

A Neutron Diffraction Study of *trans*-4-*t*-Butylcyclohexyl Toluene-*p*-sulphonate, C₁₇H₂₆SO₃

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A neutron diffraction study of *trans*-4-*t*-butylcyclohexyl toluene-*p*-sulphonate has been carried out in order to investigate possible distortion of the molecule arising from steric effects produced by the *t*-butyl group. An assessment is made of the differences in positional and thermal parameters, bond distances and angles between the results of this and a parallel X-ray analysis [Johnson, Cheer, Schaeffer, James, & Moore, *Tetrahedron* (1972), **28**, 2893–2900]. A final residual of 8.6% based on F_{obs}^2 with a full data set [4.4% on F with the data set restricted to $I > 3\sigma(I)$] was obtained.

Introduction

A widely accepted method of locking the mobile cyclohexane system into one of two chair conformations has been the use of the *t*-butyl group (Winstein & Holness, 1955). Any comparison of data on cyclohexane systems locked into two different conformations relies on assumptions that the cyclohexane ring is unaltered by the different substitutions. Experiments by Wolfe & Campbell (1967) and Shah-Malak & Utley (1967) indicated discrepancies in this assumption. Computer calculations were carried out by Altona & Sundaralingam (1970) to obtain a quantitative description of the conformation of substituted cyclohexanes. A remarkable feature of the results for *t*-butylcyclohexane is the large angle of twist of the *t*-butyl group accompanied by an asymmetrical distortion of the ring.

This neutron study forms part of a comprehensive crystallographic study on *t*-butyl substituted cyclohexanes to investigate the ring flattening and especially the steric hindrance between the hydrogens of the *t*-butyl group and those attached to the chair. Neither

this nor the related X-ray study [residual 4.7% on F with $I > 3\sigma(I)$] carried out by the authors and published jointly with the results of an independent study [residual 8.0% on F with $I > 3\sigma(I)$] executed at the University of Arizona (Johnson, Cheer, Schaeffer, James & Moore, 1972), revealed the predicted angle of twist of the *t*-butyl group though this study reveals some distortion of the *t*-butyl hydrogens.

Crystal data

trans-4-*t*-Butyl-cyclohexyl toluene-*p*-sulphonate, C₁₇H₂₆O₃S, monoclinic, space group $P2_1/c$. $a = 11.985$ (5), $b = 10.466$ (5), $c = 14.643$ (5) Å, $\beta = 107.640$ (5)°. $D_c = 1.183$ g cm⁻³. Wavelength 1.18 Å. Absorption coefficient = 2.30 ± 0.01 cm⁻¹ (measured by transmission).

Experimental

The crystal supplied by R. J. L. Martin and E. Parkinson (Department of Organic Chemistry, U.N.S.W.) was initially cut in two along the a^*b^* plane using an air abrasive unit. The better half was mounted on 1 mm thin-walled S/S tubing using Araldite and cut into a cylindrical shape (axis along a^*). The final dimensions of the crystal are given in Table 1.

Table 1. Dimensions of the crystal

Diameter of cylinder	0.678 cm
Largest length of cylinder	0.457
Shortest length of cylinder	0.368
Weight of cylinder	179.4 mg

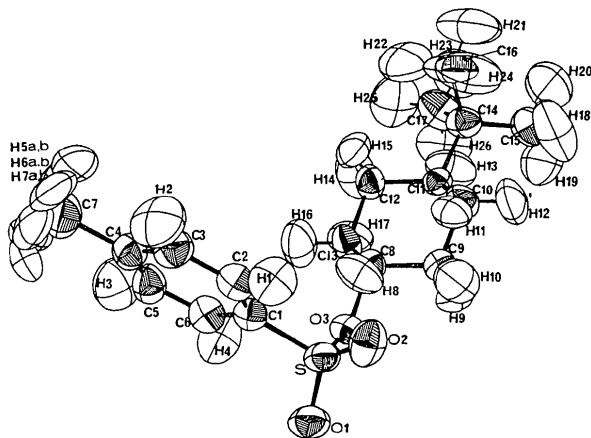


Fig. 1. A view of the molecule of *trans*-4-*t*-butylcyclohexyl toluene-*p*-sulphonate illustrating thermal vibration ellipsoids.

