−0·0001 (3)
C_{12}	0·0473 (25)	0·0049 (2)	0·0137 (6)	0·0017 (6)	−0·0034 (10)	0·0021 (3)
C_{13}	0·0403 (22)	0·0052 (3)	0·0107 (5)	−0·0013 (6)	−0·0020 (8)	0·0021 (2)
H_1	0·0216	0·0065	0·0095	−0·0015	0·0030	−0·0006
H_2	0·0691	0·0050	0·0073	0·0027	0·0056	−0·0014
H_3	0·0448	0·0042	0·0159	−0·0084	0·0044	−0·0038
H_4	0·0390	0·0054	0·0164	−0·0080	0·0040	0·0007
H_5	0·0544	0·0031	0·0063	0·0046	−0·0057	−0·0019
H_6	0·0701	0·0095	0·0118	−0·0099	−0·0168	0·0009
H_7	0·0349	0·0041	0·0078	0·0034	0·0051	−0·0026
H_8	0·0245	0·0055	0·0144	0·0039	0·0053	−0·0037
H_9	0·1465	0·0067	0·0104	0·0235	−0·0014	−0·0057
H_{10}	0·1103	0·0092	0·0150	−0·0177	0·0340	0·0004
H_{11}	0·0281	0·0038	0·0103	−0·0038	−0·0096	−0·0007
H_{12}	0·0244	0·0079	0·0207	0·0033	−0·0089	0·0005
H_{13}	0·0609	0·0060	0·0103	0·0093	0·0039	−0·0060
H_{14}	0·0383	0·0055	0·0207	−0·0019	−0·0064	−0·0029
H_{15}	0·0387	0·0058	0·0107	0·0007	−0·0118	0·0006
H_{16}	0·0875	0·0075	0·0072	−0·0025	−0·0054	−0·0011
H_{17}	0·0599	0·0078	0·0053	−0·0006	−0·0066	0·0012
H_{18}	0·0616	0·0067	0·0116	0·0590	−0·0059	0·0020
H_{19}	0·0589	0·0057	0·0183	0·0019	−0·0144	0·0026
H_{20}	0·0230	0·0111	0·0167	0·0033	0·0060	0·0003
H_{21}	0·0795	0·0054	0·0153	−0·0080	−0·0114	0·0037

EXPERIMENTAL

Crystals were prepared by slow evaporation of a petroleum ether soln. Multi-film equi-inclination Weissenberg techniques with CuK$_2$ radiation were employed to collect X-ray data on layers 0kl to 5kl and h0l to h10l and intensities were estimated visually by comparison with a calibration strip. Corrections for Lorentz and polarisation factors were obtained from the common rows of the two blocks of data using the correlation program of Rae (1965).[7] This resulted in 2221 scaled reflections from 3343 intensities measured. Of these scaled reflections 1587 were observable above background. The remainder were given values equal to that of minimum observable and treated as unobserved reflections as described below.

Three-dimensional neutron diffractometer data were collected at the HIFAR reactor, Lucas Heights, N.S.W. for 2θ angles less than 80°. These were corrected for Lorentz and absorption factors and equivalent reflections averaged. A total of 923 reflections were used of which 368 were unobserved.

Structure determination and refinement. The structure was solved by direct methods using the programs of Hall and the P.D.P. 10 computer at the University of Western Australia. Using three origin-fixing reflections and one other reflection which was given only a symbol, 36 reflections were phased from the Σ_2 relationships. These were used as starting phases in a tangent refinement from which all 226 reflections with E's greater than 1·7 were phased. All non-H atoms were obtained from a 3-dimensional E map computed from these phases. The co-ordinates of the 17 atoms as obtained from the E map were refined using the least squares program ORFLS (Busing, Martin and Levy, 1962)[8] in which the function $\Sigma w(|F_o| - |F_c|)^2$ is minimised. Throughout the latter stages of the refinement, unobserved terms with $|F_c| < |F_{min}|$ were given zero weight, while those with $|F_c| > |F_{min}|$ were treated as observed reflections. The agreement index, $R = \Sigma|\Delta F|/\Sigma|F_o|$, obtained using non-H atoms was 9·1%. Three dimensional maps computed for both X-rays and neutrons at this stage revealed reasonably-located peaks for all H atoms except those in the terminal Me group, where two sets of peaks were evident for each H atom, suggesting a degree of disorder. Refinement of both X-ray and neutron data confirmed the H positions, including the six "half hydrogen" atoms for the Me group, indicating that the most probably configuration for this group was a statistical arrangement with each methyl H occupying two positions with equal probability.

After locating the H positions, further refinements were carried out varying all parameters in the case of neutrons but fixing the thermal parameters of the hydrogens at the neutron value for the X-ray refinement. The final R value was 7·4% for X-rays and 5·5% for neutrons. The final positional and thermal parameters for all atoms are given in Tables 1 and 2.

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REFERENCES

[1] E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.* **90**, 682 (1968)
[2] S. Winstein and N. J. Holness, *Ibid.* **77**, 5562 (1955)
[3] R. J. L. Martin, private communication (1969)
[4] C. Altona and M. Sundaralingam, *Tetrahedron* **26**, 925 (1970)
[5] P. L. Johnson, Clair J. Cheer and J. P. Schaeffer, A.C.A. Summer Meeting (1970)
[6] F. H. Moore and V. J. James, to be published (1971)
[7] A. D. Rae, Department of Scientific and Industrial Research Report C.D. 2093, Lr. Hutt, N.Z. (1965)
[8] W. R. Busing, K. O. Martin and H. A. Levy, *ORFLS, a Fortran Crystallographic Least Squares Program.* Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. (1962)
[9] E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Roy. Soc.* A.**247**, 1 (1958)
[10] L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **59**, 13 (1937)
[11] A. W. Hanson and F. R. Ahmed, *Acta Cryst.* **11**, 724 (1958)
[12] S. C. Abrahams, *Ibid.* **8** 661 (1955)
[13] L. Pauling, *The Nature of The Chemical Bond* Ithaca, Cornell Univ. Press (1960)
[14] A. M. O'Connell and E. N. Maslen, *Acta. Cryst.* **22**, 134 (1967)
[15] D. W. J. Cruickshank, *J. Chem. Soc.* 5486 (1961)
[16] L. S. Bartell *Tetrahedron* **17**, 177 (1962)
[17] M. Davis and O. Hassel, *Acta. Chem. Scand.* **17**, 1181 (1963)
[18] V. Kastalsky and J. F. McConnell, *Acta. Cryst.* *B***25**, 909 (1969)