

# THE CRYSTAL AND MOLECULAR STRUCTURE OF *CIS*-4-TERT-BUTYLCYCLOHEXYL *P*-TOLUENE SULFONATE

P. L. JOHNSON and J. P. SCHAEFER

Department of Chemistry University of Arizona, Tucson, Arizona 85721

and

V. J. JAMES and J. F. MCCONNELL

School of Physics, University of New South Wales, Kensington, N.S.W. 2033

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**Abstract**—Two independent X-ray analyses of *cis*-4-tert-butyl cyclohexyl-*p*-toluene sulfonate,  $C_{17}H_{20}O_3S$ , provide data which is compared with the results of the preceding paper on the analogous *trans* compound.<sup>1</sup> The crystals are orthorhombic with average cell dimensions,  $a = 11.929$ ,  $b = 22.718$ ,  $c = 6.269$  Å,  $Z = 4$ , in space group  $P2_12_12_1$ . Diffractometer data was collected in both determinations and fully refined. A detailed comparison of the cyclohexane portions of the molecule show more flattening of the ring when the compound is *cis* rather than *trans*.

## INTRODUCTION

EXPERIMENTAL and theoretical studies of the chair form of cyclohexane have established that cyclohexane is somewhat flattened from an idealized model where the bond angles are tetrahedral and the torsional angles are exactly  $60^\circ$ .<sup>2, 3, 4</sup> The most recent values are from electron diffraction work of Buys and Geise<sup>4</sup> who found that cyclohexane in the gaseous state has endocyclic valency angles of  $111.05^\circ$  which, by geometry,<sup>5</sup> yields a torsion angle of  $55.9^\circ$ . The effect of substituents on the ring would be to flatten the ring due to the size of any substituent relative to hydrogen.

Any experimental study on an equatorial and an axial substituted cyclohexane will give results that will characterize the difference in substitution. However, it will not be possible to sort out the effect of the substituent alone if the ring undergoes a flattening. The observed effect could be due to the change in the ring.

As in the preceding paper, a duplication of effort was inadvertently made at the University of Arizona (UA) and the University of New South Wales (UNSW). The duplication of structure determination provide a good example in which one can assess the accuracy of X-ray structural parameters aside from the usual statistically derived error limits. The independently derived results of both studies provide greater confidence in the details of ring flattening that can be measured.

## DISCUSSION

The bond lengths are in Fig. 1 and bond angles in Table 1. As in the related *trans* compound, the arrangement of the atoms about the sulfur is approximately tetrahedral with the large deviation being in the  $O_1-S-O_2$  angle of  $119.4^\circ$ . The conformation of the sulfonate group is similar to that found in the preceding paper. The torsional angles are in

Table 2, and the torsional angles about the S—C<sub>1</sub> bond establish the conformation of the sulfonate group. The values of these torsional angles with the benzene closest to them are  $-19.1^\circ$ ,  $-65.3^\circ$ , and  $46.3^\circ$  respectively for O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub>. Again this differs from the preferred conformation for the sulfonate group as found by Arora and Sundaralingam<sup>6</sup> in a survey of related compounds.

