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STERIC INTERFERENCE IN ALLYLIC AND PSEUDO ALLYLIC SYSTEMS VII. THE STRUCTURES OF A CYCLOHEXYLIDENE DERIVATIVE WITH A CONFORMATIONAL PREFERENCE FOR AN AXIAL t-BUTYL GROUP.

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In a previous communication[1], we demonstrated that in a six-membered carbocyclic ring, allylic strain[2] interactions of the $A^{(1,3)}$-type may involve repulsive forces of greater magnitude than those associated with 1,3-diaxial interactions. This encouraged us to search for a carbocyclic molecule that might exhibit a preference for a conformation having an axial t-butyl group, a long sought-after objective. We now report success in this endeavor.

The 1,4-addition of t-butyl magnesium chloride to 1-benzoylcyclohexene followed by trapping of the enolate with 4-nitrobenzoyl chloride leads to a variety of products. Amongst these are two enol 4-nitrobenzoates (produced in a ratio of roughly 1 : 1 which are, from their spectral characteristics, obviously geometrical isomers. Extensive chromatography leads to one of them in a pure state. This isomer, I, has m.p. 170-172°, NMR (90 MHz), $\delta^{CDCl_3}_{Me_4Si}$ 0.90(9H,s,t-butyl), 7.35 (5H, m,pH), 8.30(4H,s,p-$NO_2C_6H_4$). $C_{24}H_{27}NO_4$(Found: C,73.16; H,7.05; N 3.44. Calcd: C,73.25: H,6.92; N,3.56). Because our initial nmr studies revealed little about the stereochemical structure of I, we undertook a single-crystal X-ray diffraction analysis to determine its preferred conformation in the solid state.

The compound crystallizes in space group $P2_1/C$, with lattice parameters $\underline{a}$ = 19.737(0.015)Å, $\underline{b}$ = 6.613(0.005)Å, $\underline{c}$ = 17.075(0.019)Å and β = 74.44°(0.069). There are four molecules per unit cell. The intensities of 2914 reflections were measured in the θ-2 θ scan mode of an Enraf-Nonius CAD-4 automatic diffractometer using monochromatized Cu-Kα radiation. The structure was determined using MULTAN[3]. Twenty-four out of twenty-nine non-hydrogen atoms were unambiguously located on the E-map. The remaining five atoms were located in a partial-structure phased Fourier map. The structure was refined by a full matrix least squares[4], initially assuming isotropic thermal parameters for all atoms. During the later stages of refinement, anisotropic thermal parameters were used for all atoms. The final R-factor, $R_2 = [\Sigma\omega(F_0 - F_c)^2/\Sigma\omega F_0]^{\frac{1}{2}}$ = 6.8% for 2912 reflections, with structure amplitudes greater than twice the standard deviation. A final difference Fourier synthesis showed a maximum electron density of less than 1e/A^3, indicating that no atoms other than hydrogen remain to be located.

The molecular structure of I is shown in Fig. 1. Surprisingly, the cyclohexylidene system adopts that chair conformation *in which the t-butyl group has an axial orientation*. This, of course, removes the $A^{(1,3)}$-interaction between the *t*-butyl group and the *syn*-phenyl ring at C(9), that would exist in the alternate chair conformation.

Some flattening of the cyclohexylidene ring occurs in the vicinity of the *t*-butyl group as is evident from the following table of torsion angles. Average values for such angles in "normal" cyclohexane systems range[5] from 52.9-57.1°.

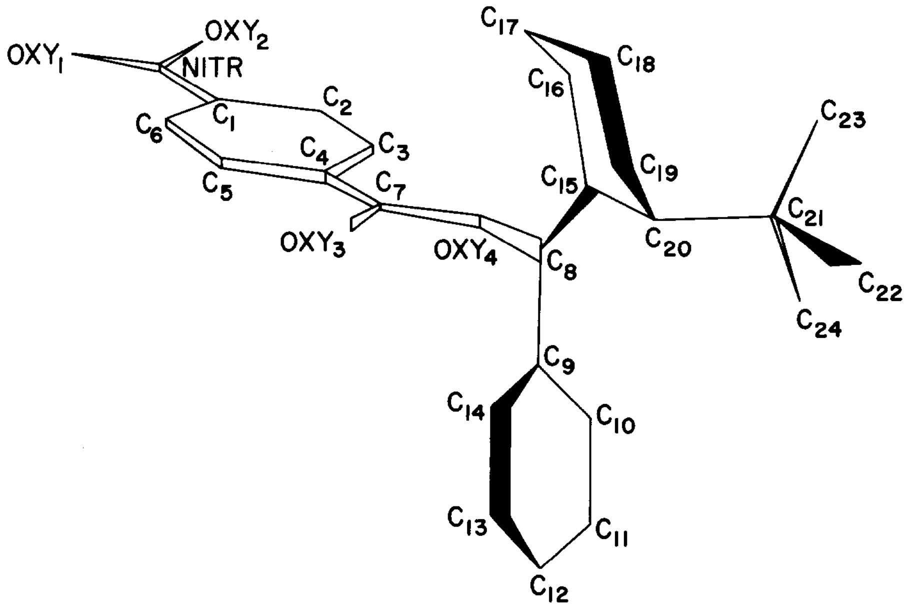
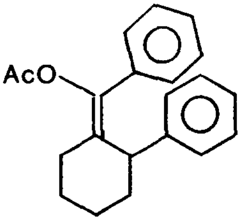