Integrated intensities were recorded for $2\theta < 72^\circ$ using an AINSE four-circle computer-controlled US1 diffractometer on the HIFAR reactor of the Australian Atomic Energy Commission, Lucas Heights. The monochromatic beam was obtained using the (111) face of a copper crystal. A θ - 2θ scan technique was used and standard reflexions were measured after every 25 reflexion measurements. To determine systematic errors and to check the absorption corrections and crystal or instrumental drift, 1616 reflexions were meas-

Table 2. *Positional and thermal parameters for X-rays (line 1) and neutrons (line 2)*

Positional parameters for S atoms are $\times 10^5$, for other atoms $\times 10^4$. The thermal parameters ($\times 10^4$) are expressed in the form: $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)]$; only neutron values are given for hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
S	604 (4) 606 (60)	6063 (6) 5835 (80)	71035 (4) 71123 (50)	96·1 (4) 59 (7)	110·4 (6) 95 (9)	71·2 (3) 60 (5)	-11 (4) -6 (6)	28·3 (3) 19 (5)	-14·8(4) -16 (6)
O(1)	1241 (1) 1245 (4)	268 (2) 264 (5)	7604 (1) 7604 (3)	83 (1) 75 (4)	184 (3) 163 (6)	98 (1) 80 (3)	-9 (1) -17 (4)	20 (1) 20 (3)	-35 (1) -35 (4)
O(2)	-167 (1) -170 (4)	1674 (2) 1675 (4)	6469 (1) 6465 (3)	166 (2) 142 (5)	111 (2) 94 (5)	90 (1) 72 (3)	-13 (2) -17 (4)	59 (1) 50 (3)	3 (1) -1 (3)
O(3)	-452 (1) -456 (3)	-636 (1) -635 (4)	6543 (1) 6542 (3)	90 (1) 73 (3)	99 (2) 85 (4)	67 (1) 56 (2)	8 (1) 11 (3)	10 (1) 9 (2)	-15 (1) -14 (3)
C(1)	-743 (2) -742 (3)	795 (2) 788 (3)	7916 (1) 7914 (2)	86 (1) 69 (3)	95 (2) 64 (4)	63 (1) 50 (2)	-13 (1) -8 (3)	17 (1) 14 (2)	-12 (1) -8 (2)
C(2)	-1275 (2) -1280 (3)	1943 (2) 1945 (4)	7966 (2) 7964 (3)	99 (2) 86 (3)	98 (3) 77 (4)	73 (1) 59 (2)	-6 (2) -7 (3)	19 (1) 16 (2)	-11 (1) -4 (2)
C(3)	-1858 (2) -1863 (3)	2109 (3) 2121 (4)	8640 (2) 8637 (3)	105 (2) 90 (3)	137 (3) 110 (5)	80 (2) 70 (3)	-4 (2) 17 (4)	23 (1) 29 (2)	-28 (2) -28 (2)
C(4)	-1915 (2) -1910 (3)	1136 (3) 1131 (4)	9265 (2) 9263 (2)	101 (2) 86 (4)	170 (4) 170 (6)	68 (1) 52 (6)	-33 (2) -32 (4)	23 (1) 21 (2)	-28 (2) -29 (3)
C(5)	-1379 (2) -1373 (3)	-9 (3) -5 (4)	9188 (2) 9196 (4)	135 (2) 115 (4)	149 (4) 125 (5)	72 (2) 56 (2)	-38 (2) -25 (4)	29 (1) 28 (3)	2 (2) -1 (3)
C(6)	-796 (2) -789 (3)	-200 (3) -208 (4)	8528 (2) 8525 (3)	128 (2) 103 (4)	107 (3) 80 (4)	75 (2) 64 (2)	-10 (2) -2 (3)	27 (1) 22 (3)	0 (2) -3 (3)
C(7)	-2541 (4) -2556 (12)	1338 (6) 1367 (15)	10001 (3) 9999 (8)	154 (4) 120 (11)	307 (9) 280 (16)	88 (2) 76 (6)	-42 (5) -70 (12)	59 (2) 45 (8)	-49 (4) -50 (9)
C(8)	-1656 (2) -1658 (3)	-647 (2) -643 (3)	5884 (1) 5888 (2)	82 (1) 73 (3)	100 (2) 76 (4)	62 (1) 46 (2)	7 (2) 1 (3)	20 (1) 16 (2)	-7 (1) -4 (2)
