The Nitration of 3,8-Diaza[10]cyclophane: Evidence for a Field Effect in Aromatic Nitration

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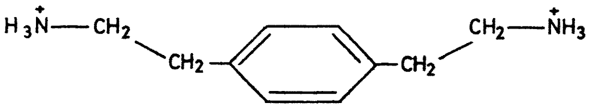
Summary The rate of nitration of the diconjugate acid of 3,8-diaza[10]cyclophane (II) is less than that of the related open-chain diconjugate acid (I) by a factor of 200.

IN aromatic nitration, the substituent $-[CH_2]_2\overset{+}{N}R_3$ (R = Me or H) gives mainly *para*-substitution with deactivation.[1,2] The preferred position of substitution can be ascribed to electron release from the methylene groups in the transition state. The deactivation can be ascribed either to the inductive effect of the nitrogen pole as relayed through the methylene groups to the 1-position or to the electrostatic interaction between the pole and the charge on the ring or on the electrophile in the transition state.

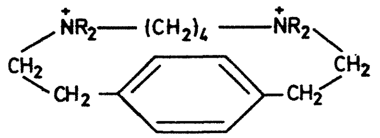
On the inductive interpretation, the extent of deactivation should be independent of the conformation of the substituent. On the electrostatic interpretation, the extent of deactivation should depend on the position of the pole in relation to the ring and the electrophile. Evidence relating to this distinction has now been obtained from the nitration of the two diconjugate acids (I) and (II).

The diamine corresponding to the diconjugate acid (I) was obtained by reduction of *para*-di(cyanomethyl)benzene. The diamine corresponding to the diconjugate acid (II) was prepared by reduction of the cyclic diamide obtained by refluxing *para*-phenylenedi(acetyl chloride) with butane-1,4-diamine in benzene.[3] The mass spectrum and n.m.r. spectrum of the cyclic diamine accord with the stated structure.

These ions undergo smooth mono-nitration in aqueous sulphuric acid. The rate profiles (see Figure) have the same slope as that for the nitration of benzene[4] and hence indicate reaction through the diconjugate acids; this interpretation is supported by the similar reactivity of the methylated ion (III). The partial rate factors for substitution in these ions are: $f_{\mathrm{I}} = 3{\cdot}2 \times 10^{-2}, f_{\mathrm{II}} = 1{\cdot}6 \times 10^{-4}$ $f_{\mathrm{III}} = 1{\cdot}1 \times 10^{-4}$. The bridged ion (II) is therefore less reactive than the open chain ion (I) by a factor of *ca.* 200.



(I)



(II; R = H)
(III; R = Me)

Steric interaction is unlikely to make a significant contribution to this rate factor because the approach of the nitronium ion to one side of the bridged ion is unimpeded. The transmission of the inductive effect of each pole through the longer arm of the saturated bridge should be negligible because of the number of atoms involved. It appears therefore that the factor of 200 must come mainly from the dependence of the field effect on the position of the pole. In the transition state of the open chain structure (I), the side-chains would be expected to adopt the extended conformation as illustrated; the distance from each pole to the centre of the ring is then reduced from 5·2 to *ca.* 3·5 Å in going from the open to the bridged structure.

This work shows that the interpretation of the deactivation in terms of the inductive effect of the pole is incomplete; the results suggest that the movement of a single protonated nitrogen pole from the position in structure (I) to that in structure (II) should decrease the rate of nitration of the benzene ring by a factor of *ca.* 10, irrespective of any concurrent change in the inductive effect. A similar change in the distance of the pole from the centre of the ring occurs in the comparison of the substituents $-CH_2{\cdot}\overset{+}{N}H_3$ and $-[CH_2]_2NH_3$ and it is probably significant that the

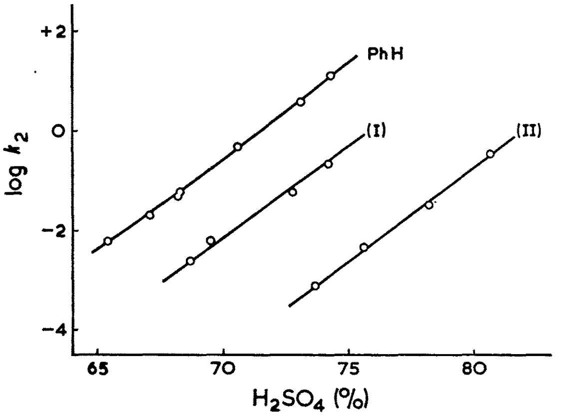


FIGURE. *Comparison of the rate profiles* (k_2 *in* mol^{-1} s^{-1} l) *for the nitration of the ions* (I) *and* (II) *with that for the nitration of benzene* (*ref.* 4).

meta partial rate factors for the nitration of the corresponding mono-substituted benzenes are $3{\cdot}4 \times 10^{-3}$ and $4{\cdot}7 \times 10^{-2}$ respectively, the ratio being 13·8. For substitution at the *meta*- position, the difference in the inductive contribution from these substituents appears to be small. However, it is unlikely that the deactivating effect of a pole can be simply related to its distance from the centre of the ring; it is more important to consider its position with reference to the whole molecular cavity.[5]

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