The Twisted t-Butyl Group. Crystal and Molecular Structure of *cis,trans*-2-5-di-t-Butylcyclohexyl Toluene-*p*-sulphonate and Valence-force Calculations

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Summary An *X*-ray study of the title compound shows that the t-butyl groups at C(2) and C(5) are twisted away from the staggered position by −11° and +9°, respectively, this detail of the structure as well as bond distances, bond angles and torsional angles are well reproduced by valence-force energy minimization calculations of various t butyl rotamers of the corresponding alcohol

THE thermodynamic, conformational, and chemical properties of the four stereoisomeric 2,5-di t-butylcyclohexanols have been studied by Pasto and Rao [1] It was concluded that the *cis trans*-isomer (**1**) (all chair, axial hydroxy-group) is thermodynamically more stable than the *trans,cis*-isomer (**2**) which exists in a chair conformation with an equatorial hydroxy-group, this behaviour is contrary to the usual trend in stabilities Nevertheless the axial tosylate (**1t**) solvolyses faster than its equatorial isomer (**2t**) Valence-force calculations[2] on t-butylcyclohexane and 1-methyl-4-t-butylcyclohexanes led to the theoretical prediction that the minimum energy conformation of the t-butyl group in this type of compound is *not* perfectly staggered but twisted or skewed (±17°) concomitant with an asymmetric distortion of the ring In this case an *X*-ray analysis would show a time average picture, *i e* exact staggering accompanied by anomalously high anisotropic temperature factors of the methyl carbon atoms Asymmetric substitution, if accompanied by sufficiently strong steric interference, will render the + and − rotamers non-equivalent and a time average twist between 0° and ±17° will occur

In order to verify these points experimentally a preliminary *X*-ray survey of compounds (**1**) (**2**) (**1t**) and (**2t**) was undertaken Unfortunately, (**1**) and (**2**) did not yield crystals suitable for single-crystal work Compound (**2t**) crystallized in the orthorhombic system $a = 22\ 11$ $b =$

11·00, c = 16·72 Å, Z = 8, space group $Pbcn$. However, poor mechanical properties of the crystals blocked further progress and we turned our attention to the axial tosylate (**1t**).

Compound (**1t**) crystallizes in the monoclinic system, a = 12·562, b = 28·402, c = 5·964 Å, β = 94·91°, Z = 4, space group $P2_1/m$. 1642 Independent non-zero reflections were measured on an automatic three-circle Enraf–Nonius diffractometer, employing the θ–2θ scan mode with Ni-filtered Cu-K_α radiation. The structure was solved by the three dimensional vector-convergence method, using the sulphur atom as the heavy atom. Refinement of the positional and thermal parameters by means of least-squares calculations proceeded smoothly to a final R of 0·042. An ORTEP[3] projection of the molecule is shown in Figure 1 and Newman projections along the C(2)–C(7) and C(5)–C(11) bonds in Figure 2.

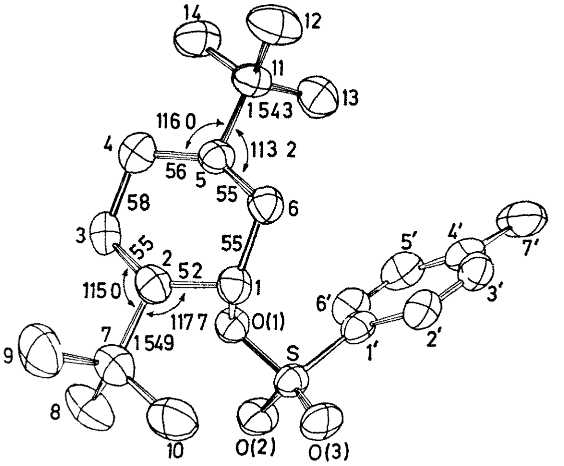

FIGURE 1. *The atomic numbering, ring torsion angles, some exocyclic valency angles and bond distances, and thermal ellipsoids scaled to enclose* 40% *probability of* cis,trans-2,5-*di-t-butylcyclohexyl toluene*-p *sulphonate. The e.s.d. of the carbon–carbon bond distances is* 0·005 *Å and of the valency angles* 0·5°. *The values quoted are uncorrected for thermal motion.*

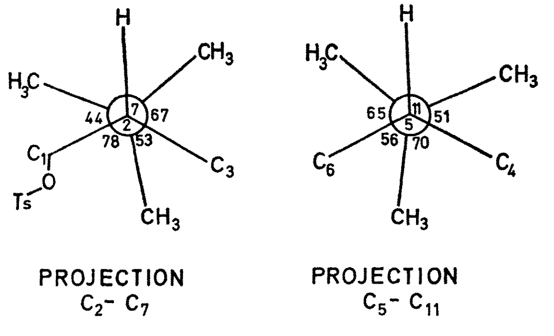

FIGURE 2. *The twist angles of t-butyl groups as seen from the cyclohexane ring.*

The tosyl group adopts a folded conformation with the O(1)–S bond perpendicular to the plane of the benzene ring and almost eclipsing the equatorial carbon–hydrogen bond at C(1) [the torsion angle H–C(1)–O(1)–S is −19°]. A similar situation occurs in the tosylate of *exo*-norbornan-2-ol.[4] This eclipsing behaviour of the tosyl group perhaps precludes exact comparison of the experimental geometry of the hydrocarbon part with the calculated geometries of the various possible t-butyl conformations of the alcohol (**1**) for which reasonably staggered hydroxy-geometries are predicted.

