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The Conformation of Non-Aromatic Ring Compounds. LXXXII.* The Crystal and Molecular Structure of *cis*, *trans*-2,5-Di-t-butylcyclohexanol Toluene-*p*-sulphonate

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The structure has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/n$ with $Z=4$. The unit-cell dimensions are $a=12{\cdot}562$, $b=28{\cdot}402$, $c=5{\cdot}964$ Å and $\beta=94{\cdot}9°$. The final conventional R value is 4·2%. The cyclohexane ring has a chair conformation with the two t-butyl groups in equatorial position. The t-butyl groups are twisted away from the staggered form by about -12 and $+7°$ respectively. The thermal motion has been analysed in terms of a rigid body, and suggests a fairly large torsional motion of the t-butyl groups.

Introduction

The presence of t-butyl groups in cyclohexane-like molecules introduces a considerable amount of 'strain', perhaps mainly due to short intramolecular contacts between the hydrogen atoms of the t-butyl group and the nearest hydrogens of the rest of the molecule. In the case of t-butylcyclohexane and related molecular systems this strain is partly relieved by an extra flattening of the ring in the C(3)–C(4)–C(5) region as well as by an increase of the exocyclic C–C–C bond angles to about 114°. Empirical force-field calculations (Altona & Sundaralingam, 1970) led to the prediction that in the minimum energy conformation of t-butylcyclohexane the t-butyl group does not occupy a staggered position, but is twisted ($\pm 17°$) with respect to the ring bonds, accompanied by an asymmetric distortion of the ring itself. Since the barrier separating the two equivalent forms was calculated to be only 0·2–0·3 kcal mole^{-1}, an X-ray analysis would show a time-average picture, *i.e.* staggering of the t-butyl group accompanied by large temperature factors of its methyl carbon atoms. Asymmetric substitution, causing sufficiently strong steric interference, will render the two forms non-equivalent and this would result in a time-average twist different from zero. Further theoretical work threw some doubt on the existence of a double minimum potential energy well – it might result from deficiencies in the force field employed (Altona & Faber, 1973) – but a potential energy well with a wide 'flat' minimum would still lead to the same predictions.

A number of X-ray studies on symmetrically substituted 4-t-butylcyclohexanes and related compounds has since appeared in which the off-staggering of the t-butyl group did not exceed 3° (Cook, Glick, Rigau & Johnson, 1971; Berti, Macchia, Macchia, Merlino & Muccini, 1971; Lectard, Metras, Petrissans & Gaultier, 1971; Parthasarathy, Ohrt, Kagan & Fiaud, 1972; Johnson, Cheer, Schaefer, James & Moore, 1972; Johnson, Schaefer, James & McConnell, 1972; de

* Part LXXXI: de Wolf, Wepster & Havinga (1973). *Rec. Trav. Chim. Pays-Bas* (to be published).

Graaff, Giesen, Rutten & Romers, 1972), in agreement with the force-field predictions. However, in *cis*-4-t-butylcyclohexane-1-carboxylic acid (van Koningsveld, 1972) the t-butyl group is twisted by about 8°. The temperature parameters of the t-butyl group in this compound are relatively high, as predicted. This part of the prediction was also confirmed by the X-ray study of *cis*-2-chloro-4-t-butylcyclohexanone (de Graaff, Giesen, Rutten & Romers, 1972) where the analysis of the thermal motion in terms of a rigid body suggested a substantial librational motion of the t-butyl group. The idea of twisting of the t-butyl group as a means of strain-relieving in crowded molecules has gained some strength by the observation of twists of 10° or more in the interesting and highly crowded molecule of tri-t-butylmethane (Burgi & Bartell, 1972; Bartell & Burgi, 1972).

The title compound, *cis,trans*-2,5-di-t-butylcyclohexanol toluene-*p*-sulphonate (hereafter referred to as BCT), is an interesting one for several reasons. First, the cyclohexane ring is asymmetrically substituted. Second, in their study of the four isomeric 2,5-di-t-butylcyclohexanols, Pasto & Rao (1970) concluded that the *cis,trans* isomer (axial hydroxyl group) is thermodynamically more stable than the *trans,cis* isomer (equatorial hydroxyl group) and it was hoped that BCT might provide a model to understand the cause of this unusual behaviour. Force-field calculations (preliminary publication Faber & Altona, 1971) reasonably reproduced the twist of the t-butyl groups in BCT, but the unusual preference of the hydroxyl group for the axial position could not easily be explained.

Experimental

A sample of BCT was kindly provided by Professor D. J. Pasto. Slow evaporation of a solution in methylene chloride yielded colourless needles, elongated along [001]. Preliminary rotation and Weissenberg photographs indicated monoclinic symmetry. A carefully selected crystal with approximate dimensions 0·3 × 0·3 × 0·7 mm was mounted on a goniometer head and the final cell dimensions were measured on a three-circle diffractometer. The axes were choosen in such

Table 1. *Crystal data for cis, trans-2,5-di-t-butylcyclohexanol toluene-p-sulphonate*

	$C_{21}H_{34}O_3S$
M.W.	266·6
m.p.	73·5 °C
Monoclinic	
Space group	$P2_1/n$
a	12·562 ± 0·005 Å
b	28·402 ± 0·008
c	5·964 ± 0·003 Å
β	94·9°
V	2121·1 Å³
D_m^{20}	1·148
D_x^{20}	1·16 g cm⁻³
Z	4
μ(Cu $K\alpha$)	14 cm⁻¹

