Inductive and Field Effects in Aromatic Substitution. Part IX.[1] Assessment of Results

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Earlier work on rates of nitration of the ions $Ph[CH_2]_nX$ ($X = \overset{+}{N}R_3, \overset{+}{S}R_2, \overset{+}{P}R_3$, *etc.*) is analysed in terms of the non-conjugative and conjugative interaction of $[CH_2]_nX$ with the aromatic ring. Partial rate factors for *meta*-substitution are taken as a measure of the non-conjugative interaction. The variation of the deactivation at the *meta*-position with the distance of the pole from the ring is shown to be more consistent with the operation of a field effect than with that of an inductive effect. Apparent exceptions occur when the methylene chain is U shaped for the deactivation is then less than expected. From this and studies with bridged substrates, it is concluded that the transmission of the field effect occurs almost entirely through the molecular cavity but, unlike the inductive effect, is not restricted to the direction of chemical bonds within that cavity. In the ions $Ph[CH_2]_nX$, there is no simple relationship between the orientation of substitution and the deactivation at the *meta*-position. The additional factor involved is identified as conjugative interaction and an approximate linear free energy relationship is derived relating the *para* : *meta* ratio to the σ°_R value for the substituent. This relationship is used to provide information on the relative importance of conjugative and non-conjugative interaction, the comparison of nitrogen and phosphorus poles, and the possible effects of the conformation of the $CH_2\overset{+}{N}H_3$ substituent on the deactivation of the ring.

THE previous papers in this series and in the preceding series[2] on 'The Substituent Effects of Positive Poles in Aromatic Substitution' have been concerned mainly with the way in which a charged substituent of the form $[CH_2]_n\overset{+}{X}$ ($\overset{+}{X} = \overset{+}{N}Me_3, \overset{+}{N}H_3, \overset{+}{P}Me_3$, *etc.*) modifies the reactivity of an aromatic ring to electrophilic reagents. Some aspects of the interpretation now presented have appeared in previous papers but this final assessment is needed because of apparent inconsistencies in the complete set of results and because related studies published in the course of the work have an important bearing on our final conclusions.

It is convenient to consider the evidence relating to these substituent effects first in terms of the deactivation at the *meta*-position and then in terms of the orientation of the substitution. The first is taken as a measure of the non-conjugative interaction (inductive + field) and the second is taken to reflect the balance between the non-conjugative interaction and the conjugative interaction (mesomeric, π-inductive, and orbital penetration).[3]

Non-conjugative Interactions.—Values of the partial rate factors (f_m) for nitration *meta* to the substituents $[CH_2]_n\overset{+}{X}$ are collected in Table 1 and are used in equation (1) to calculate the change in the free energy of activation ($\delta\Delta G^\ddagger$) when the terminal hydrogen atom of the group $[CH_2]_nH$ is replaced by $\overset{+}{X}$. In the equation, the term (f^0_m) is the *meta* partial rate factor for substitution in the hydrocarbon $Ph[CH_2]_nH$. Thus when $n = 0, f^0_m = 1$ and when $n \neq 0, f^0_m$ has been taken[4] as 3. The resulting values of $\delta\Delta G^\ddagger$ are plotted against the maximum distance (r) of the positive pole from the centre of the aromatic ring in Figure 1.

$$\delta\Delta G^\ddagger = -RT\ \ln(f_m/f^0_m) \qquad (1)$$

The results in Figure 1 include also the values for the electrostatic interaction ($\delta\Delta G^0_e$) between the charges in the diconjugate bases of the dicarboxylic acids $HO_2C\text{-}[CH_2]_nCO_2H$ ($n = 1 - 4$) calculated on Bjerrum's theory[5] from equation (2). In this equation, the terms K_1 and K_2 refer to the first and second dissociation

