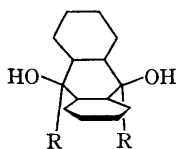
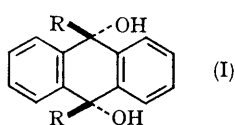


The Use of π -Complex Formation to Modify Anisotropic Effects in Nuclear Magnetic Resonance Spectra in the 9,10-Dihydroanthracene Series

By C. R. M. BUTT, D. COHEN, L. HEWITT, and IAN T. MILLAR
(*Chemistry Department, University of Keele, Staffs.*)

WE have shown that it is possible to assign stereochemical conformations in the 9,10-dialkylanthracene-9,10-diol system by making use of the anisotropic effect of the aromatic ring on the alkyl groups.¹ When an alkyl group R is in the pseudo-axial position, peaks due to protons attached to the β -carbon atom are shifted about 0.6 p.p.m. upfield.



FIGURE

We have now synthesised 9,10-di-n-propylanthracene-9,10-diol (I and Figure; R = Prⁿ) and find that the propyl groups are in the *cis*-configuration in which the alkyl groups are both in the pseudo-axial conformation. In this conformation the chemical shift of the β -methylene protons becomes identical (τ 9.4) with that of the γ -methyl group and under these conditions no spin-spin coupling is observed between these two groups. Thus the propyl groups appear as a triplet at τ 7.75 (four protons; two α -methylene groups), and a singlet superposed on a triplet at τ 9.4 (ten protons; two β -methylene and two γ -methyl groups).

It was believed that on addition of tetranitromethane, the anisotropic effect of the aromatic ring current would be modified sufficiently to induce the normal splitting pattern associated with a propyl group. This is found to be so; the ¹H n.m.r. spectrum of the deep-red π -complex shows a methyl triplet at τ 9.2, the low-field methylene triplet is slightly displaced at τ 8.3 (previously τ 7.8) and the β -methylene is an unresolved multiplet at τ 8.5.

We find that similar modifications of the spectra can be observed in other cases where aromatic anisotropic effects occur. Thus the 9,10-diethylanthracene-9,10-diol, as previously reported,¹ shows the β -methyl group at unusually high field (τ 9.8) but on adding tetranitromethane a deep-red complex is formed and the β -methyl group appears at τ 9.1. All spectra were recorded at 60 Mc./sec. on a Perkin-Elmer instrument in deuteriochloroform solution.

It is clear that the displacement is due to a modification of the ring anisotropic effect since, for example, the ¹H n.m.r. spectrum of the alkyl group in n-propylbenzene is virtually unaltered on formation of a π -complex with tetranitromethane; only small shifts (less than 0.04 p.p.m.) are observed in such cases, in which the alkyl group does not lie above the ring in the shielding region.

(Received, February 24th, 1967; Com. 179.)

¹ D. Cohen, L. Hewitt, and I. T. Millar, *Chem. and Ind.*, 1966, 1532.