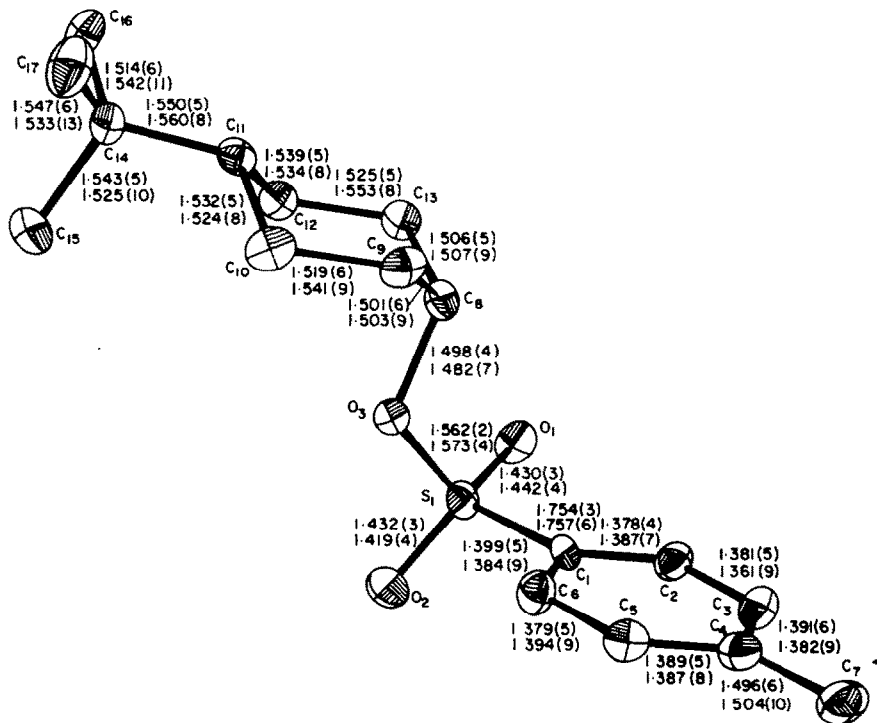


FIG. 1. Bond lengths involving nonhydrogen atoms for *cis*-4-*tert* butylcyclohexyl-*p*-toluene sulfonate with estimated standard deviations in parentheses. The bond lengths on top of each pair are from UA, while the lower are from UNSW.

The C—C bonds in the benzene ring show the same pattern of bond lengths as the *trans* compound. The short C—C bonds are C<sub>2</sub>—C<sub>3</sub> and C<sub>5</sub>—C<sub>6</sub> of average length 1.379 Å while the long C—C bonds are those remaining at 1.387 Å. This variation agrees well with the calculations of O'Connell *et al.* regarding the displacement of the carbon atoms toward the centre of a benzene ring due to the hydrogen substituents.

The anomalous bond lengths in the cyclohexane ring moiety of the structure are in accord with those observed in the *trans* compound. The C—C distances for C<sub>8</sub>—C<sub>9</sub>, and C<sub>8</sub>—C<sub>13</sub> average 1.504 Å for the *cis* compound and 1.500 for the *trans* compound and are ascribed to sp hybrid bonding with oxygen.

The *t*-butyl group shows evidence of strain with angles less than tetrahedral for those atoms in the group. Atoms C<sub>10</sub> and C<sub>12</sub> are distorted away from the *t*-butyl group as shown by the increase in angles C<sub>14</sub>C<sub>11</sub>C<sub>10</sub> and C<sub>14</sub>C<sub>11</sub>C<sub>12</sub> from the tetrahedral (average is 113.9°).

The torsional angles within the cyclohexane portion of the molecule average  $54.8^\circ$  in contrast to the average torsional angle of  $55.9$  found in the *trans* compound. The flattening of the ring as expressed by the decrease in torsional angle ( $1.1^\circ$ ) compares

TABLE 1. INTRAMOLECULAR ANGLES BETWEEN NONHYDROGEN ATOMS OF *cis*-4-*tert* BUTYL CYCLOHEXYL-*p*-TOLUENE SULFONATE.