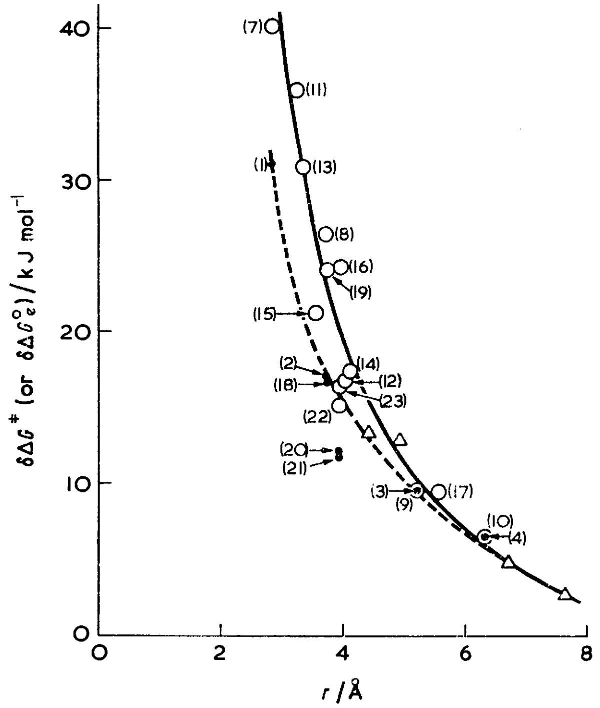

FIGURE 1 Plot of $\delta\Delta G^\ddagger$ [equation (1)] and $\delta\Delta G^0_e$ [equation (2)] at 25° against the distance (r) between the charges. For the ammonium poles, the distances are those given in ref. 4: for the other poles the distances are calculated from these values and the corresponding covalent bond radii (L. Pauling, 'Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960, 3rd edn., p. 224): ○ $\delta\Delta G^\ddagger$ for methylated poles; ● $\delta\Delta G^\ddagger$ for protonated poles; △ values of $\delta\Delta G^0_e$ for the dicarboxylic acids. The numbering corresponds to that in Table 1

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[1] Part VIII, R. Danieli, A. Ricci, and J. H. Ridd, preceding paper.

[2] A. Gastaminza, J. H. Ridd, and F. Roy, *J. Chem. Soc.* (*B*), 1969, 684 and earlier papers in this series.

[3] For the distinctions between these terms see A. R. Katritzky and R. D. Topsom, *J. Chem. Educ.*, 1971, **48**, 427.

[4] T. A. Modro and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 528.

[5] F. H. Westheimer and M. W. Shookhoff, *J. Amer. Chem. Soc.*, 1939, **61**, 555.

constants of the dicarboxylic acid. These values and the maximum distances (r) between the charges are taken from the work of Westheimer and Shookhoff.[5]

$$\delta\Delta G^0{}_e = RT\ \ln(K_1/4K_2) \qquad (2)$$

The plots in Figure 1 bring out the following points. (a) For $r > 4.5$ Å, the values of $\delta\Delta G^\ddagger$ appear to depend on the distance of the pole from the ring and not on the nature of the pole. The values of $\delta\Delta G^0{}_e$ lie effectively on the same line as those of $\delta\Delta G^\ddagger$. Since the magnitude of K_1/K_2 is generally considered to be determined by electrostatic interaction this gives a reason for interpreting the $\delta\Delta G^\ddagger$ values in terms of the electrostatic interaction between the charge on the substituent and that on the ring in the transition state. This accords with our previous observations[4] based on only four values of $\delta\Delta G^\ddagger$. (b) For values of $r < 4.5$ Å, the values of $\delta\Delta G^\ddagger$ for the fully methylated poles * are scattered about a smooth curve. No exact relation between $\delta\Delta G^\ddagger$ and r could be expected partly because the substituent effect is sensitive to the number of methyl groups on the pole[1] and different poles have different numbers of methyl groups. However, the agreement with the curve is sufficient to suggest that the weaker deactivation produced by such substituents as $\overset{+}{S}bMe_3$ and $\overset{+}{A}sMe_3$ relative to $\overset{+}{N}Me_3$ arises mainly from the variation in the C–X bond lengths. This is consistent with the electrostatic interpretation. The alternative interpretation in which the curve is ascribed to the attenuation of the inductive effect by methylene groups is unsatisfactory because very different transmission factors (t) have to be ascribed to the methylene group depending on whether the polar group is positive,[6a] e.g., $-\overset{+}{N}Me_3$ (t 0.59) or neutral, *e.g.* CCl_3 (t 0.28). (c) For values of $r < 4.5$ Å, the values of $\delta\Delta G^\ddagger$ for the substrates with protonated poles ($\overset{+}{N}H_3$) are significantly lower than the curve defined by those with methylated poles presumably because the protonated poles have the centroid of charge nearer to the polar solvent. (d) Certain substituents, notably those numbered (20)—(23) (Table 1) give points that lie significantly below the relevant line. The reason for this is discussed later.

