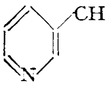
490. meta-*Interactions and Inductive Effects in Heterocyclic Systems.*

By D. A. Brown and M. J. S. Dewar.

The apparently anomalous behaviour of β-picoline, and of certain *meta*-substituted benzene derivatives, has been examined theoretically. Two possible explanations have been considered. The first, which postulates a direct *meta*-interaction in aromatic systems, has proved unsatisfactory. The second, based on the conception of an inductoelectromeric effect by which abnormally electronegative carbon atoms exert appreciable electromeric effects, provides a satisfactory explanation of the above anomalies. A general theoretical explanation of the absence of *meta*-interaction effects, based on perturbation theory, is given in the Appendix.

It is well known that α- and γ-picoline differ from the β-isomer in undergoing a number of typical prototropic reactions, for instance, base-catalysed condensations with aldehydes; and this difference is believed to be due to the electromeric electrophilic effect of the annular nitrogen atom. Recently, however, Brown and Murphey (*J. Amer. Chem. Soc.*, 1951, **73**, 3308) have observed that the prototropic reactivity of β-picoline, while less than that of its isomers, is nevertheless very much greater than that of toluene; for β-picoline is readily alkylated by alkyl halides and sodamide in liquid ammonia, conditions under which toluene does not react at all. A similar anomaly was observed by Bevan and Bye (*Chem. and Ind.*, 1952, 981) in the methanolysis of 1-fluoro-3 : 5-dinitrobenzene, the rate of which is similar to that of the methanolysis of *p*-fluoronitrobenzene under similar conditions; here again the electromeric effect of the nitro-group is apparently transferred to the *meta*-position in a six-membered aromatic ring. Brown and Murphey (*loc. cit.*) suggested that the β-picolinyl anion (I) might be stabilized by contributions from the *meta*-quinonoid structure (II). A recent investigation into the relation between the resonance and the molecular orbital theory (M.O.) (Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, 1952, *A*, **214**, 482) implies that the M.O. parallel of this suggestion would be that (I) is stabilized by direct interaction between pairs of *meta*-carbon atoms, the resonance integral between them being appreciable. In the usual M.O. treatment, which leads to the same conclusions as the classical or resonance theory, resonance integrals between non-adjacent atoms are neglected; according to Brown and Murphey, the new effect implies that the neglect of such integrals is not justifiable.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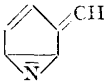
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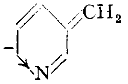
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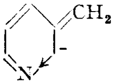

(IV)

An alternative explanation was given by Dewar (*J. Amer. Chem. Soc.*, 1952, **74**, 3357). The polarity of the C–N σ-bonds in pyridine should raise the electron affinity of the α-carbon atoms, and these electronegative carbon atoms should then activate the β-methyl to prototropy. Such an activation would be due to the electromeric effect of two electronegative atoms in the usual (*o* : *p*) relations to the methyl; since the activating atoms owe their electronegativity to an inductive effect, the overall effect might be termed " inducto-electromeric." In resonance terminology, the stabilization of (I) is here ascribed to the importance of unexcited structures (III, IV) in which the negative charge resides on abnormally electronegative carbon atoms. A theoretical investigation of *o* : *p*-ratios in substitution of benzene derivatives (Dewar, *J.*, 1949, 463) had already shown that this effect must be important, and as an explanation of a novel phenomenon it has the attraction of involving only accepted concepts.

The relative importance of these two possible types of phenomenon have now been studied theoretically.

Method.—Energy levels and charge distributions were calculated for benzene and pyridine by standard L.C.A.O. techniques with and without inclusion of resonance integrals between *meta*-atoms. From these, energy levels and charge distributions were calculated for the benzyl anion by the L.C.M.O. modification of the usual L.C.A.O. method (Dewar, *Proc. Camb. Phil. Soc.*, 1948, **45**, 638). This procedure greatly reduces the labour involved in such calculations. Several parameters were required in addition to the usual C–C resonance integral. The ratio of the C–C resonance integrals between adjacent (1 : 2) and *meta* (1 : 3) atoms in the ring was taken to be 10; the ratio of the corresponding overlap integrals is about 6 (Slater, *J. Chem. Phys.*, 1949, **17**, 1248), and the ratios of the resonance and overlap integrals should be similar. The parameters involving the N atom followed those recommended by Dewar (*J.*, 1949, 463; 1950, 2329):

Resonance integral of CN bond = resonance integral for similar CC bond
Coulomb term for nitrogen = β
Coulomb term for carbon adjacent to nitrogen = $0{\cdot}4\beta$
Coulomb term for carbon separated by one atom from nitrogen = $0{\cdot}1\beta$

Approximate charge distributions were also calculated for a number of larger heterocyclic systems by the perturbation method of Coulson and Longuet-Higgins (*J.*, 1949, 971), the values indicated above being used for the various Coulomb integrals.

