Crystal Structure of 9-t-Butyl-9,10-dihydroanthracene

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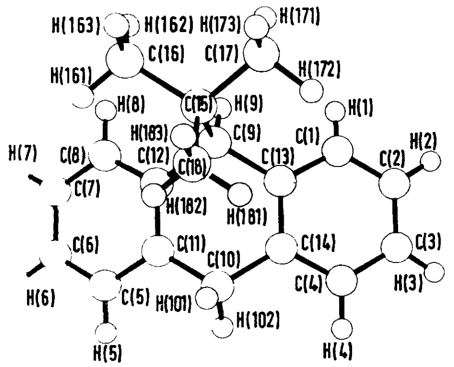
Summary The crystal structure of the title compound shows an 'axial' orientation for the t-butyl group and a dihedral angle of about 147° between the benzene ring planes.

THE preferred orientation of the t-butyl group in 9-t-butyl-9,10-dihydroanthracene (I) has been a subject of much controversy. Chemical studies[1] indicated that the t-butyl group prefers the 'axial' position, while n.m.r. results[2,3] suggested 'equatorial' orientation. More recent studies[4,5,6] showed that the group exists preferentially in the axial orientation. The present structure analysis of (I) was undertaken to confirm its molecular conformation and provide accurate C–C bond distances, C–C–C bond angles and conformations for the fused ring system and the t-butyl function.[7] While the *X*-ray work was in progress, an n.m.r. study,[8] employing the nuclear Overhauser enhancements (NOE), showed that the t-butyl group was in the 'axial' orientation in solution.

Compound (I) $C_{18}H_{20}$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 5{\cdot}98(1)$, $b = 11{\cdot}065(1)$, $c = 20{\cdot}712(2)$ Å, $U = 1370{\cdot}7 \times 10^{-24}$ cm^3, $M = 236{\cdot}4$, $D_m = 1{\cdot}148$, $D_c = 1{\cdot}145$ for $Z = 4$. A total of 1325 independent non-zero reflections ($2\theta_{max} = 120°$) were measured on a Picker automated diffractometer with Ni-filtered Cu-K_α radiation using the θ—2θ scan technique. The structure was solved by direct methods, employing the structure invariants cos $(\phi_{h1} + \phi_{h2} + \phi_{h3})$.[9] Full matrix least-squares refinement with anisotropic thermal parameters for the carbon atoms and isotropic thermal parameters for the hydrogen atoms resulted in a final R factor of 0·043. The average estimated standard deviations in the C–C bonds and C–C–C bond angles are 0·004 Å and 0·2° respectively.

The molecular conformation is shown in the Figure. The t-butyl group is in the 'axial' orientation, in agreement with the solution NOE studies.[8] The methyl groups are staggered with respect to the substituents on C(9). Similarly, the methyl hydrogen atoms are staggered with respect to the substituents on C(15). The molecule is folded about the C(9)–C(10) axis with a dihedral angle between the benzene rings of 146·6°. This value may be compared with the values found in other 'butterfly' molecules.[10] The central ring is in the boat conformation, C(9) being more displaced (0·420 Å) than C(10) (0·292 Å) with respect to the four-atom least-squares plane C(11),C(12), C(13), and C(14).



FIGURE

Average carbon–carbon bond distance

Bonds	Range (Å)	Average Distances (Å)
C(1)–C(2), C(2)–C(3) C(3)–C(4) C(5)–C(6), C(6)–C(7), C(7)–C(8)	1·372—1·379	1·374
C(1)–C(13), C(13)–C(14), C(14)–C(4) C(5)–C(11), C(11)–C(12), C(12)–C(8)	1·383—1·397	1·392
3(10–C(11, C(10)–C(14)	1·498—1·502	1·500
C(9)–C(12), C(9)–C(13)	1·513—1·517	1·515
C(15)–C(16), C(15)–C(17), C(15)–C(18)	1·517—1·528	1·524
C(9)–C(15)		1·578

The twenty C–C bond distances of (I) fall into six groups as shown in the Table. The C(9)–C(15) bond length of 1·578 Å is not only significantly longer than the normal carbon–carbon single bond distance of 1·533 Å, but also the diamond (1·544 Å) carbon–carbon bond distance.

Both the increased puckering at C(9) and the lengthening of the C(9)–C(15) bond are apparently due to the nonbonded interactions between the t-butyl group and the rest of the molecule, in particular the central ring and the neighbouring *peri* positions. Furthermore, the nonbonded repulsion between the C(18) methyl group and H(101) are relieved by an increase in the C(14)–C(15)–C(18) valency angle from the normal tetrahedral value to 112·1°, and by a rotation of the t-butyl group about the C(9)–C(15) bond of *ca.* 4° from an exactly staggered conformation. From theoretical calculations a rotation angle of about ±17° was found for an equatorial t-butyl group attached to a cyclohexane ring in the chair conformation. The contacts between H(101) and H(181) and H(182) are 2·38 and 2·43 Å, respectively. There are similar van der Waals contacts, averaging 2·41 Å, involving the equatorial hydrogens H(9) and H(102) and their neighbouring *peri* hydrogen atoms.

Apparently, the 'axial' isomer appears to be preferred, since in the 'equatorial' orientation there are forbidden van der Waals contacts between the methyl groups and the *peri* hydrogen atoms H(1) and H(8). Thus the observed conformation of compound (I) results from a balance between the various intramolecular forces.

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