TABLE 1

Partial rate factors for nitration at 25° at the *meta*-position of the ions $Ph[CH_2]_n\overset{+}{X}$ and the related phenylcyclohexylammonium ions. Numbers in parentheses define the points in the Figures. Except where indicated, the figures refer to nitration in aqueous sulphuric acid.

$\overset{+}{X}$	log f_m			
	$n = 0$	$n = 1$	$n = 2$	$n = 3$
$\overset{+}{N}H_3$	-5.45 [a] (1)	-2.51 [b] (2)	-1.27 [b] (3)	-0.67 [b] (4)
$\overset{+}{N}H_2Me$	-5.90 [a] (5)			
$\overset{+}{N}HMe_2$	-6.47 [a] (6)			
$\overset{+}{N}Me_3$	-7.04 [b] (7)	-4.16 [b] (8)	-1.20 [b] (9)	-0.67 [b] (10)
$\overset{+}{P}Me_3$	-6.31 [c] (11)	-2.41 [d] (12)		
$\overset{+}{A}sMe_3$	-5.42 [c] (13)	-2.58 [d] (14)		
$\overset{+}{S}bMe_3$	-3.74 [c] (15)			
$\overset{+}{S}Me_2$		-3.97 [b,e] (16)	-1.18 [b,e] (17)	
(III; $\overset{+}{X} = \overset{+}{N}H_3$)		-2.45 [f] (18)		
(III; $\overset{+}{X} = \overset{+}{N}Me_3$)		-3.74 [f] (19)		
(IV; X = *trans*-$\overset{+}{N}H_3$)			-1.64 [f] (20)	
(IV; X = *cis*-$\overset{+}{N}H_3$)			-1.58 [f] (21)	
(IV; X = *trans*-$\overset{+}{N}Me_3$)			-2.18 [f] (22)	
(IV; X = *cis*-$\overset{+}{N}Me_3$)			-2.39 [f] (23)	

[a] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851. [b] Ref. 6*b*. [c] A. Gastaminza, T. A. Modro, J. H. Ridd, and J. H. P. Utley, *J. Chem. Soc.* (*B*), 1968, 534. [d] For nitration by nitric acid in nitromethane; F. L. Riley and E. Rothstein, *J. Chem. Soc.*, 1964, 3872. [e] H. M. Gilow, M. de Shazo, and W. C. Van Cleave, *J. Org. Chem.*, 1971, **36**, 1745. [f] Ref. 11. The values of f_m derived from notes *a* and *c* have been corrected (by a factor of *ca.* 2) to accord with the value of f_m for the $\overset{+}{N}Me_3$ group in note *b*.

The fact that the values of $\delta\Delta G^\ddagger$ and $\delta\Delta G^0{}_e$ lie on the same curve is, in part, an accident deriving from the choice of nitration as the standard reaction. Results are also available for the substituents $\overset{+}{N}Me_3$, $CH_2\overset{+}{N}Me_3$, $[CH_2]_2\overset{+}{N}Me_3$, $CH_2\overset{+}{S}Me_3$, and $[CH_2]_2\overset{+}{S}Me_2$ in bromination by positive bromine[6b] and the corresponding values of $\delta\Delta G^\ddagger$ [equation (1)] define a line of the same form as that shown for the methylated poles in Figure 1 but shifted to the left by *ca.* 0.5 Å. This is, however, only a little outside the scatter of the points shown for nitration and does not alter the arguments in favour of electrostatic interaction.

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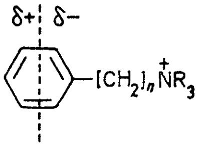
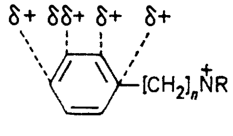
* Partly methylated poles, *e.g.* $\overset{+}{N}MeH_2$ are excluded from the plot in Figure 1.

[6] (*a*) F. De Sarlo, G. Grynkiewicz, A. Ricci, and J. H. Ridd, *J. Chem. Soc.* (*B*), 1971, 719; (*b*) R. Danieli, A. Ricci, H. M. Gilow, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 1477.

