Absence of the Expected Field Effect in the Hydrogen-isotope Exchange Reactions of a Bridged Anthracene Derivative carrying a Nitrogen Pole

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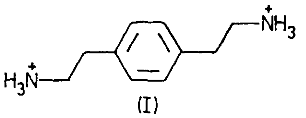
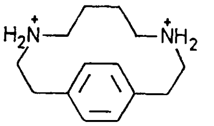
Summary In hydrogen-isotope exchange, the overall reactivities of the two aromatic rings of the conjugate acid of 9,10-dihydro-9,10- (*trans*-11-amino-12-methylethano)-anthracene (III) are the same, in spite of the fact that the nitrogen pole is much nearer one ring than the other.

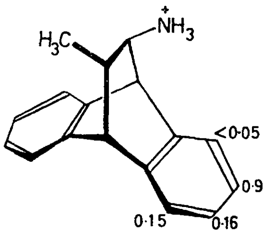
Recent work has established that the open-chain ion (I) is more reactive than the bridged ion (II) by a factor of 100 in nitration and this difference has been ascribed to the greater field effect of the nitrogen poles in the bridged ion.[1] The distances of the nitrogen pole from the centres of the nearer and further rings in the ion (III) (3·5 and 5·2 Å) are very similar to those in the ions (II) and (I) respectively† and so, if the ring–pole distance is the main factor in determining the field effect, the reactivities of these rings would differ by a factor of *ca.* 10 in nitration and by rather more in hydrogen-isotope exchange.[2] The study of the nitration reaction is complicated by the multiplicity of the products formed but we now report the results for hydrogen–deuterium exchange at 25° in a CF_3CO_2D–D_2SO_4–D_2O mixture of composition 79·6–12·5–7·9 mol %. Reaction under these conditions gives exchange without significant sulphonation.



(I)



(II)



(III)

The reaction was followed from the n.m.r. spectra of extracted samples of the free amine in the presence of $Eu(dpm)_3$. The use of this shift reagent expands the aromatic signal and permits the extent of exchange at different positions to be determined. The analysis of the expanded spectrum was based on the correlation of the induced shifts with the relative values predicted by the equation for pseudo-contact interactions[3] using a position for the europium atom in accord with the shifts of the aliphatic protons. The main features of the resulting assignment (and in particular the division of the signals into those of the two rings) were confirmed by spin-decoupling experiments.[4]

The rate of isotope-exchange shows that reaction must involve the protonated amine (III). Nevertheless, the overall reactivity of the two rings was found to be the same within experimental error (±10%). Approximate partial-rate factors for substitution in the ring nearer the nitrogen pole have been obtained (III) and we believe that essentially the same values apply to the corresponding positions in

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† This argument assumes that the open-chain ion reacts in the extended conformation shown (I).

the other ring.‡ This pattern of reaction rates can be considered to derive from the expected difference in the reactivities of the α- and β-positions (*cf.* hydrogen-isotope exchange in triptycene which gives $k_\beta/k_\alpha = 7$)[5] combined with some relative deactivation of the positions *ortho* and *para* to the shorter of the two carbon chains leading to the nitrogen pole.

The apparent conflict between the results for structures (I) and (II) and those for structure (III) is not easy to resolve. It may however be significant that the transition-state electrostatic interaction in structure (II) is across the molecular cavity whereas that between the nitrogen pole and the nearer aromatic ring in structure (III) is across a region occupied by the solvent. The effective dielectric constant should be much less for the former interaction. Thus these results suggest that the lower reactivity of the bridged structure (II) relative to the open-chain structure (I) derives from the difference in the forms of the molecular cavities not the difference in the distances of the positive poles from the aromatic ring.

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‡ Exchange in the further ring gives the same set of relative reactivities but the identification of the individual α and β-positions is less clear-cut.

[1] A. Ricci, R. Danieli, and J. H. Ridd, *J.C.S. Perkin II*,1972, 1547.

[2] Hydrogen-isotope exchange in these substrates is a more selective reaction: R. Danieli, A. Ricci, and J. H. Ridd, *J.C.S. Perkin II*, 1972, 2107.

[3] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

[4] For further details see J. H. Rees, Ph.D. Thesis, London, 1973.

[5] R. Taylor in 'Comprehensive Chemical Kinetics,' ed. C. H. Bamford and C. F. H. Tipper, Elsevier, 1972, vol. 13, p. 245.