Table 2. *Fractional coordinates* (× 10⁴) *and standard deviations of the non-hydrogen atoms*

	x	y	z
S	2131·6 (0·6)	1711 (0·3)	4811 (1)
O(1)	2857 (2)	1283·1 (0·7)	4296 (3)
O(2)	2091 (2)	1697·3 (0·9)	7183 (3)
O(3)	1159 (2)	1694·0 (0·8)	3394 (4)
C(1′)	2838 (2)	2212 (1)	4107 (5)
C(2′)	2607 (3)	2434 (1)	2064 (6)
C(3′)	3135 (3)	2842 (1)	1611 (6)
C(4′)	3876 (3)	3046 (1)	3151 (8)
C(5′)	4102 (3)	2810 (2)	5163 (7)
C(6′)	3594 (3)	2403 (1)	5662 (6)
C(7′)	4386 (3)	3506 (2)	2672 (9)
C(1)	2851 (2)	1083 (1)	1996 (5)
C(2)	2872 (3)	549 (1)	2204 (5)
C(3)	3954 (3)	396 (1)	3356 (6)
C(4)	4893 (3)	583 (1)	2172 (6)
C(5)	4877 (2)	1121 (1)	2061 (5)
C(6)	3808 (2)	1275 (1)	910 (5)
C(7)	1889 (3)	305 (1)	3092 (6)
C(8)	1870 (3)	338 (1)	5644 (7)
C(9)	1899 (4)	−217 (1)	2456 (7)
C(10)	858 (3)	516 (2)	1954 (7)
C(11)	5840 (3)	1354 (1)	1064 (5)
C(12)	5837 (3)	1264 (2)	−1459 (6)
C(13)	5833 (3)	1884 (1)	1495 (7)
C(14)	6891 (3)	1160 (2)	2232 (6)

Table 3. *Fractional coordinates* (× 10³) *and B values* (Å²) *of the hydrogen atoms with standard deviations*

	x	y	z	B
H(1)	213 (2)	231 (1)	108 (5)	4·91
H(2)	297 (2)	299 (1)	19 (5)	6·69
H(3)	457 (2)	293 (1)	623 (5)	6·76
H(4)	374 (2)	224 (1)	699 (5)	6·23
H(5*A*)	403 (4)	375 (2)	333 (8)	8·46
H(6*A*)	456 (4)	354 (2)	119 (9)	7·73
H(7*A*)	519 (4)	350 (2)	340 (9)	6·41
H(8*B*)	500 (6)	347 (3)	226 (13)	10·81
H(9*B*)	448 (6)	371 (3)	421 (13)	5·78
H(10*B*)	390 (6)	372 (3)	186 (13)	7·66
H(11)	219 (2)	119 (1)	119 (4)	3·23
H(12)	287 (2)	46 (1)	67 (4)	4·27
H(13)	401 (2)	7 (1)	340 (4)	4·21
H(14)	404 (2)	54 (1)	498 (5)	5·52
H(15)	553 (2)	46 (1)	294 (5)	6·47
H(16)	486 (2)	46 (1)	63 (5)	5·21
H(17)	489 (2)	124 (1)	353 (4)	3·45
H(18)	374 (2)	163 (1)	81 (4)	2·84
H(19)	377 (2)	117 (1)	−58 (4)	4·72
H(20)	177 (2)	65 (1)	617 (5)	6·97
H(21)	252 (3)	21 (1)	646 (7)	10·45
H(22)	125 (3)	16 (1)	615 (5)	7·02
H(23)	187 (3)	−25 (1)	79 (6)	8·84
H(24)	125 (3)	−39 (1)	294 (6)	8·23
H(25)	251 (3)	−39 (1)	311 (6)	8·64
H(26)	24 (2)	35 (1)	245 (5)	6·36
H(27)	85 (3)	54 (1)	26 (6)	9·22
H(28)	73 (2)	83 (1)	257 (5)	6·90
H(29)	515 (3)	143 (1)	−234 (6)	8·87
H(30)	576 (3)	90 (1)	−184 (5)	6·75
H(31)	642 (3)	139 (1)	−210 (5)	7·29
H(32)	584 (2)	195 (1)	315 (5)	7·24
H(33)	523 (3)	203 (1)	71 (6)	8·34
H(34)	645 (2)	200 (1)	96 (5)	6·86
H(35)	695 (2)	83 (1)	188 (5)	6·24
H(36)	684 (2)	119 (1)	388 (5)	6·71
H(37)	754 (2)	133 (1)	177 (5)	6·48

H(5*A*), H(6*A*), H(7*A*) and H(8*B*), H(9*B*), H(10*B*) are the two disordered positions of the toluene methyl group, approximately $A/B = 60/40$.

a way that the systematic extinctions ($0k0$ for k odd, $h0l$ for $h+l$ odd) are consistent with the space group $P2_1/n$. Diffraction intensities of 1898 independent non-zero reflexions were measured at room temperature on an automatic three-circle Enraf–Nonius diffractometer, employing the $\theta/2\theta$ scan mode with Ni-filtered Cu $K\alpha$ radiation. An additional 1251 reflexions having counts less than twice the standard deviation were considered to be non-observed. Further details of the measuring technique have been published elsewhere (Portheine, Romers & Rutten, 1972). The intensities were reduced to structure factor moduli in the usual way by dividing by Lorentz, polarization and absorption factors calculated by a computer program developed by de Graaff (1973). The crystal data are listed in Table 1.