Atoms	UA	UNSW
O <sub>1</sub> —S—O <sub>2</sub>	119.3 (2)	119.5 (3)
O <sub>1</sub> —S—O <sub>3</sub>	110.3 (1)	110.1 (2)
O <sub>1</sub> —S—C <sub>1</sub>	107.8 (2)	108.1 (3)
O <sub>2</sub> —S—O <sub>3</sub>	104.7 (1)	104.6 (2)
O <sub>2</sub> —S—C <sub>1</sub>	109.4 (2)	109.5 (3)
O <sub>3</sub> —S—C <sub>1</sub>	104.3 (2)	104.1 (3)
S—C <sub>1</sub> —C <sub>2</sub>	119.0 (3)	119.3 (5)
S—C <sub>1</sub> —C <sub>6</sub>	120.7 (2)	120.4 (4)
C <sub>2</sub> —C <sub>1</sub> —C <sub>6</sub>	120.2 (3)	120.2 (6)
C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	119.7 (4)	119.7 (6)
C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	121.3 (3)	121.8 (6)
C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	118.2 (4)	118.5 (6)
C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	121.4 (4)	120.7 (6)
C <sub>5</sub> —C <sub>6</sub> —C <sub>1</sub>	119.3 (3)	119.1 (5)
C <sub>3</sub> —C <sub>4</sub> —C <sub>7</sub>	120.8 (4)	121.1 (7)
C <sub>5</sub> —C <sub>4</sub> —C <sub>7</sub>	121.1 (4)	120.4 (7)
C <sub>8</sub> —C <sub>9</sub> —C <sub>10</sub>	112.3 (3)	111.6 (5)
S—O <sub>3</sub> —C <sub>8</sub>	118.3 (2)	120.3 (5)
O <sub>3</sub> —C <sub>8</sub> —C <sub>9</sub>	105.6 (3)	112.3 (5)
O <sub>3</sub> —C <sub>8</sub> —C <sub>13</sub>	108.4 (3)	109.1 (5)
C <sub>9</sub> —C <sub>10</sub> —C <sub>11</sub>	112.3 (3)	112.1 (5)
C <sub>10</sub> —C <sub>11</sub> —C <sub>12</sub>	107.6 (3)	108.1 (5)
C <sub>11</sub> —C <sub>12</sub> —C <sub>13</sub>	111.9 (3)	111.3 (5)
C <sub>12</sub> —C <sub>13</sub> —C <sub>8</sub>	112.6 (3)	111.9 (5)
C <sub>13</sub> —C <sub>8</sub> —C <sub>9</sub>	112.6 (3)	112.7 (5)
C <sub>12</sub> —C <sub>11</sub> —C <sub>14</sub>	114.0 (3)	113.4 (5)
C <sub>10</sub> —C <sub>11</sub> —C <sub>14</sub>	114.6 (3)	113.5 (6)
C <sub>11</sub> —C <sub>14</sub> —C <sub>15</sub>	111.7 (3)	111.5 (6)
C <sub>11</sub> —C <sub>14</sub> —C <sub>16</sub>	111.2 (3)	109.0 (5)
C <sub>11</sub> —C <sub>14</sub> —C <sub>17</sub>	109.7 (3)	107.7 (5)
C <sub>15</sub> —C <sub>14</sub> —C <sub>16</sub>	108.6 (3)	108.7 (7)
C <sub>15</sub> —C <sub>14</sub> —C <sub>17</sub>	108.4 (4)	110.9 (8)
C <sub>16</sub> —C <sub>14</sub> —C <sub>17</sub>	107.0 (4)	108.9 (7)

quite favorably with that predicted by computer calculations ( $1.3^\circ$ ).<sup>2</sup> A mean torsional angle of  $53.7^\circ$  was calculated for the *cis* compound while  $55.0^\circ$  was the prediction for the *trans* compound. However, the pattern of the individual torsional angles does not compare well. The predicted flattening is asymmetric while the observed flattening has an approximate mirror plane through C<sub>1</sub>C<sub>4</sub>. The torsional angles are smallest near the axial substituents with the average of C<sub>12</sub>C<sub>13</sub>C<sub>8</sub>C<sub>9</sub> and C<sub>13</sub>C<sub>8</sub>C<sub>9</sub>C<sub>10</sub> being  $51.3^\circ$ . The torsional angles adjacent to these (C<sub>10</sub>C<sub>11</sub>C<sub>12</sub>C<sub>13</sub> and C<sub>11</sub>C<sub>12</sub>C<sub>13</sub>C<sub>8</sub>) average  $56.2^\circ$ . The least amount of flattening is found in the torsional angles adjacent to the equatorial substituent; the values for C<sub>8</sub>C<sub>9</sub>C<sub>10</sub>C<sub>11</sub> and C<sub>9</sub>C<sub>10</sub>C<sub>11</sub>C<sub>12</sub> average  $56.8^\circ$ . The localized

flattening at the axial substituent was not predicted while the predicted asymmetric distortions were not found experimentally.

Another feature of the predicted structure was a lengthening of the  $C_{11}$ — $C_{14}$  bond. This was observed with the theoretical value being 1.564 Å while the observed value was 1.555 Å. This experimental finding of a bond length increasing to relieve strain has been observed by Schaefer and Walthers<sup>8</sup> in a survey of cyclobutane compounds.

TABLE 2. TORSIONAL ANGLES IN *cis*-4-*tert* BUTYLCYCLOHEXYL-*p*-TOLUENE SULFONATE FROM UA DATA WITH STANDARD DEVIATIONS IN PARENTHESES.