C(9)	-1617 (2) -1626 (3)	-479 (3) -479 (5)	4882 (2) 4878 (2)	91 (2) 68 (4)	163 (4) 150 (6)	64 (1) 53 (2)	-19 (2) -12 (4)	21 (1) 20 (2)	14 (2) 9 (3)
C(10)	-2856 (2) -2850 (3)	-623 (3) -623 (5)	4175 (2) 4180 (3)	97 (2) 85 (4)	153 (4) 138 (6)	64 (1) 51 (3)	-11 (2) -24 (4)	15 (1) 6 (2)	20 (2) 23 (3)
C(11)	-3401 (2) -3392 (3)	-1912 (2) -1913 (6)	4283 (1) 4284 (3)	85 (2) 94 (4)	119 (3) 163 (7)	60 (1) 47 (2)	8 (2) -47 (5)	25 (1) 19 (3)	-11 (1) -1 (3)
C(12)	-3403 (2) -3413 (3)	-2057 (3) -2062 (4)	5319 (2) 5318 (2)	119 (2) 64 (3)	152 (4) 99 (4)	67 (1) 48 (2)	-36 (2) 5 (3)	32 (1) 20 (2)	-5 (2) -8 (2)
C(13)	-2182 (2) -2172 (4)	-1903 (3) -1895 (4)	6030 (2) 6031 (3)	131 (2) 121 (5)	136 (3) 114 (5)	56 (1) 46 (2)	-28 (2) -35 (4)	21 (1) 13 (3)	5 (2) 6 (3)
C(14)	-4611 (2) -4606 (3)	-2157 (3) -2158 (4)	3517 (2) 3516 (2)	91 (2) 76 (3)	138 (3) 121 (5)	73 (1) 62 (2)	1 (2) -8 (3)	20 (1) 13 (2)	-24 (2) -26 (3)
C(15)	-4489 (3) -4490 (5)	-2097 (5) -2127 (8)	2519 (3) 2521 (3)	142 (3) 119 (6)	258 (7) 240 (10)	69 (2) 51 (3)	-11 (3) -13 (6)	11 (2) 11 (3)	-23 (3) -27 (4)
C(16)	-5067 (3) -5078 (6)	-3476 (4) -3462 (5)	3669 (3) 3654 (4)	151 (3) 139 (6)	182 (5) 134 (7)	107 (2) 92 (4)	-47 (3) -36 (5)	23 (2) 3 (4)	-38 (3) -26 (4)
C(17)	-5514 (3) -5511 (5)	-1168 (4) -1162 (8)	3590 (3) 3583 (6)	93 (2) 69 (5)	219 (6) 191 (8)	139 (3) 124 (5)	27 (3) 38 (5)	4 (2) -8 (4)	-64 (3) -69 (6)
H(1)	-1229 (22) -1234 (7)	2551 (33) 2734 (7)	7502 (21) 7487 (6)						
H(2)	-2263 (24) -2254 (8)	2848 (34) 3009 (10)	8701 (21) 8699 (6)	145 (8)	84 (8)	101 (6)	28 (7)	47 (5)	20 (6)
H(3)	-1393 (27) -1432 (9)	-658 (36) -771 (10)	9529 (24) 9688 (8)	160 (10)	160 (12)	128 (7)	40 (9)	60 (6)	-34 (7)
H(4)	-494 (27) -344 (8)	-939 (36) -1120 (8)	8490 (24) 8477 (6)	210 (13)	190 (14)	121 (7)	-20 (11)	68 (8)	42 (9)
*H(5A)	-2050 (70) -1800 (40)	1550 (120) 1360 (150)	10580 (70) 10700 (40)	190 (11)	103 (9)	117 (7)	42 (8)	72 (7)	27 (6)
*H(5B)	-2140 (60) -2300 (40)	500 (100) 670 (70)	10550 (70) 10560 (40)	130 (48)	120 (23)	40 (14)	60 (91)	0 (26)	-70 (50)
*H(6A)	-3290 (60) -2920 (50)	2100 (90) 2080 (90)	9760 (60) 9960 (40)	90 (30)	700 (100)	70 (20)	20 (4)	20 (2)	80 (4)
*H(6B)	-2360 (70) -3450 (50)	2240 (90) 1480 (40)	10400 (70) 9570 (30)	80 (47)	40 (11)	140 (39)	-70 (51)	70 (34)	-150 (60)
*H(7A)	-2690 (80) -3180 (50)	550 (100) 660 (90)	10040 (70) 10000 (60)	70 (40)	510 (40)	90 (30)	-20 (4)	40 (3)	50 (3)
*H(7B)	-3130 (70) -2310 (60)	1370 (110) 70 (30)	10200 (70) 880 (40)	240 (42)	310 (41)	140 (28)	-160 (44)	170 (32)	-70 (30)
H(8)	-2055 (21) -2118 (6)	-20 (29) -157 (8)	6006 (18) 6100 (5)	140 (50)	300 (50)	110 (30)	-70 (4)	70 (3)	-120 (4)
H(9)	-1232 (22) -1272 (7)	440 (34) 438 (10)	4786 (19) 4809 (6)	93 (7)	150 (10)	87 (5)	35 (7)	15 (5)	-38 (6)