The hypothesis that the non-conjugative part of these substituent effects derives from the electrostatic interaction between the charge on $\overset{+}{X}$ and the charge on the ring in the transition state receives support from the ^{13}C chemical shifts in these systems. The work of Reynolds and his co-workers [7] has shown that the replacement of the terminal hydrogen by $\overset{+}{N}R_3$ (R = H or Me) in the systems $Ph[CH_2]_n\overset{+}{N}R_3$ gives rise to an electron displacement as shown in structure (I); when $n = 0$ and R = H or Me the absorption of the *para*-carbon atom is shifted to low field suggesting a reduced electron density relative to benzene. The polarisation shown in structure (I) was foreshadowed by the theoretical calculations of Bishop and Craig.[8] The inductive effect would lead to a different pattern of electron densities in the aromatic ring [structure (II)].[9] If the inductive effect is unimportant in determining the charge distribution in the isolated molecule, it is unlikely to be important in determining substituent effects. Other evidence for the greater importance of the field effect over the inductive effect comes from recent papers on acid–base equilibria.[10]

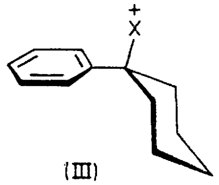


(I)

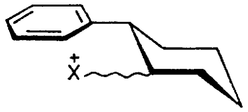


(II)

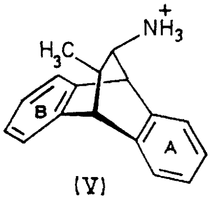
Deviations from the relationship between deactivation and distance (*r*) in Figure 1 are more marked when the substituent $[CH_2]_n\overset{+}{X}$ is constrained to the form of a U. This can be seen in the results [11] for the *meta*-nitration of the phenylcyclohexylammonium ions (III) and (IV). For the ions (III; X = $\overset{+}{N}H_3$ or $\overset{+}{N}Me_3$), the values of $\delta\Delta G^{\ddagger}$ [points (18) and (19)] lie on the appropriate plots but for the ions (IV; X = $\overset{+}{N}H_3$ or $\overset{+}{N}Me_3$), where the substituent chain is U shaped, all points lie below the relevant curve. This is particularly true for the values of $\delta\Delta G^{\ddagger}$ for the ions (IV; X = $\overset{+}{N}H_3$) [points (20) and (21)]. Related difficulties arise for hydrogen isotope exchange in the bridged anthracene derivative (V), for the two rings have equal reactivity [12] despite the fact that the nitrogen pole is nearer ring A and that, in terms of the Kirkwood–Westheimer model,[13] the effective dielectric constant between the nitrogen pole and the rings should be less for ring A than ring B.[14] In these examples, the substituent effect appears to be conducted largely or wholly through the framework of σ bonds.



(III)



(IV)



(V)

It is difficult to know to what extent these results are truly inconsistent with the field effect interpretation because the only approach available for calculating electrostatic interactions in such systems is still that of Kirkwood and Westheimer [13] and this requires that the molecules are treated as spherical or ellipsoidal cavities in the solvent. The potential at points within an S- or U-shaped cavity in a continuous dielectric due to a charge within that cavity is still an unsolved problem in classical electrostatics. When to this uncertainty deriving from the form of the cavity is added the difficulty in allowing for the molecular structure of the solvent, it is clear that the relative importance of electrostatic interaction through the cavity and through the medium cannot be reliably estimated. In view of the difficulty of explaining the complete set of results in terms of the classical inductive effect, the results for compounds with U shaped cavities are probably best accepted as deriving from a field effect which operates almost entirely through the molecular cavity rather than through the medium.

One further piece of evidence then accords with this interpretation. The open-chain ions (VI; $n = 2$ or 3) are much more reactive than the bridged ions (VII; $n = 2$ or 3) in both nitration and hydrogen-isotope exchange; [15] thus, with $n = 3$, $m = 4$, and R = Me, the open-chain ion is more reactive than the bridged ion by a factor of 6.4×10^4 in hydrogen-isotope exchange.[15b] Part of this difference in reactivity may come from the form of the bridged ion, for preliminary experiments [14] have indicated that hydrogen-isotope exchange in [10]paracyclophane is *ca.* 100 times slower than that in *para*-xylene; the reason for this is still under investigation. However, the greater retardation produced by bridging in these 'onium salts is most easily understood in terms of the greater field effect of the positive poles in the bridged ions. The difference between this situation and that with the ion (V) is that, with the brid-

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[7] W. F. Reynolds, I. R. Peat, M. H. Freedman, and J R. Lyerla, *Canad. J. Chem.*, 1973, **51**, 1857.

[8] D. M. Bishop and D. P. Craig, *Mol. Phys.*, 1963, **6**, 139.