Atoms	Torsional Angle
$O_2-S-C_1-C_2$	112.1 (3)
$O_2-S-C_1-C_6$	-65.3 (3)
$O_3-S-C_1-C_2$	-136.4 (3)
$O_3-S-C_1-C_6$	46.3 (3)
$O_1-S-C_1-C_2$	-19.1 (3)
$O_1-S-C_1-C_6$	163.5 (3)
$C_8-C_9-C_{10}-C_{11}$	-55.8 (5)
$C_9-C_{10}-C_{11}-C_{12}$	57.7 (4)
$C_{10}-C_{11}-C_{12}-C_{13}$	-56.9 (4)
$C_{11}-C_{12}-C_{13}-C_8$	54.6 (4)
$C_{12}-C_{13}-C_8-C_9$	-50.4 (5)
$C_{13}-C_8-C_9-C_{10}$	50.7 (5)
$C_{10}-C_{11}-C_{14}-C_{15}$	-60.5 (5)
$C_{10}-C_{11}-C_{14}-C_{16}$	117.9 (3)
$C_{10}-C_{11}-C_{14}-C_{17}$	59.7 (5)
$C_{12}-C_{11}-C_{14}-C_{15}$	63.9 (5)
$C_{12}-C_{11}-C_{14}-C_{16}$	-57.6 (4)
$C_{12}-C_{11}-C_{14}-C_{17}$	-175.8 (4)

TABLE 3. PHASE ASSIGNMENTS FOR SPECIFYING THE ORIGIN AND IMPLEMENTING EQUATION (1).

$h$	$\Phi_k$	E
4 15 0	$\pi$	2.61
4 0 7	$\pi/2$	1.96
3 12 0	$3\pi/2$	2.61
0 13 8	d	3.52
2 4 8	m	1.70

The most unusual result of the computer calculations for this class of compounds was not observed in this compound as was the case with the preceding paper. The *t*-butyl group was predicted to be twisted by  $\pm 17^\circ$  from the perfectly staggered form. The torsional angles about the  $C_{11}$ — $C_{14}$  bond in Table 2 show that this does not occur. If the ideal geometry were present, these angles would be  $0^\circ$ ,  $60^\circ$ ,  $-60^\circ$  and the tabulated values are near these numbers. The anomalously high thermal parameters were found for the *t*-butyl group and no peaks were found corresponding to disordered atoms of this

TABLE 4. ATOMIC COORDINATES FOR *cis*-4-*tert*-BUTYLCYCLOHEXYL-*p*-TOLUENE SULFONATE AND IN PARENTHESES THEIR STANDARD DEVIATIONS.