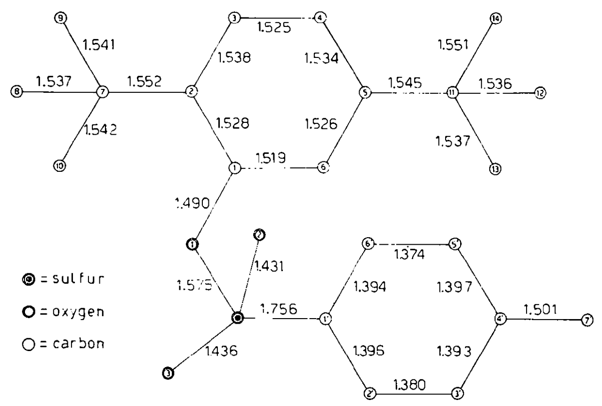

Fig. 1. Atomic numbering and corrected bond lengths in BCT.

Structure determination and refinement

The structure of BCT was solved by Patterson methods, with sulphur as the heavy atom. The refinement was carried out by the block-diagonal approximation. Isotropic refinement of all heavy atoms lowered the R value (unweighted, observed reflexions only) to 12·3%. At this stage the hydrogen atoms were included (the toluene methyl hydrogen atoms were assumed to be 50/50 disordered) and subsequent anisotropic refinement of the heavy atoms produced an R value of 5·7%. This value decreased to 4·89% by subsequent refinement of the hydrogen atom positions and isotropic temperature parameters and the heavy atoms alternately. At this stage the occupancy factors of the toluene methyl hydrogen atoms were refined; the ratio turned out to be approximately 60:40, however the improvement in R was minor (4·84%). Finally, two cycles of full-matrix refinement (one for the cyclohexane part C(1) to C(14) plus O(1) and one for the tosyl moiety) produced an R value of 4·2% (observed reflexions only). The weighted value R_w (omitting non-observed reflexions) is 4·9% and the conventional R value including non-observed reflexions is 9·2%. The largest shift in atomic positions during these last few

Table 4. *Observed and calculated U_{ij} values of non-hydrogen atoms*

The units are 10^{-4} Å^2 and the crystallographic axes are the reference system. The temperature factor is defined as

$$\exp(-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}).$$

	U_{11}		U_{22}		U_{33}		$2U_{12}$		$2U_{23}$		$2U_{13}$	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
S	487 (5)	—	634 (5)	—	464 (5)	—	104 (9)	—	−21 (9)	—	90 (7)	—
O(1)	548 (13)	558	561 (13)	572	409 (12)	402	106 (21)	−16	−32 (20)	−19	71 (19)	97
O(2)	840 (17)	—	945 (19)	—	392 (13)	—	199 (29)	—	21 (25)	—	267 (23)	—
O(3)	455 (13)	—	828 (17)	—	690 (15)	—	66 (25)	—	5 (26)	—	−138 (22)	—
C(1′)	502 (19)	505	527 (20)	503	456 (19)	491	203 (33)	219	−156 (33)	−162	49 (31)	60
C(2′)	666 (23)	681	586 (24)	589	542 (22)	525	93 (39)	147	−91 (36)	−72	−52 (35)	−70
C(3′)	791 (27)	788	593 (25)	614	692 (26)	683	208 (43)	196	66 (41)	84	254 (42)	291
C(4′)	602 (24)	579	552 (25)	573	955 (32)	976	147 (39)	87	−224 (46)	−222	496 (45)	516
C(5′)	629 (25)	606	785 (30)	767	877 (32)	889	−23 (45)	−84	−418 (50)	−398	−93 (44)	−74
C(6′)	633 (24)	653	682 (26)	731	697 (24)	579	22 (40)	87	−105 (39)	−179	−136 (38)	−172
C(7′)	832 (29)	845	704 (29)	651	1745 (48)	1731	−127 (49)	−122	−204 (61)	−194	1172 (62)	1150
C(1)	561 (21)	549	563 (22)	542	366 (18)	367	21 (33)	28	65 (30)	68	−6 (30)	29
C(2)	652 (23)	655	541 (22)	533	464 (20)	493	−145 (35)	−74	−26 (32)	−14	114 (33)	120
C(3)	757 (26)	709	476 (21)	521	706 (24)	700	86 (37)	124	231 (36)	229	85 (39)	141
C(4)	624 (23)	649	640 (24)	583	723 (25)	701	174 (38)	220	126 (39)	78	144 (37)	195
C(5)	525 (20)	552	619 (22)	581	390 (18)	428	68 (34)	61	2 (32)	61	157 (30)	95
C(6)	597 (21)	575	529 (21)	560	404 (19)	371	17 (33)	27	76 (30)	106	111 (31)	63
C(7)	748 (26)	751	634 (25)	643	592 (24)	583	−260 (41)	−309	−5 (37)	−11	197 (39)	166
C(8)	1181 (36)	777	1019 (34)	784	678 (28)	559	−765 (56)	−376	150 (48)	279	549 (49)	123
C(9)	1121 (36)	1089	635 (28)	653	1129 (36)	1052	−517 (50)	−538	−83 (49)	−187	247 (56)	477
C(10)	669 (26)	665	887 (31)	925	994 (32)	498	−444 (46)	−409	−124 (50)	−144	315 (46)	78
C(11)	572 (22)	587	737 (26)	766	479 (21)	486	−72 (38)	−64	67 (36)	4	225 (33)	193
C(12)	861 (30)	700	1396 (41)	999	539 (25)	514	−219 (55)	−206	49 (49)	−138	458 (43)	356
C(13)	723 (27)	709	769 (29)	753	1032 (32)	565	−338 (44)	−313	223 (47)	39	377 (47)	265
C(14)	553 (23)	555	1076 (34)	1053	779 (27)	699	9 (45)	55	−18 (48)	50	247 (39)	180

The calculated values were taken from rigid-body model I, with exception of atoms C(8), C(9), C(10), C(12), C(13) and C(14) which were taken from rigid-body model II (cyclohexane part).

cycles did not exceed 0·2 times the standard deviation. The scattering curves employed are those of Berghuis, 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 sulphur. Fig. 1 shows the atomic numbering used. The positional parameters of the heavy atoms are listed in Table 2, the coordinates and isotropic B values of the hydrogen atoms in Table 3. The 'observed' U_{ij} values together with the 'calculated' U_{ij} values (see next section) are to be found in Table 4. The observed and calculated structure factors are given in Table 5.

