

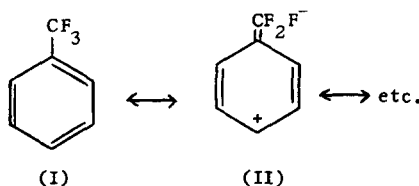
Evidence Against Negative Hyperconjugation Involving Perfluoroalkyl Groups

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There is considerable discussion and speculation in the literature concerning the basis of electronic effects of perfluoroalkyl groups and controversy still surrounds the possibility of negative hyperconjugation, as indicated by (I) and (II).¹

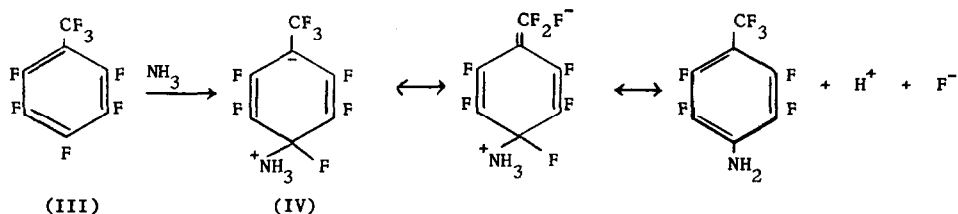


Most of the available data concern systems in the ground state and are based on equilibrium constants and n.m.r. measurements.

We have now investigated the effects of substituent perfluoroalkyl groups on the rates of nucleophilic aromatic substitution to determine whether there is any negative equivalent to a Baker Nathan order,² as found in electrophilic aromatic substitution. Second-order rate constants for the reaction of ammonia with a series of perfluoroalkylbenzenes, in aqueous dioxan (23:77), at 92° are shown below and they are all significantly activated with respect to hexafluorobenzene.

| Compound | C_6F_6 | $C_6F_5 \cdot CF_3$ | $C_6F_5 \cdot CF_2CF_3$ | $C_6F_5 \cdot CF(CF_3)_2$ | $C_6F_5 \cdot C(CF_3)_3$ |
|--|---------------------|---------------------|-------------------------|---------------------------|--------------------------|
| $10^3 k(1 \text{ mole}^{-1} \text{ s}^{-1})$ | Too slow to measure | 0.670 | 1.44 | 1.00 | 1.73 |
| | | (± 0.003) | (± 0.01) | (± 0.01) | (± 0.01) |

If the extent of negative hyperconjugation were significant this would result in appreciable stabilisation of the intermediate IV and, by implication, of the transition state leading to the formation of IV. Clearly this effect should be at a maximum for the trifluoromethyl group (in III) where there are three fluorine atoms available for this type of conjugation. As the fluorine atoms in the trifluoromethyl group are replaced by CF_3 groups in the series CF_3 , CF_2CF_3 , $CF(CF_3)_2$, $C(CF_3)_3$, the extent of negative



hyperconjugation should diminish and the rate constants decrease. This is demonstrably not the case, since all the perfluoroalkylbenzenes in the series react at comparable rates with, in fact, perfluorotoluene being the least reactive, although the differences are not very big in comparison with the degree of activation with respect to hexafluorobenzene. It could be argued that resonance involving a C-CF₃ bond is as important as that for a C-F bond, i.e. $\text{Ar}-\overset{\ominus}{\text{C}}-\text{CF}_3 \longleftrightarrow \text{Ar}=\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{C}}\text{F}_3$. However, it has been pointed out previously¹ that this clearly cannot be the case since the acidities of HF and HCF₃ differ by at least 30 powers of ten. These results are much more effectively interpreted in terms of I_π stabilisation^{1,3} of adjacent charge by perfluoroalkyl groups in the transition state since there is evidence to indicate that the inductive effects of perfluoroalkyl groups are very similar.⁴

These results reinforce doubts raised recently, concerning whether it is necessary to invoke the concept of negative hyperconjugation at all.^{1,3}

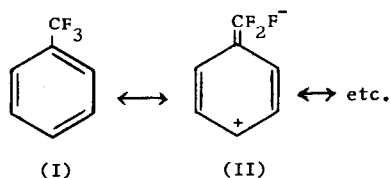
1. D. Holtz, Chem. Revs., 1971, 71, 139.
2. See e.g. R.O.C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds', Elsevier, Amsterdam, 1965.
3. R.D. Chambers, 'Fluorine in Organic Chemistry', Wiley, New York, 1973, p.70.
4. W.A. Sheppard, J. Amer. Chem. Soc., 1963, 85, 1314.

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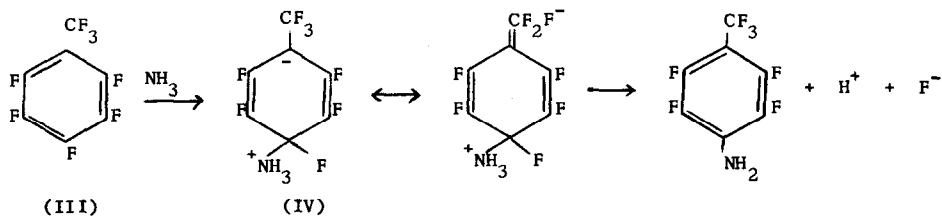


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