Fig. 1. Molecular structure of I

Table of Torsion Angles in Cyclohexylidene Ring

Group of Atoms	Torsion Angle
C(16)-C(15)-C(20)-C(19)	-48.8^0(0.6)
C(15)-C(20)-C(19)-C(18)	42.3^0(0.7)
C(20)-C(19)-C(18)-C(17)	-48.0^0(0.9)
C(19)-C(18)-C(17)-C(16)	53.1^0(0.8)
C(18)-C(17)-C(16)-C(15)	-56.3^0(0.7)
C(17)-C(16)-C(15)-C(20)	58.0^0(0.6)

These values are lower, but comparable with those (range 49.0-59.6^0) found for the corresponding angles in II, a molecule whose most thermodynamically stable conformation[6] has an axial phenyl group.



II

Further evidence of ring flattening comes from the values of the angles C(15)-C(20)-C(21) and C(19)-C(20)-C(21) which are 114.5^0(0.4) and 116.2^0(0.4) respectively. Interestingly, the internal angle C(15)-C(20)-C(19) has a normal value of 109.5^0(0.4). Most significant, however, is the value found for the angle between the t-butyl bond C(21)-C(20) and the plane represented by the atoms (15)-C(19)-C(20). In I, this is 137.9^0, whereas based on ideal cyclohexane geometry, the angle should be 125.3^0. Thus, the t-butyl group is inclined outwards from the ring by ∿ 13^0, which may be a combination of bond bending and ring flattening. However, it appears that spatial accommodation of the t-butyl group is not solely accounted for by these effects since the bond length of C(20)-C(21)[1.589(0.007$\overset{0}{\mathrm{A}}$] is considerably longer than usual. On the other hand, the bond length of C(21-C(23) is much shorter [1.484(0.010)$\overset{0}{\mathrm{A}}$] than normal and, in agreement with the idea that this is due to repulsion by the axial hydrogen atoms at C(16) and C(18), the bond angle C(23)-C(21)-C(20) is much larger [117.71^0(0.47)] than expected. Other angles around the t-butyl group are within normal limits. One other point of interest concerns the location of the methyl group, C(23), which lies over the cyclohexylidene ring. It is equidistant from the C(18) and C(16) axial hydrogen atoms. This conclusion is supported by the fact that the plane passing through C(23)-C(21)-C(20) lies at an angle of only 7.9^0 to the plane through C(21)-C(20)-C(17). However, the fact that the centers C(23), C(21), C(20) and C(17) are not quite coplaner can be accounted for by the fact that there is a twist of ∿ 3° out of planarity across the system represented by C(15)-C(16)-C(18)-C(19), and this leads to a slight lateral displacement of C(17).

Finally, it may be noted (a) that the unsubstituted phenyl ring and the double bond are not coplaner but lie at a dihedral angle of 67.47° to one another, which is substantially less than that (88.50°) found[6] in II and (b) that the atoms included by the grouping O(1) to C(8) lie perfectly in a plane.

It appears that I is the first case of a compound in which a non-rigid six-membered cycloalkane ring preferentially adopts a conformation having an axial t-butyl group. The only other compounds in which an axial t-butyl group has been identified are 1-t-butyladamantane[7], which is conformationally rigid and cis-2-alkyl-5-t-butyl-1,3-dioxacyclohexanes[8]. In the latter materials, no axial hydrogens interfere with the t-butyl group. Further work on I and its geometrical isomer will be reported in a future publication, along with a list of the coordinates of all the atoms and other molecular details.

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References and Notes

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