* $\frac{1}{2}$ hydrogens.

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
H(10)	-1136 (23)	-1253 (35)	4797 (21)						
	-1045 (6)	-1230 (0)	4732 (5)	70 (6)	290 (20)	83 (5)	15 (9)	33 (5)	-4 (8)
H(11)	-2902 (21)	-604 (32)	3531 (21)						
	-2812 (7)	-497 (10)	3549 (6)	155 (9)	270 (20)	55 (5)	-50 (10)	12 (5)	52 (8)
H(12)	-3355 (24)	49 (33)	4276 (20)						
	-3401 (7)	138 (9)	4286 (6)	110 (8)	130 (10)	113 (7)	23 (8)	6 (6)	7 (7)
H(13)	-2854 (24)	-2523 (35)	4181 (20)						
	-2827 (6)	-2625 (8)	4148 (5)	98 (7)	150 (10)	79 (5)	41 (7)	10 (5)	-28 (6)
H(14)	-3964 (21)	-1444 (29)	5422 (20)						
	-3981 (7)	-1394 (11)	5469 (6)	94 (7)	290 (20)	70 (5)	-20 (9)	39 (5)	-43 (8)
H(15)	-3699 (21)	-1444 (29)	5421 (20)						
	-3714 (9)	-3000 (10)	5422 (6)	210 (10)	190 (10)	87 (6)	-100 (10)	30 (7)	3 (8)
H(16)	-2229 (23)	-2007 (31)	6667 (22)						
	-2207 (7)	-1998 (9)	6756 (6)	180 (10)	230 (10)	70 (6)	-80 (10)	37 (6)	10 (7)
H(17)	-1652 (26)	-2549 (34)	5925 (21)						
	-1610 (8)	-2644 (9)	5945 (6)	138 (9)	110 (10)	100 (7)	13 (8)	-16 (6)	6 (3)
H(18)	-3095 (32)	-2827 (46)	2536 (24)						
	-3833 (12)	-2673 (16)	2432 (7)	190 (10)	470 (30)	84 (7)	50 (20)	59 (8)	-50 (10)
H(19)	-4127 (33)	-1404 (44)	2359 (26)						
	-4266 (13)	-1159 (13)	2324 (7)	300 (2)	230 (20)	76 (7)	-60 (20)	-3 (8)	29 (9)
H(20)	-5209 (29)	-2318 (41)	2084 (23)						
	-5337 (10)	-2278 (12)	1967 (7)	160 (10)	360 (20)	182 (6)	-50 (10)	-3 (7)	-40 (10)
H(21)	-5727 (32)	-3603 (39)	3169 (30)						
	-5863 (10)	-3660 (10)	3125 (8)	170 (10)	260 (20)	133 (9)	-100 (10)	3 (9)	-60 (10)
H(22)	-4360 (33)	-4069 (40)	3575 (28)						
	-4433 (11)	-4217 (11)	3666 (10)	200 (10)	140 (10)	180 (10)	-0 (10)	39 (9)	-30 (10)
H(23)	-5214 (30)	-3571 (42)	4291 (31)						
	-5293 (10)	-3549 (12)	4323 (10)	200 (10)	270 (10)	150 (10)	-130 (10)	60 (10)	-40 (10)
H(24)	-6218 (28)	-1309 (39)	3114 (29)						
	-6350 (9)	-1330 (11)	3058 (8)	98 (8)	300 (20)	166 (9)	40 (10)	-19 (8)	-80 (10)
H(25)	-5673 (25)	-1070 (44)	4199 (31)						
	-5653 (10)	-1155 (17)	4237 (10)	150 (10)	370 (3)	140 (10)	100 (10)	39 (9)	-60 (10)
H(26)	-5313 (33)	-357 (47)	3518 (34)						
	-5262 (10)	-223 (13)	3481 (12)	130 (10)	170 (1)	200 (10)	40 (10)	-2 (9)	-10 (10)