[9] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, 1969, 2nd edn., p. 302.

[10] L. M. Stock, *J. Chem. Educ.*, 1972, **49**, 400.

[11] A. Ricci and J. H. Ridd, *J.C.S. Perkin II*, 1972, 1544.

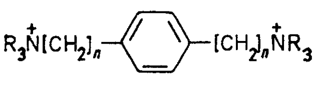
[12] J. H. Rees and J. H. Ridd, *J.C.S. Perkin II*, 1976, 285.

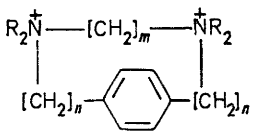
[13] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 1938, **6**, 506; F. H. Westheimer and J. G. Kirkwood, *ibid.*, p. 513.

[14] J. H. Rees, Ph.D. Thesis, London 1973.

[15] (*a*) A. Ricci, R. Danieli, and J. H. Ridd, *J.C.S. Perkin II*, 1972, 1547; (*b*) R. Danieli, A. Ricci, and J. H. Ridd, *ibid.*, p. 2107.

ged ions, the shortest distance between the pole and the ring lies within the molecular cavity and not across a region occupied by the solvent. Thus, the overall conclusion from these results is that positive substituents deactivate the aromatic ring by a field effect which operates essentially within the molecular cavity but which, unlike the inductive effect, is not restricted to the σ bonds within that cavity. This accords with the results reported in the preceding paper.[1]


(VI)


(VII)

A detailed comparison with related results for acid–base equilibria is outside the scope of this paper but it is worth noting that difficulties arise there in the electrostatic interpretation of results relating to U shaped systems [10] and that the results indicate more transmission through the molecular skeleton than would be expected on the basis of simple electrostatic models.[16,17]

Conjugative Interaction.—The following observations indicate that the field effect is insufficient to explain the orientation of substitution in the ions $Ph[CH_2]_n\overset{+}{X}$ (n = 0 or 1).

(a) There is no simple relationship between the $f_p:f_m$ ratio in the nitration of these ions (Table 2) and the magnitude of the field effect as measured by the value of log f_m (Table 1). This applies even if consideration is restricted to the substituents with nitrogen poles. Thus, the $\overset{+}{N}H_3$ substituent gives less *meta*-substitution than $CH_2\overset{+}{N}Me_3$ but is more deactivating. This cannot be explained in terms of hyperconjugative electron donation from the methylene group for such interaction would decrease the % *meta*-substitution observed with the $CH_2\overset{+}{N}Me_3$ substituent.

TABLE 2

Product compositions and related quantities for the nitration of monosubstituted benzenes

Substituent	Product composition (%) *o*	*m*	*p*	σ°_R
$\overset{+}{N}H_3$ [a]	1.5	62	36.5	-0.18 [f]
$\overset{+}{N}H_2Me$ [b]		70	30	-0.15 [f]
$\overset{+}{N}HMe_2$ [b]		78	22	-0.14 [f]
$\overset{+}{N}Me_3$ [b]		89	11	-0.15 [f]
$CH_2\overset{+}{N}H_3$ [c]	21	45	34	-0.10 [g]
$CH_2\overset{+}{N}Me_3$ [d]	2	88	10	$+0.03$ [g]
$\overset{+}{P}Me_3$ [e]		98	2	±0.08 [g]

[a] Ref. 18. [b] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851. [c] Ref. 11. [d] F. R. Goss, W. Hanhart, and C. K. Ingold, *J. Chem. Soc.*, 1927, 250. [e] A. Gastaminza, T. A. Modro, and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 534. [f] Ref. 22*b*. [g] Ref. 31. The figures quoted assume that the $CH_2\overset{+}{N}Me_3$ substituent is restricted by steric interaction to its normal geometry with the C–N bond at right angles to the ring but that the $CH_2\overset{+}{N}H_3$ substituent can turn so that the C–N bond lies in the plane of the ring.

