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THE CRYSTAL STRUCTURE OF *cis*-1-*p*-BROMOPHENYL-4-*t*-BUTYLCYCLOHEXANE

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The extremely abundant literature on *t*-butylcyclohexanes that has been published since the first proposal of the *t*-butyl function as a holding group[1] has involved surprisingly little direct experimental structural studies. This fact was recently pointed out by Altona and Sundaralingam[2] who proposed a model for *t*-butylcyclohexane, calculated by a full relaxation molecular mechanics approach, but could not check it because of the lack of experimental data. Since we were interested in conformational studies on 4-*t*-butyl-1-phenylcyclohexanes we thought it worth while to analyze a derivative of this system by X-ray diffraction and chose *cis*-1-*p*-bromophenyl-4-*t*-butylcyclohexane (**2**), which was obtained from the corresponding hydrocarbon **1**[3] by treatment with bromine in CCl_4 in the presence of iron, as needles, m.p. 66-66.5° (from ethanol). Our choice appeared justified by the fact that the presence of the two bulky *cis*-1,4 substituents was likely to induce a considerable deformation in the cyclohexane ring system and, possibly, involve a twist conformation. Garbisch and Patterson[3] have deduced from thermodynamic and n.m.r. data that an appreciable amount of a twist form is likely to be present in solutions of **1**.

1 **2**

The crystals of **2** are triclinic, space group $P\bar{1}$, with unit cell dimensions of *a* = 6.11, *b* = 10.67, *c* = 11.66 Å, α = 102°10', β = 91°50', γ = 97°0'. Intensities from the reciprocal lattice layers 0kl-4kl were recorded with Ni-filtered CuKα radiation on equi-inclination Weissenberg photographs, and corrected

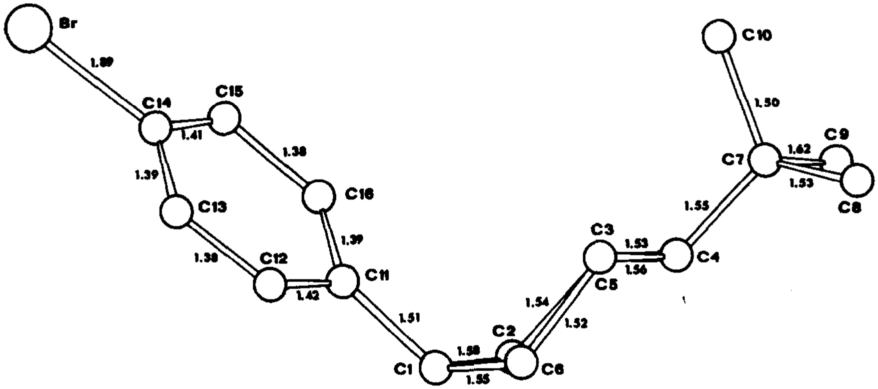
TABLE

Bond angles

	Angle	e.s.d.		Angle	e.s.d.
C(1)-C(2)-C(3)	114.2°	1.5°	C(7)-C(4)-C(3)	114.4°	1.1°
C(2)-C(3)-C(4)	111.9	1.2	C(7)-C(4)-C(5)	112.9	1.3
C(3)-C(4)-C(5)	109.1	1.2	C(11)-C(1)-C(2)	115.7	1.4
C(4)-C(5)-C(6)	109.8	1.3	C(11)-C(1)-C(6)	113.1	1.5
C(5)-C(6)-C(1)	113.1	1.3	C(12)-C(11)-C(1)	118.1	1.5
C(6)-C(1)-C(2)	106.9	1.3	C(16)-C(11)-C(1)	125.4	1.5

Torsional angles

	Angle		Angle
C(1)-C(2)-C(3)-C(4)	54.4°	C(4)-C(5)-C(6)-C(1)	62.1°
C(2)-C(3)-C(4)-C(5)	55.8	C(3)-C(4)-C(5)-C(6)	59.3
C(6)-C(1)-C(2)-C(3)	52.3	C(5)-C(6)-C(1)-C(2)	56.8



The solid state molecular conformation of cis-1-p-bromophenyl-4-t--butylcyclohexane.

for Lorentz, polarization and absorption factors. The structure was solved by the Patterson method. The refinement was made by full matrix least-squares methods, with anisotropic thermal parameters for all the heavy atoms. The hydrogen atoms of the phenyl and cyclohexyl groups were introduced in calculated positions; the positional parameters of the hydrogen atoms in the *t*-butyl group were determined by a Fourier difference synthesis. The final agreement factor was R = 0.065 for the 853 observed reflections.

The figure shows the molecular structure of **2** and the bond distances (e.s.d. 0.02 Å for C-C bonds). The internal angles of the benzene ring are normal (average 120°0'). The Table gives the internal and external angles and the torsional angles of the cyclohexane ring. The following points appear as particularly relevant:

a) The conformation of the cyclohexane ring is an asymmetrically distorted chair, in which both the axial phenyl and the equatorial *t*-butyl group are pushed outwards: the angles of the C(4)-C(7) bond with the plane C(3)-C(4)-C(5) and of the C(1)-C(11) bond with the plane C(2)-C(1)-C(6) are of about 135° as compared with the theoretical values of 125°16'.

b) The *t*-butyl group has a perfectly staggered disposition with respect to the cyclohexane ring, in contrast with the calculations by Altona and Sundaralingam[2] which indicate an angle of twist of ± 17° for the minimum-energy conformation of *t*-butylcyclohexane; it must however be pointed out that the latter conformation should be only about 0.2-0.3 kcal/mol lower in energy than the staggered one.

c) The plane of the phenyl group forms an angle of ca. 62° with the C(14)-C(11)-C(1)-C(4) plane in order to decrease the strong non-bonding interactions between hydrogens that exist in the two symmetric rotamers. Even in this position the distances between the hydrogen on C(16) and the equatorial hydrogen on C(2) and axial hydrogen on C(3) would be rather short (respectively 2.11 and 2.08 Å). These interactions are eased by an increase in the C(16)-C(11)-C(1) and C(11)-C(1)-C(2) angles and by a flattening of the cyclohexane ring which is greater on the C(2)-C(3) than on the opposite side as seen from the torsional angle values.

The complete crystallographic data will be published elsewere. We thank the Consiglio Nazionale delle Ricerche for support of this work.

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