Atoms	UA			UNSW		
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S	0.22109(7)	0.30918(4)	0.33180(15)	0.2212(1)	0.3092 (1)	0.3316(2)
O <sub>1</sub>	0.1560(2)	0.2753(1)	0.1852(5)	0.1554(3)	0.2752(2)	0.1843(7)
O <sub>2</sub>	0.3064(2)	0.3477(1)	0.2520(5)	0.3056(3)	0.3475(2)	0.2529(8)
O <sub>3</sub>	0.1433(2)	0.3497(1)	0.4678(4)	0.1426(3)	0.3499(1)	0.4787(6)
C <sub>1</sub>	0.2801(3)	0.2605(1)	0.5175(6)	0.2802(4)	0.2606(3)	0.5173(9)
C <sub>2</sub>	0.2871(3)	0.2016(1)	0.4675(7)	0.2870(5)	0.2012(2)	0.4689(1)
C <sub>3</sub>	0.3376(3)	0.1632(1)	0.6083(7)	0.3374(5)	0.1645(2)	0.6075(1)
C <sub>4</sub>	0.3815(3)	0.1827(2)	0.8010(7)	0.3816(3)	0.1837(2)	0.7997(10)
C <sub>5</sub>	0.3739(3)	0.2422(2)	0.8484(7)	0.3741(5)	0.2424(3)	0.8484(10)
C <sub>6</sub>	0.3239(3)	0.2813(1)	0.7099(7)	0.3233(5)	0.2817(2)	0.7087(10)
C <sub>7</sub>	0.4322(3)	0.1402(2)	0.9555(9)	0.4329(6)	0.1408(4)	0.9567(10)
C <sub>8</sub>	0.0349(3)	0.3249(1)	0.5480(6)	0.0358(5)	0.3249(2)	0.5461(10)
C <sub>9</sub>	0.0189(4)	0.3508(2)	0.7658(6)	0.0189(6)	0.3500(3)	0.7657(10)
C <sub>10</sub>	-0.0020(4)	0.4167(2)	0.7582(7)	-0.0027(5)	0.4169(3)	0.7576(10)
C <sub>11</sub>	-0.1020(3)	0.4327(1)	0.6165(5)	-0.1020(4)	0.4323(2)	0.6164(9)
C <sub>12</sub>	-0.0780(3)	0.4083(3)	0.3923(6)	-0.0782(5)	0.4088(2)	0.3922(9)
C <sub>13</sub>	-0.0569(3)	0.3421(2)	0.3957(7)	-0.0572(5)	0.3413(2)	0.3950(9)
C <sub>14</sub>	-0.1343(3)	0.4987(1)	0.6196(7)	-0.1333(5)	0.4991(2)	0.620(1)
C <sub>15</sub>	-0.0372(4)	0.5381(2)	0.5413(11)	-0.0363(7)	0.5372(3)	0.540(2)
C <sub>16</sub>	-0.2362(4)	0.5104(2)	0.4822(9)	-0.2356(6)	0.5094(3)	0.477(2)
C <sub>17</sub>	-0.1650(5)	0.5175(2)	0.8490(9)	-0.1645(9)	0.5155(3)	0.851(2)
H <sub>1</sub>	0.252(3)	0.188(1)	0.320(6)	0.270(11)	0.182(4)	0.269(23)
H <sub>2</sub>	0.337(3)	0.120(1)	0.566(6)	0.357(6)	0.119(3)	0.559(10)
H <sub>3</sub>	0.400(3)	0.254(2)	0.968(7)	0.405(5)	0.253(3)	0.910(10)
H <sub>4</sub>	0.323(3)	0.324(1)	0.735(6)	0.328(8)	0.330(8)	0.794(18)
H <sub>5</sub>	0.495(4)	0.125(2)	0.909(8)	0.496(7)	0.130(3)	0.928(15)
H <sub>6</sub>	0.460(4)	0.158(2)	1.082(8)	0.457(10)	0.119(11)	1.121(19)
H <sub>7</sub>	0.390(3)	0.118(2)	1.050(8)	0.379(6)	0.102(4)	0.938(18)
H <sub>8</sub>	0.046(3)	0.280(1)	0.552(7)	0.052(5)	0.273(3)	0.557(15)
H <sub>9</sub>	-0.042(3)	0.329(2)	0.831(6)	-0.043(7)	0.338(3)	0.847(12)
H <sub>10</sub>	0.096(3)	0.341(1)	0.843(6)	0.110(7)	0.332(4)	0.848(16)
H <sub>11</sub>	0.068(3)	0.437(1)	0.691(7)	0.082(6)	0.445(3)	0.682(13)
H <sub>12</sub>	-0.023(4)	0.428(2)	0.873(7)	-0.012(6)	0.435(2)	0.906(10)
H <sub>13</sub>	-0.171(3)	0.410(1)	0.671(6)	-0.167(4)	0.404(2)	0.678(11)
H <sub>14</sub>	-0.139(3)	0.413(1)	0.290(6)	-0.144(4)	0.413(2)	0.307(9)
H <sub>15</sub>	-0.011(3)	0.429(1)	0.347(6)	-0.001(6)	0.430(3)	0.340(17)
H <sub>16</sub>	-0.115(3)	0.321(1)	0.457(6)	-0.135(4)	0.323(2)	0.465(8)
H <sub>17</sub>	-0.043(3)	0.325(2)	0.240(7)	-0.033(5)	0.323(3)	0.233(9)
H <sub>18</sub>	0.028(4)	0.533(2)	0.644(8)	0.022(12)	0.569(5)	0.585(18)
H <sub>19</sub>	-0.038(4)	0.529(2)	0.388(8)	-0.027(9)	0.537(7)	0.356(14)
H <sub>20</sub>	-0.059(3)	0.576(2)	0.531(8)	0.065(7)	0.530(4)	0.638(14)
H <sub>21</sub>	-0.225(4)	0.500(2)	0.335(7)	-0.229(9)	0.522(6)	0.418(17)
H <sub>22</sub>	-0.305(4)	0.484(2)	0.504(8)	-0.321(9)	0.506(4)	0.549(14)
H <sub>23</sub>	-0.262(3)	0.549(2)	0.495(8)	-0.259(11)	0.522(4)	0.282(17)
H <sub>24</sub>	-0.110(4)	0.512(2)	0.933(8)	-0.068(6)	0.515(3)	0.899(13)
H <sub>25</sub>	-0.201(3)	0.559(2)	0.842(8)	-0.172(6)	0.542(3)	0.846(13)
H <sub>26</sub>	-0.235(4)	0.489(2)	0.879(7)	-0.139(8)	0.488(5)	0.987(15)

group. This second example of a non-twisted t-butyl group casts further doubt on the concept of a twisted t-butyl group<sup>2</sup> in this class of compounds. An intermolecular scan of bond distances reveals no anomalously short intermolecular contacts.