Thermal motion

The thermal motion of the molecule was analysed using a modification (Rutten, 1971) of Schomaker & Trueblood's (1968) *TLS* program. Different groups of atoms contributing to the assumed rigid body were inspected, omitting the hydrogen atoms. For the tosyl moiety – carbon atoms C(1′) to C(7′) – the resulting tensors are listed in Table 6(*a*). For the cyclohexane moiety, the model without the methyl carbon atoms and including O(1) gave the best fit between observed and calculated U_{ij} values (Table 4); the resulting thermal parameters are listed in Table 6(*b*). Inspection of these models with Hamilton's (1965) ratio test indicates that the combined rigid-body model cannot be rejected on a 2·5% significance level (Table 7). The direction of the largest principal libration axis L_1 of the rigid-body model II (cyclohexane moiety) almost coincides with the directions of the C(2)–C(7) and C(5)–C(11) bonds (the angles between L_1 and these bonds are 5 and 7° respectively), as might be expected in the case of a torsional libration of the t-butyl groups.

Description of the structure

The bond distances between the heavy atoms are listed in Table 8. The estimated standard deviations are 0·002 Å for S–O, 0·003 Å for S–C, 0·004 Å for O–C and

Table 5. *Observed and calculated structure factors*

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 5 (*cont.*)

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

0·006 Å for all other heavy-atom distances. The carbon–hydrogen distances range from 0·93 to 1·08 Å, resulting in an average value of 0·98 Å with a standard deviation of 0·04 Å. The valency angles between the heavy atoms are listed in Table 9, their standard deviation is 0·3°. The mean values of the C–C–H and H–C–H angles (110 and 108°) agree quite well with previous observations made by Portheine, Romers & Rutten (1972) (110 and 106°) and by Braun, Hornstra & Leenhouts (1969) (109 and 108°). Finally, some torsional angles involving heavy atoms are to be found in Table 10; their estimated standard deviation is 0·5°.

The cyclohexane moiety

The mean torsional angle in the cyclohexane ring of BCT is 55·1°, indicating a slight flattening of the ring compared with cyclohexane itself, for which Geise, Buys & Mijlhoff (1971) report a value of 55·9°. Fig. 2 shows Newman projections along the central carbon–carbon bonds of the t-butyl groups. It is seen that the C(2) and C(5) t-butyl groups are twisted away from the staggered position by −12 and +7° respectively. This off-staggering of the t-butyl groups, accompanied by twisting of their methyl groups (Fig. 3), is reflected in an asymmetric distortion of the ring, in agreement with the force-field predictions. The exocyclic bond angles at C(2) and C(5) are increased to 113·2–117·7°, indicating the presence of non-bonded strain in this region. Since this strain is expected to originate mainly from short H···H contacts, a closer examination of these contacts might be revealing (Fig. 4). Table 11 lists the relevant H···H distances in BCT, some related t-butyl compounds and 1-biadamantane (Alden, Kraut & Traylor, 1968). Some of these distances are well below the accepted van der Waals distance, thus indicating the presence of non-bonded strain in this

Table 6. *Rigid-body thermal parameters of BCT*

E.s.d.'s are given in parentheses. Axes of reference are the directions **a**, **c** × **a** and **c***.

(*a*) Rigid-body model I (tosyl moiety)

Consisting of atoms C(1′) to C(7′); r.m.s. deviation in U_{ij} = 0·0021 Å²

Principal axes of reduced $\bar{\mathbf{T}}$

	R.m.s. amplitude (Å²)	Direction cosines		
*T*1	0·27	−0·045	0·478	−0·878
*T*2	0·24	−0·716	−0·628	−0·305
*T*3	0·19	−0·697	0·614	0·370

Tensor (10³ Å²)	11	22	33	12	23	13
	47·8	53·4	66·4	9·6	6·5	−11·0
	(2·4)	(1·6)	(1·6)	(1·8)	(1·7)	(1·4)

Principal axes of $\bar{\mathbf{L}}$

	R.m.s. amplitude (deg²)	Direction cosines		
*L*1	8·3	−0·358	−0·917	0·176
*L*2	5·3	−0·843	0·398	0·362
*L*3	3·0	−0·402	−0·019	−0·916

Tensor (deg²)	11	22	33	12	23	13
	30·4	61·8	13·5	12·9	−9·6	− 6·7
	(4·0)	(6·7)	(3·1)	(4·2)	(2·2)	(3·3)

(*b*) Rigid-body model II (cyclohexane moiety)

Consisting of atoms C(1) to C(7) plus C(11) and O(1); r.m.s. deviation in U_{ij} = 0·0024 Å²

Principal axes of reduced $\bar{\mathbf{T}}$

	R.m.s. amplitude (Å²)	Direction cosines		
*T*1	0·24	−0·949	−0·314	−0·040
*T*2	0·22	−0·310	0·899	0·309
*T*3	0·20	−0·061	0·305	−0·950

Tensor (10³ Å²)	11	22	33	12	23	13
	56·7	49·9	40·2	2·3	−0·4	3·3
	(1·2)	(1·4)	(2·0)	(1·1)	(1·3)	(1·3)