Table 3. Bond lengths (Å) with standard deviations in parentheses

	X-rays	Neutrons		X-rays	Neutrons
S—O(1)	1.427 (2)	1.424 (8)	S—O(2)	1.426 (2)	1.456 (9)
S—O(3)	1.561 (2)	1.547 (8)	S—C(1)	1.754 (2)	1.742 (8)
C(1)—C(2)	1.372 (3)	1.384 (4)	C(2)—C(3)	1.381 (4)	1.383 (5)
C(3)—C(4)	1.385 (4)	1.396 (5)	C(4)—C(5)	1.382 (4)	1.397 (5)
C(5)—C(6)	1.368 (4)	1.380 (5)	C(6)—C(1)	1.388 (3)	1.386 (4)
C(4)—C(7)	1.504 (4)	1.525 (10)	O(3)—C(8)	1.474 (2)	1.469 (5)
C(8)—C(9)	1.494 (3)	1.500 (5)	C(9)—C(10)	1.540 (3)	1.521 (5)
C(10)—C(11)	1.528 (4)	1.526 (5)	C(11)—C(12)	1.525 (3)	1.530 (5)
C(12)—C(13)	1.527 (3)	1.547 (6)	C(13)—C(8)	1.501 (4)	1.489 (5)
C(11)—C(14)	1.564 (3)	1.568 (5)	C(14)—C(15)	1.513 (4)	1.505 (6)
C(14)—C(16)	1.526 (4)	1.514 (7)	C(14)—C(17)	1.525 (4)	1.529 (6)
H(1)—C(2)	0.94 (3)	1.09 (1)	H(2)—C(3)	0.94 (3)	1.06 (1)
H(3)—C(5)	0.86 (4)	1.07 (1)	H(4)—C(6)	0.87 (4)	1.11 (1)
*H(5A)—C(7)	0.89 (8)	0.86 (9)	*H(6A)—C(7)	1.11 (8)	1.05 (4)
*H(7A)—C(7)	0.91 (12)	1.14 (5)	*H(5B)—C(7)	1.20 (10)	1.07 (4)
*H(6B)—C(7)	1.00 (10)	1.07 (7)	*H(7B)—C(7)	1.15 (10)	1.06 (4)
H(8)—C(8)	0.88 (3)	1.10 (1)	H(9)—C(9)	1.11 (3)	1.07 (1)
H(10)—C(9)	1.03 (4)	1.11 (1)	H(11)—C(10)	0.94 (3)	1.08 (1)
H(12)—C(10)	0.97 (3)	1.08 (1)	H(13)—C(11)	0.98 (4)	1.06 (1)
H(14)—C(12)	0.98 (3)	1.05 (1)	H(15)—C(12)	1.00 (3)	1.07 (1)
H(16)—C(13)	0.96 (3)	1.08 (1)	H(17)—C(13)	0.97 (4)	1.06 (1)
H(18)—C(15)	1.03 (4)	1.01 (2)	H(19)—C(15)	0.92 (4)	1.11 (2)
H(20)—C(15)	0.93 (3)	1.01 (1)	H(21)—C(16)	0.91 (4)	1.04 (1)
H(22)—C(16)	1.12 (4)	1.10 (2)	H(23)—C(16)	0.97 (4)	1.09 (2)
H(24)—C(17)	0.91 (3)	1.08 (2)	H(25)—C(17)	0.98 (4)	1.02 (2)
H(26)—C(17)	0.90 (5)	1.05 (2)			

* ½ hydrogens.

ured for two equivalent positions and 242 of these were measured more than twice.