(b) The orientation of substitution in the ion $Ph\overset{+}{N}H_3$ is very sensitive to the acidity of the medium but the extent of deactivation at the *meta*-position is not.[18] Thus, over the range 98—82% sulphuric acid, the $f_p:f_m$ ratio increases by a factor of 2.8 but the value of f_m changes by merely 20%. The change in the $f_p:f_m$ ratio was shown not to arise from the incursion of reaction through the free amine.[18]

(c) In the nitration of $Ph\overset{+}{N}H_3$ in 98% sulphuric acid, the *meta*- and *para*-positions have a very similar reactivity ($f_p:f_m$ 1.2) but the secondary isotope effects per H(D) atom in the substituent differ appreciably: [18] for *para*-substitution $k_H/k_D = 1.18$; for *meta*-substitution $k_H/k_D = 1.08$. This suggests that the similar reactivity at the *meta*- and *para*-positions is achieved by a different balance of substituent effects, with the N–H bonds having greater ionic character in the transition state for *para*-substitution.

(d) The strong *meta, para* directing effect of the $\overset{+}{N}H_3$ and $\overset{+}{N}Me_3$ poles disappears in nitration and hydrogen isotope exchange when the ring is strongly activated by other substituents.[19] However, the greater part of the deactivating effect of the nitrogen pole is retained.

These observations indicate the existence of an additional type of interaction between the substituents and the ring; an interaction that discriminates sufficiently strongly between the *meta*- and *para*-positions to dominate the orientation of substitution. The conventional analysis of substituent effects does not suggest that the inductive effect discriminates in this way [20] and we are left therefore with a form of conjugative interaction.

The idea that the low $f_p:f_m$ ratios with the $\overset{+}{P}Me_3$, $\overset{+}{A}sMe_3$, and $\overset{+}{S}bMe_3$ groups derive in part from π-electron donation from the ring into the vacant *d*-orbitals of the substituent has been accepted for some time [21] but evidence that the $\overset{+}{N}H_3$ and $\overset{+}{N}Me_3$ groups show conjugative interaction with the aromatic ring is more recent and derives mainly from the work of Katritzky, Topsom, and their co-workers [22] on the intensities of the i.r. vibrations at *ca*. 1 600 cm^{-1}. Their values of σ^0_R for

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[16] E. J. Grubbs, R. Fitzgerald, R. E. Phillips, and R. Petty, *Tetrahedron*, 1971, **27**, 935.

[17] O. Exner and J. Jonáš, *Coll. Czech. Chem. Comm.*, 1962, **27**, 2296; see also K. Kalfus, M. Večeřa, and O. Exner, *ibid.*, 1970, **35**, 1195.

[18] S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 1063.

[19] (*a*) R. S. Cook, R. Phillips, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 1166; (*b*) J. R. Blackborow and J. H. Ridd, *Chem. Comm.*, 1967, 132.

[20] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 1.

[21] J. H. Ridd and J. H. P. Utley, *Proc. Chem. Soc.*, 1964, 24.

[22] (*a*) P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767; (*b*) A. R. Katritzky and R. D. Topsom, *Angew. Chem., Internat. Edn.*, 1970, **9**, 87.

some of the substituents used in these kinetic studies are included in Table 2 and show that the $\overset{+}{\mathrm{N}}\mathrm{Me}_3$ and $\overset{+}{\mathrm{N}}\mathrm{H}_3$ groups act as π-electron donors. The apparent conflict between this conclusion and the ^{13}C chemical shifts (showing that the *para*-carbon atom has a low field shift) [7] can be resolved if it is assumed that the ^{13}C shifts measure the sum of the electron displacements from the field effect and the conjugative effect while the i.r. intensities measure only the conjugative effect. As a long range interaction, the field effect should not give rise to a large oscillating dipole during vibrations and hence should not cause a major enhancement of the i.r. intensities.

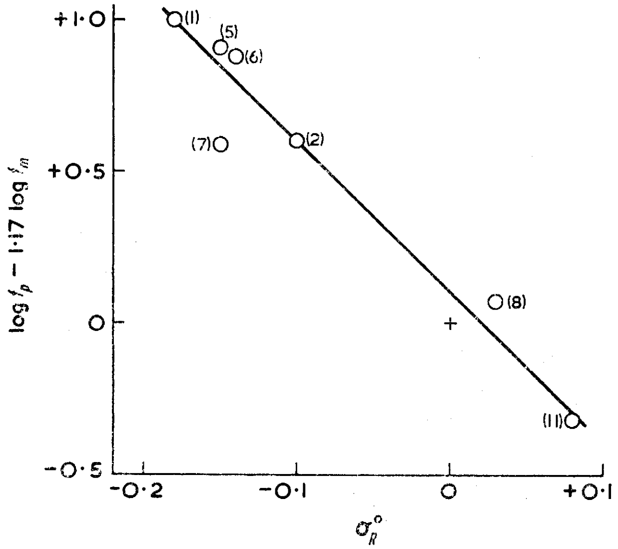

FIGURE 2 Plot to test equation (5) using the data in Tables 1 and 2. The numbering of the points corresponds to that in Table 1. The sign of σ^0_R for the $\overset{+}{\mathrm{P}}\mathrm{Me}_3$ substituent is taken as positive to accord with the chemical shift of a *para*- ^{19}F substituent (R. W. Taft and J. W. Rakshys, *J. Amer. Chem. Soc.*, 1965, **87**, 4387)