Principal axes of $\bar{\mathbf{L}}$

	R.m.s. amplitude (deg²)	Direction cosines		
*L*1	5·0	0·908	0·330	−0·261
*L*2	3·2	0·164	0·292	0·942
*L*3	1·7	0·387	−0·898	0·211

Tensor (deg²)	11	22	33	12	23	13
	21·4	6·0	10·9	7·0	−4·1	0·1
	(4·5)	(2·3)	(1·6)	(1·5)	(2·5)	(1·5)

Table 7. R_w *ratio test*

	(*a*) No constraints	(*b*) Model I+II
R_w	0·0485	0·0500
n	1897	1897
m	362	266
b	0	96

$R_w(b)/R_w(a) = 1{\cdot}031$

$R_{b,n-m,\alpha} = R_{96,1897-374,\cdot025} = 1{\cdot}031$

The symbols are explained in Hamilton (1965).

region of the molecule. The calculated amount of 'strain' caused by these short H···H contacts differs in various force fields, due to a different balance of forces (Altona & Faber, 1973). More detailed information (*e.g.* from neutron diffraction) might provide an important check on the quality of these fields.

The bond distances in the cyclohexane ring range from 1·519 to 1·538 Å. The mean value (1·528 Å) is the same as the value obtained from an electron diffraction experiment on cyclohexane (Geise, Buys & Mijlhoff, 1971). Since the standard deviation in the C–C bond lengths is 0·006 Å, the individual deviations from the mean value cannot be regarded as significant.

The average value of the quaternary carbon–methyl bond distances is 1·541 Å, the bond lengths of the two central [C(2)–C(7) and C(5)–C(11)] bonds are 1·552 and 1·545 Å respectively. These agree fairly well with the corresponding values (1·537 for quaternary carbon–methyl, 1·554 Å for the central bond) found by de Graaff, Giesen, Romers & Rutten (1972), as well as with the average values (1·536 and 1·544 Å, uncorrected for thermal motion) of the available X-ray data on this type of t-butyl compound. The stretching of the central C–C bond can be related to the strain induced by the short H···H contacts mentioned above. It is of interest to compare these values with the result of our force-field calculations: quaternary carbon–methyl 1·541 and central C–C 1·567 Å respectively. The former value agrees well, the latter is evidently too large by 0·015–0·020 Å. This effect is probably due to an overestimation of the contribution of the H···H nonbonded interactions in the force-field employed (Altona & Faber, 1973). It should be noted that in two X-ray determinations (Parthasarathy, Ohrt, Kagan & Fiaud, 1972; Cook, Glick, Rigau & Johnson, 1971) no stretching of the central bond is observed, the bond lengths being reported as 1·537 and 1·515 Å (uncorrected for thermal motion) respectively.

Let us next consider the thermal parameters of the t-butyl groups. The direction of the largest principal axes of the thermal ellipsoids (Fig. 5) indicates a torsional libration of the t-butyl groups, but it appears desirable to obtain a more quantitative picture. Therefore, we calculated the r.m.s. amplitude of the t-butyl methyl carbon atoms in the direction perpendicular to the quaternary carbon–methyl bond and the central C–C bond. Assuming the motions of the ring and the t-butyl groups to be fully uncoupled, the following r.m.s. values are found from the observed thermal parameters: C(8) 0·36, C(9) 0·34, C(10) 0·30, C(12) 0·36, C(13) 0·32 and C(14) 0·30 Å. This corresponds to a r.m.s. torsional motion of 13°. If the phases of the

Table 8. *Bond lengths* (Å) *in BCT*

u and *c* refer to values uncorrected and corrected for thermal motion.

	u	*c*		*u*	*c*
O(1)—C(1)	1·484	1·490 (*a*)	C(11)–C(13)	1·527	1·537 (*b*)
C(1)—C(2)	1·522	1·528 (*a*)	C(11)–C(14)	1·541	1·551 (*b*)
C(2)—C(3)	1·532	1·538 (*a*)	S———O(1)	1·563	1·575 (*c*)
C(3)—C(4)	1·521	1·525 (*a*)	S———O(2)	1·421	1·431 (*c*)
C(4)—C(5)	1·530	1·534 (*a*)	S———O(3)	1·430	1·436 (*c*)
C(5)—C(6)	1·519	1·526 (*a*)	S———C(1′)	1·743	1·756 (*c*)
C(6)—C(1)	1·515	1·519 (*a*)	C(1′) —C(2′)	1·381	1·396 (*d*)
C(2)—C(7)	1·548	1·552 (*a*)	C(2′) —C(3′)	1·373	1·380 (*d*)
C(5)—C(11)	1·542	1·545 (*a*)	C(3′) —C(4′)	1·378	1·393 (*d*)
C(7)—C(8)	1·527	1·537 (*b*)	C(4′) —C(5′)	1·383	1·397 (*d*)
C(7)—C(9)	1·531	1·541 (*b*)	C(4′) —C(7′)	1·493	1·501 (*d*)
C(7)—C(10)	1·532	1·542 (*b*)	C(5′) —C(6′)	1·365	1·374 (*d*)
C(11)–C(12)	1·526	1·536 (*b*)	C(6′) —C(1′)	1·380	1·394 (*d*)

(*a*) Taken from rigid-body model II.
(*b*) The quaternary carbon–methyl distances were corrected with an *average* value from rigid-body model II.
(*c*) Approximate corrections from a rigid-body calculation including atoms S, O(1), O(2), O(3) and C(1′).
(*d*) From rigid-body model I.

The corrections were made according to Cruickshank (1956), using a peak-breadth parameter of 0·10 Å.