Overlap was neglected, since its inclusion is known to make no appreciable difference in chemical applications of the M.O. method.

Results and Discussion.—(1) *Energy levels.* Table 1 shows calculated energies for M.O.'s of benzene, benzyl, and pyridine, both with and without inclusion of *meta*-interactions (*i.e.*, of resonance integrals between *meta*-positions in the ring, and between the methylene group and *ortho*-positions in benzyl). The last row shows the calculated total π-electron energies for these molecules, the three values for benzyl corresponding to the cation, radical, and anion respectively. Notice that the total energies of the even systems, and of the odd radical, are virtually unchanged by *meta*-interactions although the individual levels alter somewhat; it can be shown (see Appendix) that this is true in general for neutral alternant systems, to a first approximation, and there is therefore probably no need to consider *meta*-interactions when calculating their energies; particularly since the calculations reported here suggest that the higher-order perturbations are very small. Notice also that the " non-bonding " M.O. of benzyl becomes antibonding when *meta*-interactions are included; this result again can be shown to hold quite generally (see Appendix) and would imply that the resonance energies of a related set of odd alternant systems should fall in the order cation>radical>anion if *meta*-interactions are important. (In the absence of *meta*-interactions all three energies are of course equal.) However, the application of the simple M.O. method to such ions involves assumptions of dubious validity (Coulson and Dewar, *Discuss Faraday Soc.*, **1947**, **2**, **54**) and too much weight should not be attached to this prediction. Experimental data are lacking.

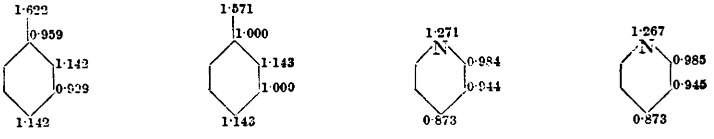
TABLE 1.

	Benzene		Benzyl		Pyridine	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Energy levels in units of β (*a*) with and (*b*) without *meta*-interaction	+1·800	+2·000	+1·880	+2·101	+1·573	+1·748
	+1·100	+1·000	+1·311	+1·260	+0·861	+0·761
	+1·100	+1·000	+1·100	+1·000	+0·628	+0·552
	−0·900	−1·000	+0·143	0·000	−1·161	−1·261
	−0·900	−1·000	−0·900	−1·000	−1·282	−1·358
	−1·800	−2·000	−1·210	−1·260	−2·619	−2·443
	—	—	−2·324	−2·101	—	—
Total π-electron energy $\times \beta^{-1}$	8·00	8·00	8·87	8·72	10·12	10·12
	—	—	8·73	8·72	—	—
	—	—	8·68	8·72	—	—

(2) *Charge densities.* The total π-electron charge distributions in the benzyl anion and in pyridine with and without *meta*-interaction are shown in Fig. 1; the charge distribution in benzene, and indeed the molecular orbitals themselves, are quite unchanged by *meta*-interaction since they are determined rigorously by the symmetry of the molecule.

It will be evident from Fig. 1 that the charge densities are virtually unaltered by *meta*-interactions, except for the methylene group and the carbon atom adjacent to it in the benzyl anion. This result is perhaps unexpected since it can easily be shown that the bond–atom polarizabilities in alternant hydrocarbons vanish only for bonds formed between atoms of opposite parity (see Appendix). A more detailed investigation may show that the change in charge density depends on the environment of the atom; comparison of Fig. 1(*a*) and 1(*b*) suggests that the charges at doubly connected atoms may prove to be virtually unaffected by *meta*-interaction, while those at singly connected atoms may be raised and those at triply connected atoms lowered. For the present purpose it is sufficient to know that the charge density at the *meta*-position in the benzyl anion is virtually unchanged by *meta*-interactions and therefore almost identical with the charge density at a *meta*-carbon atom in toluene.

