394. *Electrophilic Reactions of the Anilinium Cation*

By A. K. CHANDRA and C. A. COULSON

A wave-mechanical study is made of the electrophilic substitution reactions of an anilinium cation. It is shown that neither the charges induced on the various atoms of the benzene ring by the ammonio-group, nor the charges induced by the combined influence of the ammonio-group and the approaching electrophil (*e.g.*, NO_2^+), are able by themselves to account for the observed *meta* and *para* reactivity. But if the latter charges are used to calculate either the actual repulsive force on the electrophil, or the total electrostatic energy required to bring the electrophil from infinity to any chosen position relative to the anilinium, then it is concluded that the *para* position should be very slightly more reactive than the *meta* position, and both much more reactive than the *ortho*. This is in complete agreement with experiment. Some indications are also obtained of the most likely directions in which the electrophil should approach the benzene ring.

THE ammonio-group in the anilinium cation $Ph{\cdot}NH_3^+$ is known to have a very large influence on the reactivity of the benzene ring, despite the fact that it has very little effect on the near ultraviolet spectrum, a region which is normally highly sensitive to substitution. The effect of the ammonio-group on the benzene ring must be largely inductive. since the opportunities for conjugation are small. In the standard theory of Ingold [1] and others,[2] it is argued that electrophilic substitution in a monosubstituted benzene takes place mainly at the *meta* position when the first substituent, as in anilinium, bears a formal positive charge. This rule is explained by the hypothesis that the inductive effect removes electrons more effectively from the *ortho* and *para* positions than from the *meta*

[1] C. K. Ingold, " Structure and Mechanism in Organic Chemistry." Cornell University Press, Ithaca, New York, 1953, sect. 196.

[2] J. H. Pfeiffer and R. Wizinger. *Annalen*. 1928, **461**. 132.

position: the approaching electrophil is therefore expected to attack the latter position preferentially. However, recent work[3] on the kinetics of nitration of the anilinium cation has shown that the reactivity of the *para* position slightly exceeds that of a *meta* position. (If the substituent is NMe_3^+ instead of NH_3^+ the situation is reversed, and the *meta* positions are slightly more reactive than the *para* position.)

One of the earliest attempts to deal with directional effects in aromatic substitution was due to Wheland and Pauling,[4] who related reactivity to the charge distribution in the monosubstituted molecule. A quantum-theory justification for this was given by Coulson and Longuet-Higgins,[5] within the framework of the simple Hückel molecular-orbital theory. However, as these latter authors showed, using the mutual atom-atom polarizabilities for benzene, the effect of a change in the Coulomb term of the ring atom to which the first substituent is attached will be to take π electrons away from the *ortho* and *para* positions, and add π electrons to the *meta* positions, in the ratio 17 : 11 : 1. This charge distribution would lead to an almost exclusive nitration of anilinium at the *meta* position, in clear contradiction to what is found experimentally. This point has already been recognised by Bishop and Craig,[6] whose work we shall consider shortly.

The present Paper is an attempt to understand the high *para*-reactivity of anilinium. We first consider two improvements in the charge distribution, and show that although these do modify the simple Hückel result just described, they still do not lead to the observed situation in regard to reactivity. We then take into account the simultaneous perturbations of the π electrons of the ring due both to the original NH_3^+ and to the approach of the NO_2^+ ion. On the basis of these calculated charges the *meta* position still seems to be the most favoured. But when we use this charge distribution to estimate the actual force acting on the NO_2^+ in varying positions round the ring and at varying distances from the centre of the ring, we find that this repulsive force is slightly less when the electrophil approaches towards the *para* position than when it approaches towards the *meta* position; and both are much less than when it approaches towards the *ortho* position. A precisely similar situation holds if, instead of calculating the repulsive force on the electrophil, we compute the total electrostatic interaction between all the charges involved. It seems, therefore, as if the explanation of the experimental results lies not so much in the charge distribution of the original unperturbed anilinium, as in the global interaction between all the charges, when these are calculated in the presence of the approaching electrophil.

It will be appreciated from the above that we have adopted the implicit assumption that the transition state comes " early " and is of relatively low energy relative to the reactants. If it comes " late," then valence forces will surely play some part. This distinction between " early " and " late " corresponds roughly (see Figure) to the approaching electrophil being more than, or less than, about $1\frac{1}{2}$ bond lengths from the attacked carbon atom.