Table 9. *Bond angles involving heavy atoms in BCT*

O(1)–C(1)–C(2)	107·9°	C(2)—C(7)—C(10)	110·0°	O(2) -S——O(3)	118·8°
O(1)–C(1)–C(6)	108·4	C(8)—C(7)—C(9)	107·9	O(2) -S——C(1′)	109·1
C(2)–C(1)–C(6)	112·6	C(8)—C(7)—C(10)	109·4	O(3) -S——C(1′)	108·2
C(1)–C(2)–C(3)	109·1	C(9)—C(7)—C(10)	107·1	S——C(1′)-C(2′)	120·8
C(1)–C(2)–C(7)	117·7	C(5)—C(11)-C(12)	111·9	S——C(1′)-C(6′)	119·5
C(3)–C(2)–C(7)	115·0	C(5)—C(11)-C(13)	110·0	C(2′)-C(1′)-C(6′)	119·6
C(2)–C(3)–C(4)	112·7	C(5)—C(11)-C(14)	108·4	C(1′)-C(2′)-C(3′)	119·4
C(3)–C(4)–C(5)	111·2	C(12)–C(11)–C(13)	109·4	C(2′)-C(3′)-C(4′)	122·3
C(4)–C(5)–C(6)	108·4	C(13)–C(11)–C(14)	107·1	C(3′)-C(4′)-C(5′)	116·8
C(4)–C(5)–C(11)	115·9	C(12)–C(11)–C(14)	108·4	C(3′)-C(4′)-C(7′)	121·1
C(6)–C(5)–C(11)	113·2	C(1)—O(1)—S	121·5	C(5′)-C(4′)-C(7′)	122·0
C(5)–C(6)–C(1)	114·0	O(1)—S——O(2)	104·3	C(4′)-C(5′)-C(6′)	122·3
C(2)–C(7)–C(8)	113·2	O(1)—S——O(3)	109·8	C(5′)-C(6′)-C(1′)	119·6
C(2)–C(7)–C(9)	109·0	O(1)—S——C(1′)	105·9		

Table 10. *Some torsional angles involving heavy atoms in BCT*

C(6)–C(1)–C(2) -C(3)	51·9°	O(1) -S——C(1′)-C(6′)	−85·0°
C(1)–C(2)–C(3) -C(4)	−54·7	O(2) -S——C(1′)-C(6′)	26·8
C(2)–C(3)–C(4) -C(5)	58·5	O(3) -S——C(1′)-C(6′)	157·3
C(3)–C(4)–C(5) -C(6)	−56·1	S——C(1′)-C(2′)-C(3′)	176·5
C(4)–C(5)–C(6) -C(1)	54·9	C(6′)-C(1′)-C(2′)-C(3′)	0·0
C(5)–C(6)–C(1) -C(2)	−54·6	C(1′)-C(2′)-C(3′)-C(4′)	−1·5
S——O(1)–C(1) -C(2)	−138·3	C(2′)-C(3′)-C(4′)-C(5′)	2·6
S——O(1)–C(1) -C(6)	99·5	C(2′)-C(3′)-C(4′)-C(7′)	−176·0
O(2)-S——O(1) -C(1)	161·3	C(3′)-C(4′)-C(5′)-C(6′)	−2·4
O(3)-S——O(1) -C(1)	33·0	C(7′)-C(4′)-C(5′)-C(6′)	176·2
C(1′)-S——O(1) -C(1)	−83·6	C(4′)-C(5′)-C(6′)-C(1′)	1·0
O(1)-S——C(1′)-C(2′)	98·6	C(5′)-C(6′)-C(1′)-C(2′)	0·2
O(2)-S——C(1′)-C(2′)	−149·6	C(5′)-C(6′)-C(1′)-S	−176·3
O(3)-S——C(1′)-C(2′)	−19·1		

motions are partially coupled this value might range anywhere from 4° (in phase) to 23° (180° phase shift); these values are found by subtracting (adding) the r.m.s. amplitude from the calculated thermal parameters from (to) the observed ones. A torsional libration of 13° lies in the same order of magnitude as the r.m.s. amplitude calculated from the shape of the potential energy curve in our force-field calculations. It appears however, that this complex problem cannot be successfully tackled without the aid of spectroscopic methods. Further work in this direction is in progress.

The tosyl moiety

The geometry of this part of the molecule is consistent with earlier observations (Johnson, Cheer, Schaefer, James & Moore, 1972; Johnson, Schaefer, James & McConnell, 1971; Altona & Sundaralingam, 1972; James & McConnell, 1971), as far as bond lengths and bond angles are concerned. The C(2')–C(3') and C(5')–C(6') bonds are shortened (1·380 and 1·374 Å), compared to a mean value of 1·395 Å for the other four bonds. The benzene ring exhibits a small but significant deviation from planarity, C(1'), C(2') and C(4') lying respectively 0·005, 0·001 and 0·013 Å above the least-squares plane through all six atoms, C(3'), C(5') and C(6') lying respectively 0·010, 0·008 and 0·001 Å below this plane. The methyl carbon atom is lying 0·090 Å below the plane.

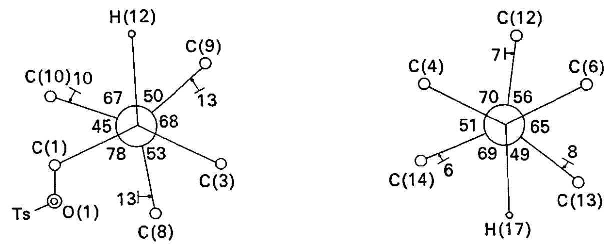

Fig. 2. Newman projections along (*a*) C(2)–C(7) (average twist angle −12°) and (*b*) C(5)–C(11) (average twist angle 7°).