FIG. 1. *Charge distributions in the benzyl anion and in pyridine* (a) *with and* (b) *without* meta-*interactions.*



Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39) showed that the change in π-electron energy on replacement of a carbon atom in a mesomeric system by a hetero-atom is given approximately by $q\alpha$, where q is the π-electron density at that position in the isoconjugate hydrocarbon and α is the coulomb term of the hetero-atom, provided that the substitution alters none of the bond resonance integrals, as is probably the case for nitrogen. If then the charge density at the *meta*-position in the benzyl anion is approximately the same as in the *meta*-position of toluene, the π-electron energy of each will be altered equally if that carbon atom is replaced by nitrogen. Such a replacement would then leave the relative energies of toluene and its conjugate base ($Ph{\cdot}CH_2^-$) unaltered, and so β-picoline would resemble toluene in its prototropic reactivity. The greater prototropic reactivity of β-picoline cannot therefore be ascribed to *meta*-interactions as Brown and Murphey suggested.

The alternative explanation, in terms of the inductoelectromeric effect, does account for the observed facts. The energy levels of the three picolinyl anions, with neglect of *meta*-interaction, are listed in Table 2; and the differences (ΔE) in total π-electron energy between toluene and the three picolines on the one hand, and their conjugate anions on the other, are given in Table 3. Since prototropic activity should be greater the greater ΔE, it is evident that β-picoline should show a reactivity intermediate between that of toluene on the one hand, and that of α- or γ-picoline on the other.

TABLE 2. *Energy levels of the picolinyl ions, in units of* β.

α-Picolinyl	β-Picolinyl	γ-Picolinyl	α-Picolinyl	β-Picolinyl	γ-Picolinyl
−0·1784	−0·1140	−0·1797	−1·470	−1·576	−1·616
−1·356	−1·307	−1·261	−2·535	−2·484	−2·472

TABLE 3. *Total* π-*electron energies of* $R{\cdot}CH_3$ *and* $R{\cdot}CH_2^-$, *and the differences between them, in units of* β.

R =	Phenyl	β-Pyridyl	α-Pyridyl	γ-Pyridyl
$E_{R{\cdot}CH_2^-}$	8·72	10·96	11·08	11·05
$E_{R{\cdot}CH_3}$	8·00	10·12	10·12	10·12
ΔE	0·72	0·84	0·96	0·93

The unusual acidity of β-picoline should therefore be ascribed to the inductoelectromeric effect rather than to *meta*-interactions of the type considered by Brown and Murphey; and this, together with the results obtained earlier (Dewar, *loc. cit.*), suggests strongly that the increase in electronegativity of carbon atoms in heterocyclic systems, due to the inductive effect of the hetero-atoms, must be taken explicitly into account in any theoretical treatment. Note that the inductive effect in question is one operating on the σ-bonds of a molecule; the polarization of the π-electrons may also lead to changes in electronegativity of carbon atoms, but when explicit allowance is made for them (cf. Wheland and Mann, *J. Chem. Phys.*, 1949, **17**, 264) the charge distributions show little qualitative change, the magnitudes of the net charges being reduced more or less proportionately. Consequently, the π-polarizations can probably be absorbed into the empirical parameters used in the simple M.O. treatment.

A further argument for the importance of the inductoelectromeric effect is provided by the basic strengths of the three picolines. The precise mode of action of the methyl group in such compounds is uncertain, but since the effect is undoubtedly nucleophilic, the charge densities on the nitrogen atoms of the picolines should run parallel to those on the nitrogen atoms of the conjugate anions. The charge densities in these anions (with neglect of *meta*-interaction) are listed in Fig. 2. The basic strengths of the picolines do in fact run parallel to the calculated charge densities on nitrogen in these ions (*i.e.*, $\gamma > \alpha \gg \beta$; the observed pK_a are 6·03, 5·94, and 5·66, respectively; Herrington, *Discuss. Faraday Soc.*, 1950, **9**, 26).

Longuet-Higgins (*J.*, 1949, 971) used a perturbation method to calculate the charge distributions in heterocyclic compounds from those in the isoconjugate hydrocarbons.