Charge Distribution in the Anilinium Cation.—We now make improved calculations of the anilinium charge distribution. The first improvement is to suppose that the NH_3^+ group behaves as a point positive charge, and that this provides an additional electrostatic potential of the form $e/\varepsilon R$ at distance R, where ε is some effective dielectric constant. In discussions of acid strength ε has often been given the value 2: Bishop and Craig[6] have given additional justification for this value, so we adopt it. This potential modifies the Coulomb term α_r of carbon atom r, by adding to it (in atomic units) an amount $1/\varepsilon R_r$. This is numerically largest for the carbon atom to which the NH_3^+ is attached, and it falls steadily as we pass to the *ortho*, *meta*, and *para* positions. This use of $1/\varepsilon R_r$ means that we consider the ammonio-group to influence not only the carbon atom to which it is attached

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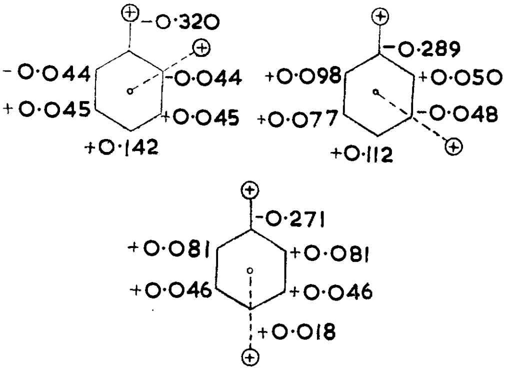
[3] M. Brickman, S. Johnson, and P. Ridd, *Proc. Chem. Soc.*, 1962. 228.
[4] G. W. Wheland and L. C. Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2091.
[5] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **192**, 16.
[6] D. M. Bishop and D. P. Craig, *Mol. Phys.*, 1963, **6**, 139.

but also, by a field effect, all the other carbon atoms of the ring. The second improvement is to replace the Hückel theory, and the various derived atom–atom polarisabilities, by the molecular-orbital perturbation theory formulated by Pople,[7] which is based on a Hamiltonian that includes electron interaction. We are, of course, assuming all the time that the π electrons are involved in this phenomenon.

Criticisms are possible of both our improvements. The field effect is likely to be of shorter range than is implied by a formula $1/\varepsilon R$, since there will be some electrostatic screening by the dipoles of the solvent molecules (usually water). It is probable that an additional factor of exponential form should be incorporated. But there does not seem to be any simple way of estimating it, and so, following Bishop and Craig,[6] we neglect it. Bishop and Craig add a repulsive term and write for the electrostatic potential due to the NH_3^+ an expression of the form



Net π-electron charges on the carbon atoms of an anilinium ion perturbed by an electrophil approaching in the *ortho, meta,* and *para* directions

$$V = \frac{1}{\varepsilon}\left(-\frac{\alpha}{R} + \frac{3}{R^2}\right)$$

where α is about 1·8. In the range of R which is of interest for our problem this differs relatively little from our simpler expression. Criticism may also be made of our use of perturbation theory. However the full calculations would be much more clumsy to make, and would probably not differ very significantly from the simpler perturbation ones. In any case, the error arising in this way is not likely to be more than that implicit in our model. For the purposes of a qualitative understanding, these criticisms do not seem to us to be valid.

We have extended our calculations of charge distributions by supposing that the NH_3^+ charge is located at 1, 2, or 3 bond distances (*i.e.*, 1·4, 2·8, or 4·2 Å) radially from the ring. Our reason for doing this is to show that the sequence of charges is not critically dependent on this distance, but is always such that the *para* position carries the largest resultant positive charge. The whole set of charges also gets progressively smaller as the distance of the cation increases. The results are given in Table 1. It can be seen from this Table that in the normal anilinium molecule, all three types of atom carry a net positive charge, but the sequence is *para* > *ortho* > *meta*. If the simple argument from π-charges were valid,

TABLE 1

The net π-electron charges on the carbon atoms of the benzene ring perturbed by a positive pole which is placed at various distances radially out from a carbon atom in the plane of the ring

Distance from nearest C atom	*ortho*	*meta*	*para*
1·4 Å	+0·05249	+0·04842	+0·11451
2·8	−0·00272	+0·02829	+0·04569
4·2	−0·00653	+0·01686	+0·02557

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[7] J. A. Pople, *Proc. Roy. Soc.*, 1955, *A*, **233**, 233.

this should lead to a prediction of nitration in the *meta* position, the *para* position being least reactive of all.