The tosyl group adopts a folded conformation with the O(1)–S bond perpendicular to the plane of the benzene ring, a situation similar to that in 2-*exo*-norbor-

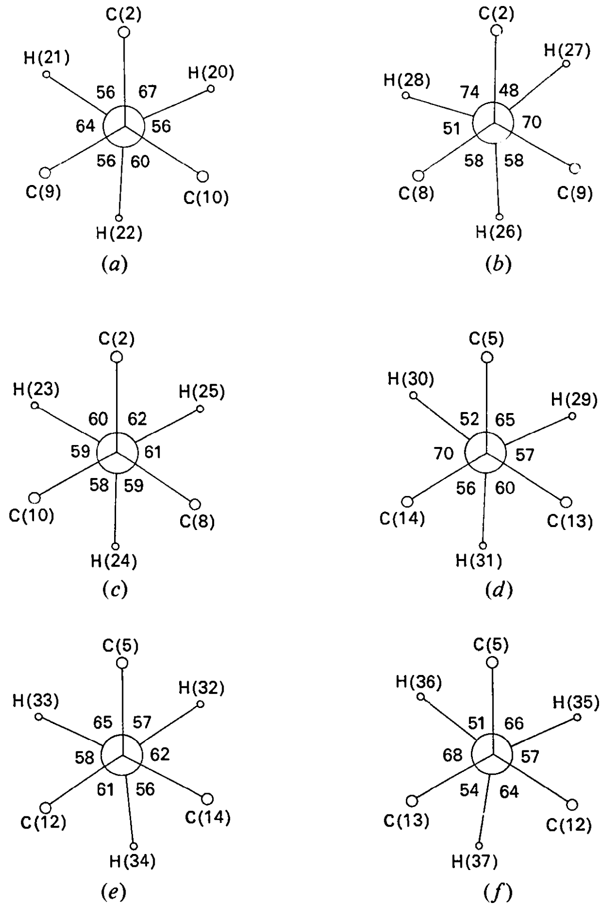

Fig. 3. Newman projections along the following C–C bonds in the t-butyl groups (with average twist angles in parentheses): (*a*) C(7)–C(8) (4°), (*b*) C(7)–C(10) (−8°), (*c*) C(7)–C(9) (0°), (*d*) C(11)–C(12) (5°), (*e*) C(11)–C(13) (−3°), (*f*) C(11)–C(14) (6°).

Table 11. *Short* H···H *distances in BCT and some related compounds*

The atomic numbering used is depicted in Fig. 4.

	t-Butyl twist	16–30	19–29	15–35	18–33	17–36	17–32
This work*	+7	2·30	2·23	2·21	2·20	2·45	2·36
This work†	−12	2·37	—	2·29	2·31	2·38	2·54
K	+8	2·22	2·36	2·17	2·14	2·45	2·54
POKF	—	2·17	2·18	—	2·07	—	—
JSJC	−1·4	2·25	2·31	2·21	2·25	2·55	2·35
JCSJM	+1·6	2·28	2·31	2·11	2·13	2·42	2·46
JCSJM	+1·4	2·31	2·30	2·16	2·07	2·39	2·37
GGRR	+2·2	2·31	2·25	2·17	2·17	2·47	2·49
CGRJ	−2·1	2·73	2·23	2·39	2·73	2·34	2·48
LMPG	0	2·34	2·34	2·07	2·07	2·44	2·44
AKT	—	2·14	2·16	2·14	2·14	—	—

K: van Koningsveld (1972); POKF: Parthasarathy, Ort, Kagan & Fiaud (1972); JSJC: Johnson, Schaefer, James & McConnell (1972); JCSJM: Johnson, Cheer, Schaefer, James & Moore (1972); GGRR: de Graaff, Giesen, Rutten & Romers (1972); CGRJ: Cook, Glick, Rigau & Johnson (1971); LMPG: Lectard, Metras, Petrissans & Gaultier (1971); AKT: Alden, Kraut & Traylor (1968).

* C(5) t-butyl group.
† C(2) t-butyl group.

nanol toluene-p-sulphonate (Altona & Sundaralingam, 1972). It is of interest to note that the S–O(1) bond comes fairly close to eclipsing the C(1)–H(11) bond, the torsional angle S–O(1)–C(1)–H(11) being $-19°$. The possibility cannot be entirely excluded that this behaviour of the tosyl group may perhaps be responsible for part of the distortion in the molecule.

The packing arrangement

A projection of the structure is shown in Fig. 6, some of the shortest intermolecular heavy atom distances are indicated. From Table 12 it can be seen that the shortest intermolecular contacts are found along the short c axis. The number of intermolecular H···H contacts below 3 Å is 22, the shortest being 2·52 Å. Both t-butyl groups occur in hydrocarbon-like surroundings; no carbon–carbon contact shorter than 3·95 Å is found, suggesting that the main forces determining the conformation in the solid are intramolecular rather than intermolecular (packing forces) in this case.

In conclusion, the force-field predictions are substantiated by the X-ray analysis of BCT. Furthermore, no other known investigations on t-butylcyclohexane compounds disagree with these predictions, perhaps with the exception of *cis*-4-t-butyl cyclohexane-1-carboxylic acid (van Koningsveld, 1972) where a symmetrically substituted ring exhibits a t-butyl twist of 8°. However, this unexpected feature might be related to the eclipsing of a carbonyl oxygen atom with the C^{β} atom in this compound; this seems to be more than an accidental package effect, since this eclipsing is known to occur in many carbonyl compounds of this type (van Koningsveld, 1972). The existence of a torsional libration of t-butyl groups seems very likely. A better quantization of this interesting phenomenon can perhaps be obtained by combining the results of spectroscopic investigations with those of diffractometric work.

