The Stereochemistry of Meso-substituted 9,10-Dihydroanthracenes: the use of 9-Alkyl-1,4-dimethyl-9,10-dihydroanthracenes as Model Compounds

By A. L. TERNAY, JUN.,* A. W. BRINKMANN, S. EVANS, and J. HERRMANN
(*Case Western Reserve University, Cleveland, Ohio* 44106 *U.S.A.*)

Summary N.m.r. evidence suggests that 9-alkyl-9,10-dihydroanthracenes may exist in the pseudo-axial conformation.

BECKETT and MULLEY[1,2] have suggested that, for simple 9-substituted 9,10-dihydroanthracenes, the *meso*-substituent (the substituent at C-9) should prefer the pseudo-axial (*ax′*) position. This was supported by Caspar, *et al.*,[3] who assigned the methyl group of 9-methyl-9,10-dihydroanthracene (I) to the *ax′* orientation. Recently, it has been suggested that 9-ethyl-9,10-dihydroanthracene[4] (II), 9-n-butyl-9,10-dihydroanthracene[4] (III) and 9-tert-butyl-9,10-dihydroanthracene[5] (IV) exist in that conformation in which the alkyl group at C-9 is *eq′*. We report a group of 9,10-dihydroanthracene derivatives in which the *meso*-substituent must be *ax′* by virtue of the presence of a substituent adjacent to it. We have examined the following 9-alkyl-1,4-dimethyl-9,10-dihydroanthracenes: 1,4,9-trimethyl-9,10-dihydroanthracene (V), 1,4-dimethyl-9-ethyl-9,10-dihydroanthracene (VI), and 1,4-dimethyl-9-isopropyl-9,10-dihydroanthracene (VII).

The chemical shift (100 MHz., $CDCl_3$, Me_4Si), of the methyl resonance of (I) is a quartet, δ 1·43 (J 7 Hz) p.p.m. The corresponding signal of the model compound (V) occurs at δ 1·28 (J 8 Hz.) p.p.m. and we must conclude, in agreement with Nicholls and Szwarc,[4] that (I) is conformationally inhomogeneous.

The signal from the methyl portion of the ethyl group of (VI) is a triplet δ 0·85 (J 7 Hz.) and a multiplet for the (slightly) anisochronous methylene protons, δ 1·58, similar to the corresponding resonances observed for (II), δ 0·85 and 1·66, respectively. The resonances of the anisochronous methyl signals of the isopropyl group of (VII) are doublets (J 7 Hz.), δ 0·93 and 0·68. The arithmetic centre of this pattern is δ 0·81 and is similar to the centre of the doublet for the corresponding signal in 9-isopropyl-9,10-dihydroanthracene (VIII), also δ 0·81. Furthermore, the centre of the multiplet corresponding to the methine proton of the isopropyl group of (VII) occurs at almost the same frequency as does the corresponding proton of (VIII) (δ 1·92 *vs.* δ 1·86, respectively).

The similarity in the chemical shifts of the ethyl signals of (II) and (VI) and isopropyl signals of (VII) and (VIII) strongly suggests that 9-ethyl- and 9-isopropyl-9,10-dihydroanthracene (II) and (VIII) prefer the pseudo-axial conformation. These results, then, support the conclusions of Beckett[1,2] but differ from those of Szwarc.[4] We predict that (IV) also exists in the *ax′* conformation. An *ax′* t-butyl group should interact with the *ax′* proton at C-10, cause the dihedral angle between the aryl planes in (IV) to increase, and thereby[6] increase (in the negative sense) the geminal coupling constant of the C-10 methylene group. Indeed, the reported [4,5] geminal coupling constant of (I) is 18·0 Hz. while that of (IV) is 19·0 Hz.

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