An approximate relationship between the $f_p : f_m$ ratios and the σ^0_R values in Table 2 has been derived as follows. For electrophilic aromatic substitution, the equations of Exner [23] take the forms (3)—(5): * a plot of log f_p − λlog f_m against σ^+_R should therefore be linear with a slope of ρ (1 − $\alpha\lambda$). The values of σ^0_R have been used here as an approximation for σ^+_R and λ has been taken as 1.17. The resulting plot for those positive substituents for which σ^0_R values are available is shown in Figure 2 and is approximately linear.

$$\log f_m = \rho(\sigma_I + \alpha\sigma^+_R) \tag{3}$$

$$\log f_p = \rho(\lambda\sigma_I + \sigma^+_R) \tag{4}$$

$$\log f_p - \lambda\log f_m = \rho\sigma^+_R(1 - \alpha\lambda) \tag{5}$$

For several reasons, the above approach can be only a very approximate one. Charged substituents do not usually give satisfactory correlations in linear free energy relationships because the σ values depend on the conditions; [25] σ^+_R values are not usually proportional to σ^0_R values; [3] and with the $\overset{+}{\mathrm{N}}\mathrm{H}_3$ substituent, at least, the orientation of substitution depends on the conditions.[18] Nevertheless, the slope of the plot in Figure 2 (−5.0) suggests that the correlation is significant for, with $\alpha = 0.2$,[24] the value of ρ comes out to be −6.53, a value close to that usually assigned to nitration (−6.0).[26,27] This is, of course, partly a consequence of the value assigned to λ but the fact that the value of λ giving a linear plot also gives an approximately correct slope is worth noting for it supports the significance of the correlation and suggests that these σ^+_R values and the corresponding σ^0_R values are not very different, perhaps because these positive substituents are not very polarisable. The main purpose in presenting this correlation is qualitative rather than quantitative, to provide evidence that the orientation of these substitution reactions is determined in part by conjugative interaction with the substituent.

Such conjugative interaction clearly provides an explanation of why there is no correlation between the orientation of substitution and the extent of deactivation at the *meta*-position [observation (a) p. 297]. The reason why the directing effect of the $\overset{+}{\mathrm{N}}\mathrm{H}_3$ and $\overset{+}{\mathrm{N}}\mathrm{Me}_3$ poles disappears when the ring is strongly activated by other substituents [observation (d) p. 297] is less obvious but can be rationalised in the following way.

Since λ needs to be >1 to obtain the correlation shown in Figure 2, it follows that, on this interpretation, the non-conjugative interaction deactivates the *para*- (and presumably also the *ortho*-) more than the *meta*-position. For the substituents with $\sigma^0_R < 0$, this relative deactivation of the *para*-position is partly or completely compensated by the conjugative electron donation. However, the conjugative interaction is believed to act less strongly at the *ortho*- than at the *para*-position,[28] a result which provides an explanation of the *meta*, *para* orientation observed with such groups. In the presence of a strongly activating group or groups, this directing effect would be expected to change, for the transition state should become more similar to the initial state and the conjugative effect then appears to activate the *ortho*- and *para*-positions to a similar extent (*cf.* the $f_o : f_p$ ratio for hydrogen-isotope exchange in toluene when the electrophile is a strong acid [29]). The deactivation of

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* Exner's equations [23] are needed here because no correlation is obtained using the more conventional equations [24] with $\lambda = 1$. The value of λ is very close to that chosen by Exner (1.14) but this may be an accident since λ is treated here as an adjustable parameter and need not have the same value for electrophilic substitution and acid–base equilibria.

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[25] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[26] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35 (see especially p. 99).

[27] Ref. 24, p. 43.

[28] *Cf.* C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Chem. Soc.* (*B*), 1969, 15.

[29] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, pp. 211, 305 *et seq.*

the *ortho*- relative to the *para*-position should then be reduced.