Charge distributions showing the *para* position as the least reactive have been obtained by Bishop and Craig (ref. 5, Figure 4), though their numerical values for the net charges are smaller than ours. It is interesting that Bishop and Craig used an entirely different approach from ours, building up their final charges by a superposition of several distinct states of unperturbed benzene. The presence of the NH_3^+ charge mixes together otherwise non-interacting states; and by appeal to experiment to get the appropriate energy differences, and by calculation of the required matrix components due to the perturbation V, it is possible to compute the charges. It seems probable that our net charges are too large, since Bishop and Craig report preliminary proton magnetic resonances which indicate smaller variations between the various carbons. However, only relative values of the charges are needed for our later work. A larger value of ε would, of course, reduce the magnitudes of these calculated net charges.

Effect of a Positive Ion on Anilinium Charge Distribution.—It is clear from the previous paragraph that no explanation of the observed *para* nitration of anilinium is to be found from the charge distribution of an isolated anilinium ion. We therefore consider what happens when an electrophil such as NO_2^+, regarded as a point-positive charge, approaches the anilinium. In this way we attempt to calculate the charge distribution at various points along the reaction path. We therefore adopt the perturbation theory of Pople,[7] but now there are two perturbations acting simultaneously. One is the ammonio-group, placed at 1·42 Å from the attached carbon atom: the other is the NO_2^+ group, placed at varying positions in the plane of the anilinium, and also at varying positions out of the plane. We do not yet know the geometrical shape of the transition state, and may therefore hope to get some indications by varying the angle between the approaching electrophil and the plane of the ring. We have made calculations for several distinct distances of the electrophil, but shall content ourselves here by describing those that relate to a distance equal to three bond lengths (4·2 Å) from the centre of the ring.

First let us suppose that the NO_2^+ lies in the same plane as the ring. The Figure shows the charges on all six ring carbon atoms when the NO_2^+ lies radially outwards in the direction of the *ortho*, *meta*, or *para* carbons. It will be seen that these charge distributions differ considerably from those in Table 1. It is not surprising, therefore, that we need to include the perturbing influence of the approaching NO_2^+, even when it is twice as far away from its appropriate carbon atom as is the bonded ammonio-group. There are some obvious differences between these numerical values, and those for a similar geometrical situation obtained by Bishop and Craig. But both sets of values agree in suggesting that under the combined influence of the NH_3^+ and NO_2^+ groups, the direction of attack that leads to the greatest electron density on the attacked carbon is toward the *meta* position. In both sets the *para* position appears considerably less favourable. We have found that the same situation is obtained if the distance of the NO_2^+ group from the ring is varied between one and three bond lengths from the atom being attached.

Our conclusion is that the charge distribution under the joint perturbation of NH_3^+ and NO_2^+ does not, by itself, allow us to predict the position of nitration. It is true that in this purely electrostatic argument we have not allowed for the formation of any incipient bond from the NO_2^+ to the ring carbon atom.[8] However, this bond requires that the ring carbon should donate some fraction of an electron to the approaching electrophil. We should expect this donation to be most easily accomplished if the ring carbon atom already possesses a large electron density. Thus our neglect of any possible covalent bond formation is not likely to influence our conclusion as to the position of attack.

Next we consider the situation that arises when the NO_2^+ group is moved out of the anilinium plane. We keep the distance between the NO_2^+ and the centre of the ring

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[8] R. D. Brown, *J.*, 1951, 1955; 1952, 2229.

constant and equal to three bond lengths. but we suppose that the angle between the line joining it to the centre of the ring makes an angle θ with the plane of the ring. Our previous results therefore relate to $\theta = 0$. and the value $\theta = 90°$ corresponds to attack directly above the centre of the ring. Table 2 shows the charges calculated in precisely the same way as before. for a series of values of θ. Once again it appears that the *meta* position carries the greatest net negative charge, and the *para* position the least, for all values of θ.