TABLE 5. THERMAL PARAMETERS FROM UA AND UNSW WITH STANDARD DEVIATIONS IN PARENTHESES. THE FIRST LINE REFERS TO THE UA VALUE WHILE SECOND TO THE UNSW VALUE. TEMPERATURE FACTORS ARE OF FORM  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	0.0069(1)	0.0018(0)	0.0225(2)	-0.0002(0)	-0.0007(1)	0.0005(1)
	0.0070(1)	0.0020(0)	0.0257(4)	-0.0002(1)	-0.0009(2)	0.0006(1)
O <sub>1</sub>	0.0101(2)	0.0026(1)	0.0265(8)	-0.0003(1)	0.0037(4)	-0.0014(2)
	0.0099(3)	0.0024(1)	0.026(1)	-0.0001(1)	0.0047(7)	-0.0008(2)
O <sub>2</sub>	0.0093(2)	0.0027(1)	0.0386(9)	0.0003(1)	-0.0046(4)	0.0025(2)
	0.0082(3)	0.0026(1)	0.041(2)	0.0003(1)	-0.0048(7)	0.0026(3)
O <sub>3</sub>	0.0061(2)	0.0017(1)	0.0300(8)	-0.0001(1)	-0.0013(3)	0.0000(2)
	0.0060(3)	0.0015(1)	0.029(1)	-0.0003(1)	-0.0010(6)	0.0006(3)
C <sub>1</sub>	0.0061(2)	0.0018(1)	0.0243(9)	-0.0003(1)	-0.0006(5)	0.0005(2)
	0.0057(4)	0.0017(1)	0.025(2)	-0.0001(2)	0.0003(8)	0.0002(3)
C <sub>2</sub>	0.0068(2)	0.0020(1)	0.0308(11)	-0.0004(1)	-0.0002(5)	-0.0011(2)
	0.0066(4)	0.0017(1)	0.034(1)	-0.0002(2)	-0.0015(9)	-0.0010(4)
C <sub>3</sub>	0.0077(3)	0.0018(1)	0.0366(14)	-0.0006(1)	-0.0007(6)	-0.0008(3)
	0.0065(4)	0.0019(1)	0.040(3)	-0.0004(2)	-0.0015(9)	0.0000(5)
C <sub>4</sub>	0.0054(2)	0.0024(1)	0.0319(13)	-0.0004(1)	-0.0024(5)	0.0015(3)
	0.0052(4)	0.0023(2)	0.030(2)	-0.0003(2)	-0.0030(8)	0.0011(5)
C <sub>5</sub>	0.0077(3)	0.0028(1)	0.024(10)	0.0002(1)	0.0003(5)	0.0000(3)
	0.0073(4)	0.0027(1)	0.025(2)	-0.0004(2)	0.0004(9)	0.0005(5)
C <sub>6</sub>	0.0084(3)	0.0018(1)	0.0283(12)	-0.0002(1)	0.0008(5)	-0.0005(2)
	0.0079(4)	0.0018(1)	0.029(2)	-0.0001(2)	0.0004(9)	-0.0005(4)
C <sub>7</sub>	0.0077(3)	0.0034(1)	0.0389(16)	-0.0011(1)	-0.0004(6)	0.0041(4)
	0.0079(6)	0.0031(2)	0.041(3)	-0.0011(3)	0.001(1)	0.0041(6)
C <sub>8</sub>	0.0065(2)	0.0018(1)	0.0272(11)	0.0001(1)	-0.0006(5)	0.0010(2)
	0.0064(4)	0.0016(1)	0.027(2)	0.0002(2)	0.0002(8)	0.0012(4)
C <sub>9</sub>	0.0075(3)	0.0027(1)	0.0221(11)	-0.0004(1)	0.0009(5)	0.0019(3)
	0.0085(5)	0.0025(1)	0.021(2)	-0.0002(2)	0.0003(8)	-0.0010(4)
C <sub>10</sub>	0.0083(3)	0.0028(1)	0.0168(9)	-0.0004(1)	0.0018(5)	-0.0007(3)
	0.0085(5)	0.0025(1)	0.021(2)	-0.0007(2)	0.0032(8)	-0.0010(4)
C <sub>11</sub>	0.0062(2)	0.0019(1)	0.0203(10)	0.0002(1)	-0.0007(4)	0.0006(2)
	0.0052(4)	0.0018(1)	0.022(2)	0.0000(2)	0.0011(7)	0.0000(3)
C <sub>12</sub>	0.0075(3)	0.0022(1)	0.0194(10)	-0.0002(1)	0.0024(5)	0.0007(2)
	0.0074(4)	0.0021(1)	0.021(2)	-0.0006(2)	-0.0027(8)	-0.0007(4)
C <sub>13</sub>	0.0070(3)	0.0020(1)	0.0227(11)	0.0001(1)	0.0022(4)	-0.0005(2)
	0.0067(4)	0.0019(1)	0.027(2)	-0.0002(2)	-0.0023(7)	0.0000(4)
C <sub>14</sub>	0.0079(3)	0.0018(1)	0.0339(13)	-0.0001(1)	-0.0016(5)	-0.0001(3)
	0.0077(5)	0.0017(1)	0.035(2)	0.0000(2)	0.0017(9)	-0.0008(4)
C <sub>15</sub>	0.0107(4)	0.0022(1)	0.0615(22)	0.0009(2)	-0.0019(9)	0.0019(4)
	0.0104(6)	0.0020(2)	0.082(5)	0.0007(3)	0.006(2)	-0.0020(8)
C <sub>16</sub>	0.0099(3)	0.0024(1)	0.0450(16)	-0.0012(2)	0.0006(7)	0.0007(3)
	0.0088(5)	0.0024(2)	0.052(3)	-0.0012(2)	-0.001(1)	-0.0006(6)
C <sub>17</sub>	0.0143(5)	0.0029(1)	0.0420(17)	-0.0012(2)	-0.0030(9)	-0.0030(4)
	0.0151(9)	0.0027(1)	0.048(3)	-0.0014(4)	0.005(2)	0.0040(7)