The calculations involved two parameters—the coulomb term of nitrogen, and the allowance for the inductive effect of nitrogen. We think that his value (2β) for the former was too large, and for the latter (factor 1/8) too low. We have accordingly repeated the calculations with our values for the parameters, and the results, in terms of net charge at the various positions, are compared with his in Fig. 3. The two sets of values agree quite well, a satisfactory conclusion in view of the uncertainty in the choice of parameters. It should in any case be emphasised that calculations of charge density by the simple M.O. method cannot be expected to have more than a qualitative significance in view of the known errors introduced in the treatment of systems containing hetero-atoms. Charges and charge densities have nevertheless been given throughout to three places of decimals, since their qualitative interrelations should be significant and since they may be of use in other connexions.

FIG. 2.

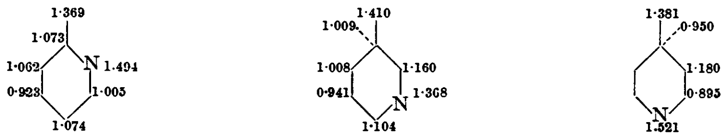
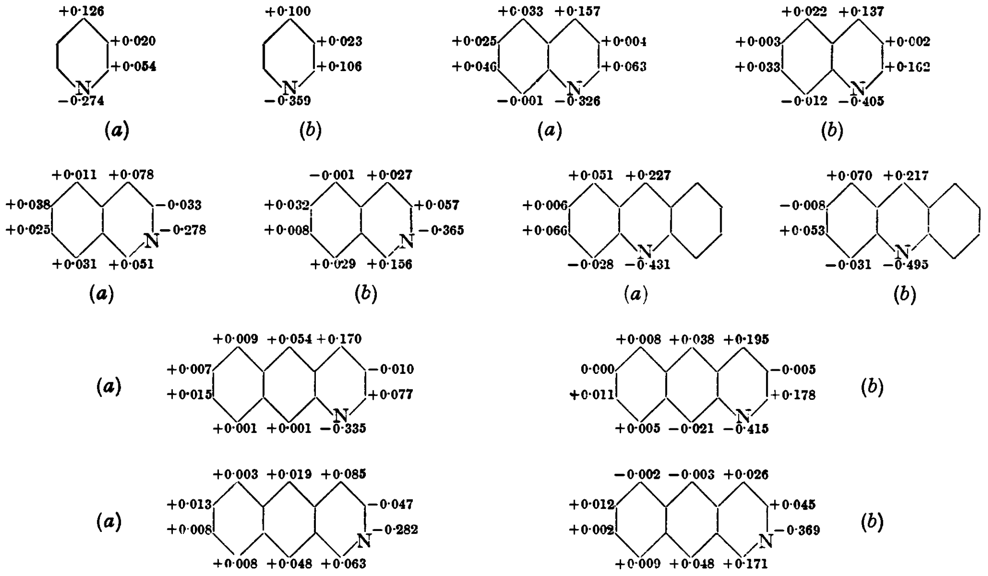


FIG. 3. *Distributions of net charge in heterocyclic compounds calculated* (a) *by us and* (b) *by Longuet-Higgins.*



(3) *Strengths of heterocyclic bases.* The basic strengths of heterocyclic bases can be related, as Coulson and Longuet-Higgins (*loc. cit.*) showed, to the charge distributions in them. These authors assumed, however, that the determining factor was the change in the coulomb term of the annular nitrogen atom on salt formation; however, the σ-inductive effect will also lead to a change in the coulomb terms of adjacent carbon atoms, presumably proportional to the change in the coulomb term of nitrogen. These being included, the relation between the acid dissociation constant of the acid conjugate to the base becomes:

$$C - 2{\cdot}303\boldsymbol{R}T\ \mathrm{p}K_a = \Delta\alpha\{q_{\mathrm{N}} + 0{\cdot}4\Sigma q_\alpha + 0{\cdot}1\Sigma q_\beta\} \equiv \mathrm{f}(q)\Delta\alpha \quad . \quad . \quad . \quad (1)$$

where q_N is the charge density at the nitrogen atoms, q_α that at carbon atoms α to nitrogen, and q_β that at carbon atoms β to nitrogen. The acid dissociation constants of five of the bases are given in Table 4. It will be seen that the relation of q to pK_a is far from linear; a similar discrepancy had already been noticed by Coulson and Longuet-Higgins, using their original relation between pK_a and q_N. Dyatkina (*Doklady Akad. Nauk, U.S.S.R.*, 1948, **59**, 517) suggested that it might be due to a change in the CN resonance integrals accompanying salt formation; but it seems unlikely that this second-order effect could be appreciable, let alone comparable with the main effect given by equation (1). Another possible explanation would be that the second-order terms, due to the change in charge distribution during salt formation, are appreciable; the main second-order term $\Delta E'$ is given by

TABLE 4.