For each staggered hydroxy-rotamer there are four energetically different combinations of twist of the two t-butyl groups, assuming the existence of a small barrier.† Using our previous sign convention[2] we have + +, + −, − − and − + conformations [the first sign of each pair describes the sense of twist of the t-butyl at C(2) and is positive if the rotation is clockwise as seen from the ring carbon] which differ but little in their calculated 'strain' energies and in the magnitude of their twist (Table). The observed mean angles of twist are −10·9° [along C(2)–C(7)] and +8·6° [along C(5)–C(11)]. From the data in the Table and assuming as a rough approximation a Boltzmann distribution over the four states time-average angles of −5·7° and +4·0°, respectively are obtained, in satisfactory agreement with experimental values, both regarding sign and order of magnitude.‡ The second part of the earlier prediction, that of large anisotropic thermal motion of the methyl carbon atoms, is substantiated by the observed directions of the long axes of their thermal ellipsoids (Figure 1).

TABLE

Calculated angles of t-butyl twist conformations and strain energies of compound (**1**)[a]

Conformer	Twist (°) 2-t-Butyl	Twist (°) 5-t-Butyl	Relative strain energy (kcal mol⁻¹)
− +	−20·1	+16·1	0
− −	−20·7	−17·6	0·10
+ +	+17·6	+20·8	0·11
+ −	+16·6	−16·7	0·46

[a] In this case, the O–H was anticlinal to C(1)–C(2).

Other noteworthy features of the structure are (i) the torsion angles of the cyclohexane ring are but slightly affected by the three-fold substitution, the mean value being 55° as compared to 55·9° in cyclohexane itself,[5] the mean angle calculated for compound (**1**) is 56°. (ii) The presence of non-bonded strain in the C(2) and C(5) regions is in agreement with an increase of the exocyclic bond angles at these carbons to 113·2—117·7° at the cost of bending the axial hydrogens on C(2) and C(5) (not shown) toward the centre of the ring.[1,2] Our calculations on compound (**1**) reproduce these features, yielding exocyclic C–C–C angles of 114·5—117·6°, the magnitude depending on the sense of twist, *e.g.* a − rotation about C(2)–C(7),

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† The assumption is not critical. It rests on the finding that each calculated structure converged to a stable minimum, but the existence of a skewed potential energy well with a wide single minimum would still result in a mean twist different from zero.

‡ The crystal packing shows that both t-butyl groups occur in typical hydrocarbon-like surroundings. The packing in these areas seems rather loose (all carbon–carbon contacts ⩾3·95 Å,) which suggests that in this case the main forces that determine the conformation in the solid are intramolecular in nature (steric strain) rather than intermolecular (packing forces).

reducing the torsion angle C(1)–C(2)–C(7)–C(10), *increases* the valency angle C(1)–C(2)–C(7) and *vice versa*. (iii) The observed and calculated trends in the carbon–carbon bond distances are: cyclohexane ring, observed mean 1·523 Å (calc. 1·536 Å), quaternary carbon–primary carbon 1·531 Å (calc. 1·541 Å), and ring carbon–quaternary carbon 1·546 (calc. 1·567 Å). Corrections for thermal motion[6] should bring the figures for the first two types of bonds into line with the calculations but is seems likely that for the tertiary–quaternary combination our force-field[7] predicts bonds that are too long by 0·010–0·015 Å. This conclusion is strengthened by a recent *X*-ray study of *cis*-2-chloro-4-t-butylcyclohexanone[8] in which the exocyclic carbon–carbon bond has a (corrected) length of 1·555 ± ·0005 Å.

The cause of the anomalous relative thermodynamic stabilities of compounds (**1**) and (**2**) is a complex problem. 14 stable energy minima were found in all, six for compound (**1**) and eight for (**2**). The calculated composition of the equilibrium (**2**) $\rightleftharpoons$ (**1**), based on the relative valence-force 'strain' energies, yields $\Delta G^{298} = +0{\cdot}24$ kcal mol^{-1}, in contrast to the experimental value of $-0{\cdot}26$ kcal mol.$^{-1}$ The discrepancy between calculation and experiment is not excessive and might be ascribed to several causes, *e.g.* deficiencies in the force field, neglect of rotational–vibrational contributions, or hydrogen bonding affecting certain hydroxy-rotamer populations selectively. Whatever the case may be, it is of interest that a plot of theoretical ln K values against $1/T$ shows only apparent linearity in the temperature range 300–450 °K; extrapolation from this range did not yield a true (input) ΔH value.

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