We gratefully acknowledge the help of Dr G. Verschoor with the diffractometric work, which was carried out in the laboratory of Dr C. Romers.

Table 12. *Shortest intermolecular distances*

C–C, C–O, O–O below 4 Å, O–H below 3 Å. Code for symmetry-related molecules:

Superscript	Molecule at		
None	x	y	z
i	x	y	$1+z$
ii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
iv	x	y	$-1+z$
v	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
vi	$1-x$	$-y$	$1-z$

O(2)–C(6)	(i)	3·20 Å	O(2)–H(7)	(ii)	2·62 Å
O(2)–C(1)	(i)	3·42	O(2)–H(11)	(i)	2·78
O(2)–C(7′)	(ii)	3·48	O(2)–H(19)	(i)	2·83
O(2)–C(2′)	(i)	3·60	O(2)–H(18)	(i)	2·87
O(2)–O(3)	(i)	3·93	O(2)–H(1)	(i)	2·90
O(3)–C(5′)	(iii)	3·39	O(3)–H(3)	(iii)	2·52
O(3)–C(7′)	(ii)	3·57	O(3)–H(8)	(ii)	2·80
O(3)–C(7′)	(iii)	3·95			
C(1′)–C(13)	(ii)	3·95			
C(3′)–C(6′)	(iv)	3·85			
C(7′)–C(9)	(v)	3·97			
C(3)–C(3)	(vi)	3·86			
C(5)–C(12)	(i)	3·97			

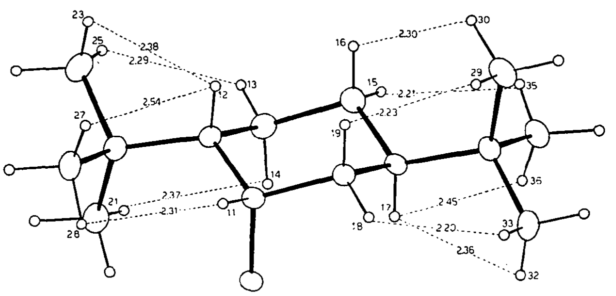

Fig. 4. *ORTEP* plot (Johnson, 1967) showing some short intramolecular H···H contacts.

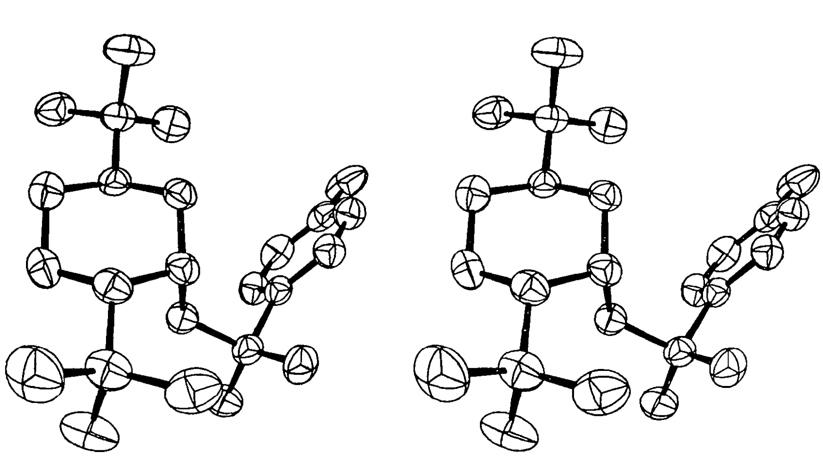

Fig. 5. Stereoscopic *ORTEP* plot (Johnson, 1967) of BCT.

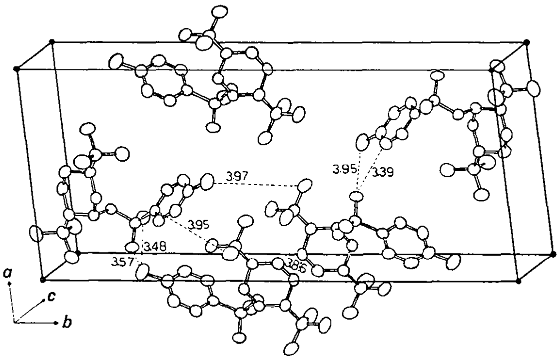

Fig. 6. *ORTEP* plot (Johnson, 1967) of the crystal structure of BCT, showing some short intermolecular distances.

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The Crystal Structure of Orthorhombic Antimony Trioxide, Sb_2O_3

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The crystal structure of orthorhombic Sb_2O_3 has been reinvestigated with three-dimensional single-crystal X-ray diffractometer data. The crystals are orthorhombic, space group *Pccn*, with $a=4{\cdot}911$, $b=12{\cdot}464$ and $c=5{\cdot}412$ Å. The structure was refined by full-matrix least-squares with 340 independent reflexions to $R=0{\cdot}032$. The idealized geometry of the antimony coordination can be described as a tetrahedron with oxygens at three corners, at the approximately equal distances 1·98, 2·02 and 2·02 Å, and the lone pair of electrons of antimony at the fourth corner. The coordination polyhedra are joined by sharing corners to form double infinite chains with the lone pairs pointing out from the chains.

Introduction

The structures of solid α- and β-Bi_2O_3 have recently been redetermined and refined (Malmros, 1970; Aurivillius & Malmros, 1972). Within this research programme, and also in order to obtain accurate antimony-(III)-oxygen distances, a refinement of orthorhombic Sb_2O_3 has been undertaken. The results of this in-