The data were corrected for background and assigned standard deviations based on Poisson counting statistics. The values of I and $\sigma(I)$ were corrected for the Lorentz effect and for absorption, the cylindrical shape being approximated by 16 boundary planes in the absorption correction. The individual weights assigned to the reflexions used in the least-squares refinement were equal to the inverse of the estimated variance of the observation $\sigma^2(F^2)$ where

$$\sigma^2(F^2) = \sigma_1^2 F^2 + \sigma_2^2 F^2,$$

$\sigma_1 F^2$ = purely random error based on Poisson statistics and $\sigma_2 F^2$ = the systematic error = $(\alpha + \beta F^2 + \gamma F^4)^{1/2}$, where α, β, γ were obtained from a plot of $[\Delta F^2 / 0.7979 - \sigma_1^2(F^2)]$ versus F^2 since ΔF^2 was shown to be equal to $[0.7979\sigma^2(F^2)]$ by taking the mean deviation as $1/2\pi$ of one standard deviation from the mean. The best

quadratic fit computed for this graph gives the values of 0.2734, 0.00261 and 0.0000313 respectively for α, β and γ . A $\lambda/2$ correction (0.00234) obtained with a copper crystal was applied.

The equivalent sets of F^2 were sorted together and the values of F^2 were averaged. These F^2 values were scaled to a proper absolute level by means of a Wilson plot. Starting with the positional parameters from the X-ray refinement and individual isotropic thermal parameters, the structure was refined by full-matrix least-squares calculations minimizing the value $\sum w(F_o^2 - F_c^2)^2$. An attempt to refine the neutron data using the thermal parameters from the X-ray refinement was not successful. The scattering lengths were held constant at 0.280 (S), 0.577 (O), 0.665 (C) and -0.372 (H) $\times 10^{-12}$ cm (Neutron Diffraction Commission, 1969). The refinement, which used all observed data was based on F_{obs}^2 to retain the sign of F_{obs}^2 (Moore, 1972) from intensities observed as negative, and resulted

Table 4. Bond angles ($^\circ$)

Neutron results only for angles involving hydrogens.

	X-rays	Neutrons		Neutrons
O(1)—S—O(2)	119.5 (1)	118.5 (6)	H(15)—C(12)—H(14)	108.3 (8)
O(2)—S—O(3)	110.1 (1)	109.2 (5)	H(15)—C(12)—C(13)	107.6 (6)
O(2)—S—C(1)	108.5 (1)	107.9 (5)	H(16)—C(13)—C(12)	109.6 (6)
S—C(1)—C(2)	119.6 (2)	120.3 (4)	H(16)—C(13)—C(8)	111.5 (5)
C(1)—C(2)—C(3)	119.5 (3)	119.8 (4)	H(17)—C(13)—C(12)	110.5 (5)
C(3)—C(4)—C(5)	117.9 (3)	119.4 (4)	H(17)—C(13)—C(8)	109.1 (6)
C(5)—C(6)—C(1)	118.6 (3)	119.3 (3)	H(17)—C(13)—H(16)	104.8 (7)
C(3)—C(4)—C(7)	120.4 (4)	118.3 (7)	H(18)—C(15)—C(14)	114.5 (8)
S—O(3)—C(8)	120.1 (1)	120.7 (4)	H(18)—C(15)—H(19)	103 (1)
O(3)—C(8)—C(13)	106.5 (2)	106.2 (3)	H(18)—C(15)—H(20)	114 (1)
C(9)—C(10)—C(11)	111.8 (2)	112.0 (3)	H(19)—C(15)—C(14)	112 (7)
C(11)—C(12)—C(13)	111.2 (2)	110.8 (3)	H(19)—C(15)—H(20)	101 (1)
C(13)—C(8)—C(9)	112.5 (2)	112.0 (3)	H(20)—C(15)—C(14)	112.0 (7)
C(12)—C(11)—C(14)	114.6 (2)	113.8 (3)	H(21)—C(16)—C(14)	111.6 (8)
C(11)—C(14)—C(16)	109.8 (2)	110.8 (4)	H(21)—C(16)—H(22)	106 (1)
C(15)—C(14)—C(16)	108.8 (2)	107.2 (4)	H(21)—C(16)—H(23)	109.8 (9)
C(16)—C(14)—C(17)	108.2 (2)	108.8 (4)	H(22)—C(16)—C(14)	111.1 (7)
O(1)—S—O(3)	103.5 (1)	104.7 (5)	H(22)—C(16)—H(23)	104.2 (9)
O(1)—S—C(1)	110.0 (1)	110.9 (5)	H(1)—C(2)—C(1)	120.8 (5)
O(3)—S—C(1)	104.0 (1)	104.6 (4)	H(1)—C(2)—C(3)	119.3 (3)
S—C(1)—C(6)	119.7 (2)	118.8 (4)	H(2)—C(3)—C(2)	119.3 (7)
C(2)—C(3)—C(4)	121.0 (3)	120.0 (4)	H(2)—C(3)—C(4)	120.7 (7)
C(4)—C(5)—C(6)	122.3 (3)	120.6 (4)	H(3)—C(5)—C(4)	117.1 (7)
C(6)—C(1)—C(2)	120.7 (3)	120.9 (3)	H(3)—C(5)—C(6)	122.4 (7)
C(5)—C(4)—C(7)	121.7 (4)	122.3 (7)	H(4)—C(6)—C(5)	121.1 (5)
O(3)—C(8)—C(9)	109.0 (2)	109.3 (3)	H(4)—C(6)—C(1)	119.4 (5)
C(8)—C(9)—C(10)	109.8 (2)	110.1 (3)	H(8)—C(8)—C(9)	110.8 (5)
C(10)—C(11)—C(12)	108.8 (2)	108.9 (3)	H(8)—C(8)—C(13)	112.5 (5)
C(12)—C(13)—C(8)	110.6 (2)	111.0 (4)	H(8)—C(8)—O(3)	106.8 (4)
C(10)—C(11)—C(14)	113.7 (2)	113.8 (3)	H(9)—C(9)—C(8)	109.1 (6)
C(11)—C(14)—C(15)	110.3 (2)	110.7 (3)	H(9)—C(9)—C(10)	110.9 (5)
C(11)—C(14)—C(17)	111.2 (2)	111.4 (3)	H(10)—C(9)—C(8)	108.2 (5)
C(15)—C(14)—C(17)	109.8 (2)	108.2 (4)	H(10)—C(9)—C(10)	109.4 (5)
			H(10)—C(9)—H(9)	109.1 (7)
			H(11)—C(10)—C(9)	109.1 (5)
			H(11)—C(10)—C(11)	110.6 (6)
			H(11)—C(10)—H(12)	102.6 (7)
H(23)—C(16)—C(14)		113.3 (7)	H(12)—C(10)—C(9)	109.8 (5)
H(24)—C(17)—C(14)		111.6 (7)	H(12)—C(10)—C(11)	110.0 (6)
H(24)—C(17)—H(25)		107 (1)	H(13)—C(11)—C(10)	106.7 (5)
H(24)—C(17)—H(26)		107 (1)	H(13)—C(11)—C(12)	108.4 (5)
H(25)—C(17)—C(14)		112.8 (8)	H(13)—C(11)—C(14)	104.9 (4)
H(25)—C(17)—H(26)		105 (1)	H(14)—C(12)—C(11)	110.4 (6)
H(15)—C(12)—C(11)		109.9 (6)	H(14)—C(12)—C(13)	109.6 (6)