## EXPERIMENTAL

The crystals of *cis*-4-*tert* butyl cyclohexyl-*p*-toluene sulfonate were colorless orthorhombic prisms. A crystal was mounted along the longest axis of a prism, which was found to be the shortest unit cell axis. Preliminary photographs of this crystal exhibited axial extinctions only which indicates the space group  $P2_12_12_1$ . The unit cell parameters were measured at UNSW to be  $a = 11.932(5)$ ,  $b = 22.718(5)$ ,  $c = 6.257(5)$  Å while at UA they were measured as  $a = 11.926(2)$ ,  $b = 22.718(3)$ ,  $c = 6.280(1)$  Å.

At UNSW, the integrated intensities were measured using the five value method of Hoppe<sup>9</sup> with the scan range varying from  $1.0^\circ$  to  $2.0^\circ$ . The scan speed, although automatically controlled by the instrument, was set with an upper time limit of 0.6 seconds per step of  $0.01^\circ$ . A standard reflection was recorded after every fifteen measurements to check on crystal and instrument drift; no crystal decomposition was noted. 1882 reflections were measured, being approximately 95.8% of those with  $\theta < 70^\circ$ , the angular limitation of the diffractometer. The intensities were corrected for Lorentz and polarization factors, approximately scaled to the proper absolute level and corrected for vibration by means of a normalization curve and the normalized structure factor magnitudes (E values) were derived.

At UA, data was collected on a Picker automatic diffractometer with Cu  $K\alpha$  radiation that had passed through a monochromator. A  $\theta-2\theta$  continuous scan was used with the scan rate being  $1^\circ$  per minute and 10 second background counts were measured before and after each scan. There was slight decomposition for the *cis* compound; the intensity of the standard was 95% of the original at the completion of data collection. This was corrected for by assuming the decrease in intensities for the full data set followed the decrease in the standard. 1617 reflections were measured of which 1491 were observed. The intensities were corrected for Lorentz and polarization factors but not for absorption.