Consequences of Above Interpretation.—The relationships expressed by equations (3) and (4) with $\lambda = 1.17$, $\alpha = 0.2$, and $\rho = 6.5$ have other significant implications. Thus the relative importance of the conjugative and non-conjugative interactions is then as in Table 3 for the $\overset{+}{N}H_3$ substituent in terms of the values for $\delta\Delta G^\ddagger$ at 25°. These figures are obtained by using the observed values of $\log f_m$ and $\log f_p$ together with the values of ρ, α, and λ used above to calculate from equations (5) and (6) the appropriate values of $\sigma_I(0.87)$ and σ^+_R (-0.20). These values are then substituted in

$$\sigma_I = (\log f_m - \alpha \log f_p)/\rho(1 - \alpha\lambda) \qquad (6)$$

equations (3) and (4) to calculate the contributions of the conjugative and non-conjugative interaction to the partial rate factors at each position. The resulting values of $\log f$ are converted to free energies of activation using $\delta\Delta G^\ddagger = -RT \ln f$. The results show that the non-conjugative interaction is by far the more important in determining the reactivity at each position but that the conjugative interaction, because it discriminates more between the *meta*- and *para*-positions is important in determining the orientation. Indeed, the figures in Table 3 imply that if the value of σ^+_R were set at zero the percentage of *para*-substitution would fall from 38% to *ca.* 5% (this calculation ignores the small amount of *ortho*-substitution).

TABLE 3

Relative importance of conjugative and non-conjugative interactions for $\overset{+}{N}H_3$ in terms of $\delta\Delta G^\ddagger$

	Non-conjugative		Conjugative	
	meta	*para*	*meta*	*para*
$\delta\Delta G^\ddagger$/kJ mol^{-1}	32.4	37.9	−1.3	−7.4

The marked difference between the extents of *para*-substitution in the poles $\overset{+}{N}R_3$ (R = H or Me) and $\overset{+}{P}Me_3$ (Table 2) has been attributed previously to conjugative electron withdrawal into the empty *d*-orbitals of the $\overset{+}{P}Me_3$ substituent.[21,30] However, the results above imply that much of this difference could arise from weaker conjugative electron donation from the $\overset{+}{P}Me_3$ group, possibly as a consequence of the difference in the Ar–$\overset{+}{P}$ and Ar–$\overset{+}{N}$ bond lengths. It seems unlikely that this factor can explain the whole of the difference in the directing effects of the nitrogen and phosphorous poles, but the relative importance of a decrease in the conjugative electron donation and the introduction of conjugative electron withdrawal is not yet clear.

Another consequence of the above interpretation is to provide, for some substituents, a method of calculating how the substituent effect depends on the conformation of the substituent. Katritzky, Topsom, and their co-workers[31] have estimated values of σ^0_R for the substituent $CH_2\overset{+}{N}H_3$ with the C–N bond in the plane of the aromatic ring (conformation A, σ^0_R −0.10) and with the C–N bond at right angles to the aromatic ring (conformation B, σ^0_R 0.00). If we assume that, with this substituent, the non-conjugative interaction is insensitive to the conformation (because both conformations have the same distance between the pole and the centre of the ring) then the consequence of the change from conformation A to B is to change the values of f_p and f_m in nitration by factors of 4.6 and 1.3 respectively. This can be seen by calculating σ_I (0.41) from equation (6) and then using this value together with the given values of σ^0_R in equations (1) and (2). The partial rate factor for *ortho*-substitution is probably reduced by a factor between 4.6 and 1.3 for conjugative effects are normally less important at the *ortho*- than at the *para*-position.[28]

It is important to have even a crude estimate of these factors to assess the magnitude of the retardation from this source in going from the open-chain ion (VI; n = 1, R = H) to the bridged ion (VII; n = 1, m = 8, R = H). In the open-chain ion, reaction would occur more readily with the substituents in conformation A but, in the bridged-ion, the $ArCH_2\overset{+}{N}$ groups are held in conformation *B*. Since each free position in the aromatic ring is *ortho* to one substituent and *meta* to the other, the change in the reactivity of the ring resulting from the conformational change is a factor of *ca.* 6. The observed retardation in going from this open-chain ion to the bridged ion is a factor[15a] of 1 050. It is clear therefore that the conformational change involving rotation about the ArC bond is unlikely to be a major contribution to the rate retardation on bridging.

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