Table 2

The net π-electron charges at *ortho*, *meta*, and *para* positions for an electrophil being placed at various points in relation to the NH_3 substituent

Angle θ	*ortho*	*meta*	*para*	Angle θ	*ortho*	*meta*	*para*
0°	−0·04406	−0·04787	+0·01795	60°	+0·02230	+0·01822	+0·08432
30°	−0·01899	−0·05032	+0·04325	90°	+0·05249	+0·04842	+0·11451
45°	+0·02176	−0·00179	+0·06419				

Electrostatic Force on Electrophil.—Our previous arguments have shown that neither the charge distribution of the non-reacting anilinium ion. nor the charge distribution in the presence of the approaching electrophil. is able to explain the high *para* reactivity experimentally observed. But there is another possible way of studying this matter. Instead of concentrating on the formal charges. let us calculate the actual force acting on the electrophil in any position. According to the Hellmann–Feynman theorem this force may be calculated by classical electrostatics, using the wave-mechanical charge distribution. In our case we may approximate the wave-mechanical charge distribution by the set or formal charges. as in the Figure or Table 2. We have then to form the vector sum of the many inverse-square law attractions and repulsions acting on the NO_2^+ ion. Table 3 shows the numerical results thus obtained. using the same distances and charges as in Table 2. The columns headed F_o, F_m, F_p relate to the forces when the NO_2^+ ion is approaching the *ortho*. *meta*. or *para* position, respectively. It will be seen from this that the forces F_m and F_p in the *meta* and *para* positions are approximately equal. and (except for the degenerate situation when $\theta = 90°$ and there is no distinction between all three) they are considerably less than F_o. Thus if the electrophil approaches toward the *ortho* carbon it will experience a greater repulsion than if it approaches toward the *meta* or *para* carbons. The actual difference between F_m and F_p is so small as probably not to be significant. But it is noteworthy that. apart from a small region near $\theta = 30°$, $F_p < F_m$. It should be emphasised that in making these calculations of the force. all electrostatic interactions have been taken into account. But no dispersion or repulsive overlap forces have been considered. There seems no particular reason why either of the latter should vary significantly from one direction of attack to another.

Table 3

Electrostatic force exerted on, and the energy of, the electrophil which is placed at various points above the plane at 3 bond distances from the ring centre radially out from *ortho*, *meta*, and *para* positions. (Force and energy are expressed in atomic units)

Angle	F_o	F_m	F_p	E_o	E_m	E_p
0°	+0·00824	+0·00384	+0·00377	+0·01805	+0·00602	+0·00833
30°	+0·00775	+0·00396	+0·00405	+0·01827	+0·00625	+0·00826
45°	+0·00731	+0·00453	+0·00423	+0·01681	+0·00815	+0·00728
60°	+0·00655	+0·00481	+0·00448	+0·01097	+0·00949	+0·00855
90°	+0·00549	+0·00549	+0·00549	+0·01069	+0·01069	+0·01069

There is another way of looking at this matter. Instead of calculating the force acting on the electrophil. let us calculate the total electrostatic energy (E_o. E_m, E_p. respectively) by summing all the contributions of type q_1q_2/R_{12}. Our previous force must be the gradient of this total electrostatic energy with respect to movement of the NO_2^+ ion. The last three columns of Table **3** show that E_m and E_p are closely alike, and differ greatly from E_o. So these numerical values confirm the greater reactivity of the *meta* and *para* positions. Now, however, for $0 < \theta < 40°$ $E_m < E_p$, and for $40° < \theta < 90°$ $E_p < E_m$. The differences are small, and may not be significant. But they suggest that *para*-substitution will be favoured if the angle θ of attack exceeds about 40°. This is likely to be the case in practice. However, even if we do not accept the details of Table 3, their general character is likely to be more accurate. We may therefore conclude with rather more confidence that since the minimum of E_o occurs at $\theta = 90°$, and of E_m and E_p at 0° and 45°, and the rates of change of these quantities are much bigger for E_o than for either E_m or E_p, therefore the geometry of the activated complex for *ortho*-substitution will differ from that for either *meta*- or *para*-substitution.

Our conclusions can be put simply: and although they have been obtained for the particular case of attack by NO_2^+ on the anilinium ion, they are likely, if correct, to apply much more generally. The position of electrophilic substitution in the anilinium cation is not adequately predicted either by the charge distribution of an isolated anilinium, nor by the charges on the *ortho*, *meta*, and *para* positions under the joint influence of the original ammonio-group and the approaching NO_2^+; but it is correctly predicted by comparisons of the repulsive force acting on the approaching electrophil, or of the total electrostatic energy of the charges induced by the NH_3^+ and NO_2^+ ions.

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