Completely different methods were used to solve the structure in the two laboratories. The determination at UNSW was direct from the observed intensities in the manner described in detail by Karle and Karle.<sup>10</sup> To initiate the phase determination, the origin was specified by assigning phases to three independent reflections shown in Table 3. Unknown symbols were assigned to two other reflections to implement the relationship

$$\theta_k \approx \langle \theta_k + \theta_{k-k} \rangle_k \quad [1]$$

which is valid for reflections with large  $|E|$  magnitudes. In the course of applying equation (1) to obtain 67 new phases from those already known, it appeared from multiple indications that the symbols  $d$  and  $m$  had values near  $\pi/2$  and  $3\pi/2$  respectively. Additional phases were obtained by using these 67 phases in a tangent refinement<sup>11</sup> from which all reflections with  $E > 1.0$  were phased.

The E-map based on the phases obtained from the tangent formula revealed the 21 nonhydrogen atoms. The initial R value based on these coordinates and an overall temperature factor of  $4.6 \text{ \AA}^2$  was 31.3%. Refinement proceeded to an R of 8.3% with anisotropic motion. A high angle refinement ( $\sin \theta/\lambda > 0.3$ ) was carried out to check whether the parameters of the nonhydrogen atoms had been affected by bonding asphericity. This resulted in slight moves in the coordinates of sulphur and some carbons. At this stage, 14 hydrogen atoms were clearly visible in a difference map and the 12 methyl hydrogens were indicated weakly.

The hydrogen atoms were given constant anisotropic temperature factors equal to those of the carbon atoms to which they were attached and no attempt was made to determine their individual motions. Their positions were refined along with the positions and thermal parameters of the heavier atoms leading to an R value of 0.057. It was noticed that refinement of the methyl hydrogens resulted in large oscillatory shifts.

At UA, the heavy atom method was used to solve the structure. The Patterson map revealed the position of the sulfur atom and subsequent rounds of structure factor calculations and Fourier maps revealed the remaining atoms. All hydrogen atoms were found on a difference map including the methyl hydrogens. The refinement was carried out in two parts which consisted of the methyl benzene and the *t*-butyl cyclohexane group being refined separately. The  $\text{SO}_2$  group was common to all refinements. The final R value was 0.043 on all observed data. The thermal motion of all non-hydrogen atoms was refined anisotropically while the hydrogen atom temperature factors were fixed at isotropic values of 4.0 and 6.0 respectively for the hydrogens attached to the ring and to the methyl groups. The hydrogen atoms were included in both studies in order to most accurately describe the parameters of the heavy atoms rather than to provide accurate locations for hydrogen atoms.

The scattering factors used were those of Hanson, Herman, Lea, and Skillman.<sup>12</sup> The coordinates from UNSW and UA are in Table 4 and thermal parameters in Table 5.

## REFERENCES

- <sup>1</sup> P. L. Johnson, C. J. Cheer, J. P. Schaefer, V. J. James, and F. M. Moore, *Tetrahedron* **27**, (1972)
- <sup>2</sup> C. Altona and M. Sundaralingam, *Ibid.* **26**, 925 (1970)
- <sup>3</sup> H. R. Buys and H. J. Geise, *Tetrahedron Letters* 2991 (1970)
- <sup>4</sup> M. Davis and O. Hassel, *Acta Chem. Scand.* **17**, 1181 (1963)
- <sup>5</sup> L. Pauling, *Proc. Nat. Acad. Sci. (USA)* **35**, 495 (1945)
- <sup>6</sup> S. K. Arora and M. Sundaralingam, *Acta Cryst.* **B27**, 1293 (1971)
- <sup>7</sup> A. M. O'Connell, A. I. M. Rae, and E. N. Maslen, *Acta Cryst.* **21**, 208 (1966)
- <sup>8</sup> J. P. Schaefer and K. K. Walthers, *Tetrahedron* **27**, 5281 (1971)
- <sup>9</sup> W. Hoppe, *Angew. Chem.* **77**, 484 (1965)
- <sup>10</sup> I. L. Karle and J. Karle, *Acta Cryst.* **21**, 849 (1966)
- <sup>11</sup> J. Karle and H. Hauptman, *Ibid.* **9**, 635 (1956)
- <sup>12</sup> H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Ibid.* **17**, 1040 (1964)