in an R of 8.6%. (The same parameters give an R of 4.4% if the data set is incorrectly restricted to I > 3σ(I) and R based on F_obs instead of F_obs^2.) The final position and thermal parameters for both the

X-ray and neutron refinements are listed in Table 2. Bond distances and angles for both X-rays and neutrons are given in Tables 3 and 4 respectively. Neutron structure factors are given in Table 5.

Table 5. Neutron structure factors for trans-4-t-butylcyclohexyl toluene-p-sulphonate

Table with 10 columns and 25 rows of numerical data representing neutron structure factors. The columns are labeled with 'h' values and the rows with 'k' values. The data consists of multiple numerical values for each (h, k) pair, representing the structure factors.

Discussion

The weighted standard deviations (Hamilton, 1969) indicate significant differences between the X-ray and neutron values for the thermal parameters of the heavy atoms. These differences result most probably from inadequacies in the free-atom approximation for the X-ray scattering factors (Hamilton, 1969; Coppens, 1968). The estimated standard deviations are lower in the X-ray method for the heavy atoms; this reflects the larger number of observations in the X-ray study but consideration of the final values of $[\omega(F_o^2 - F_c^2)^2 / (N_o - N_{var})]^{1/2}$, 1.3829 for neutrons and 4.6988 for X-rays, would indicate that $\sigma(F_o)$ for X-rays was underestimated. In the case of X-rays, $\sigma(F_o)$ was based on counting statistics alone. The largest difference in the experimental thermal parameters for this experiment is 0.074 which is smaller than the corresponding value for oxalic acid dihydrate (Coppens & Sabine, 1969).

Significant differences in the y coordinates of S, C(5) and C(15), the x coordinate of C(16) and the hydrogen positional parameters lead to differences in bond length for bonds involving these atoms. The mean neutron S–O distance exceeds that for X-rays by 0.009 Å, after a correction for thermal motion is applied (Cruickshank, 1956). This difference agrees with those obtained for β -sulphanilamide (O'Connell & Maslen, 1967) and orthanilic acid (Lum, Maslen & Hall, 1970) and those predicted by O'Connell, Rae & Maslen (1966) from theoretical calculations as the net result of an apparent decrease in the bond length due to the S–O π bonding and an apparent increase in the bond length due to the displacement of the centroid of the charge cloud towards the lone pair (Dawson, 1964). The mean discrepancy between the X-ray and neutron results for the bond lengths of the benzene ring is 0.012 ± 0.006 Å, which agrees favourably with the theoretical calculations for a benzene ring with these substituents (O'Connell, Rae & Maslen, 1966), and a difference Fourier synthesis with Fourier terms

$$(|F^x| - |F'| \exp i\varphi),$$

where $|F^x|$ is the observed X-ray structure factor, $|F'|$ is the calculated X-ray structure factor and φ is the calculated phase factor, the last two terms being obtained by using the neutron thermal and positional parameters, show the expected central negative region in the ring and the central positive regions in the bonds.

The differences in the individual C–H bonds, the average value for X-rays being 0.09 Å shorter than that for neutrons, are similar to those encountered for other structures which have been studied by both X-rays and neutron techniques. A justification has been given by Stewart, Davidson & Simpson (1965) for this apparent contraction of C–H bond lengths determined by least-squares procedures from X-ray data when a spherical scattering factor for hydrogen is assumed.

Atomic numbering and vibrational ellipsoids for neutrons are shown in Fig. 1. The most striking feature

of the illustration is the view of the disordered hydrogen system where the methyl hydrogens, which are undergoing large torsional oscillations, obviously confirm the view of Johnson (1969) that the density functions for such hydrogen atoms are skewed in an arc about the axis of torsional oscillation. The hydrogens attached to the t-butyl group are also very anisotropic, indicating a high degree of oscillation. The high degree of freedom of oscillation of the carbon atoms attached to these methyl hydrogens is indicated by comparison with the carbon atoms of the ring and the chair. The terminal oxygen atoms also have values which are considerably higher than those of the sulphur atom or the carbon atoms, with those of O(1) being understandably larger. This agrees with the higher degree of freedom they enjoy and their modes would indicate a free rotation about the S–C(1) bond. The X-ray results are similar to those from neutrons for all atoms with the neutron values being, as expected, always less than the corresponding X-ray value. The difference would arise from the valence shell contribution to the scattering factor of the X-ray refinement since the valence electron distribution is associated with the errors in the scattering factors which result in errors in thermal-motion corrections.

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References

- ALTONA, C. & SUNDARALINGAM, M. (1970). *Tetrahedron*, **26**, 925–939.
- COPPENS, P. (1968). *Acta Cryst.* **B24**, 1272–1274.
- COPPENS, P. & SABINE, B. (1969). Paper G2, Buffalo Meeting of A.C.A.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–757.
- DAWSON, B. (1964). *Acta Cryst.* **A25**, 12–29.
- HAMILTON, W. C. (1969). *Acta Cryst.* **A25**, 194–206.
- JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187–194.
- JOHNSON, P. L., CHEER, C. J., SCHAEFFER, J. P., JAMES, V. J. & MOORE, F. H. (1972). *Tetrahedron*, **28**, 2893–2900.
- LUM, R. P. K., MASLEN, E. N. & HALL, S. R. (1970). Private communication.
- MOORE, F. H. (1972). Paper XXV-15, 1Xth Congress of the International Union of Crystallography, Kyoto.
- NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* **A25**, 391–392.
- O'CONNELL, A. M. & MASLEN, E. N. (1967). *Acta Cryst.* **22**, 134–145.
- O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208–219.
- SHAH-MALAK, F. & UTLEY, J. H. P. (1967). *Chem. Commun.* pp. 69–70.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WINSTEIN, S. & HOLNESS, N. J. (1955). *J. Amer. Chem. Soc.* **77**, 5562–5578.
- WOLFE, S. & CAMPBELL, J. R. (1967). *Chem. Commun.* pp. 872–874.