Compound	f(q)	pK_a †	Compound	f(q)	pK_a †	Compound	f(q)	pK_a †
Pyridine	1·227	5·23	Quinoline	1·312	4·94	Acridine ...	1·434	5·60
*iso*Quinoline...	1·263	5·33	6 : 7-Benzoquinoline	1·321	5·05			

† Albert, Goldacre, and Phillips, *J.*, 1948, 2240.

$$\Delta E' = \tfrac{1}{2}\pi_{NN}\,(\Delta\alpha)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when π_{NN} is the self-polarizability of the nitrogen. Since $\Delta\alpha$ is negative, it is easily seen that ΔE should be negative but $\Delta E'$ positive; since the self-polarizability in naphthalene is greater in the α- than in the β-position, this effect should reduce the basicity of quinoline in comparison with that of *iso*quinoline. The observed anomaly is in this direction.

(4) *Dipole moments.* The M.O. method can also be used in principle to estimate dipole moments of conjugated molecules, but the results of such calculations are invariably unsatisfactory in a quantitative sense. This discrepancy cannot be ascribed to the inductoelectromeric effect, as the results in Table 5 show: not only do the calculated and observed mesomeric moments differ greatly, but they also show opposite variations with changes in structure. (The observed mesomeric moments were calculated from the observed dipole moments by subtracting 1·3 D, as recommended by Coulson and Longuet-Higgins, *loc. cit.*)

TABLE 5. *Comparison of calculated and observed dipole moments.*

Compound	Mesomeric moment, in D : calc.	obs.
Pyridine	2·33	0·91
Quinoline	3·40	0·84
Acridine	4·90	0·65

Conclusions.—It appears that *meta*-interactions can probably be neglected in most connexions, their effect being negligible; but that the σ-inductive effect of hetero-atoms must nearly always be taken into account. With inclusion of this inductoelectromeric effect, the M.O. method seems to give a reasonably satisfactory account of resonance energies in heterocyclic systems; but the calculations of charge density and quantities derived from it are still very disappointing. This is not surprising, since it is well known that the energy of a system given by any variation method is relatively insensitive to variation in the parameters of the trial eigenfunction, and that such methods, of which the M.O. method is one, commonly give much better approximations to the energies of systems than to their eigenfunctions.

Appendix.

(1) *Inclusion of* meta-*interactions does not, to a first approximation, alter the total energy of a neutral alternant system.* Consider, first, an even alternant hydrocarbon. The energy

levels appear in pairs, of energy $\pm E_m$ (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193), the corresponding M.O.'s ψ_{m^+}, ψ_{m^-} being given by

$$\psi_{m^+} = \overset{*}{\underset{r}{\Sigma}} a_{mr}\phi_r + \overset{0}{\underset{t}{\Sigma}} a_{mt}\phi_t \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\psi_{m^-} = \overset{*}{\underset{r}{\Sigma}} a_{mr}\phi_r - \overset{0}{\underset{t}{\Sigma}} a_{mt}\phi_t \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where ϕ_r is the atomic orbital of atom r and $\overset{*}{\Sigma}$, $\overset{0}{\Sigma}$ imply summation over starred and unstarred atomic orbitals respectively. Then the corrections for *meta*-interactions, ΔE_{m^+}, ΔE_{m^-}, are given approximately by first-order perturbation theory as

$$\Delta E_{m^+} = -2\beta'\left\{\underset{r<d}{\overset{*}{\Sigma}\,\overset{*}{\Sigma}} a_{mr}a_{md} + \underset{t<u}{\overset{0}{\Sigma}\,\overset{0}{\Sigma}} a_{mt}a_{mu}\right\}$$

$$\Delta E_{m^-} = -2\beta'\left\{\underset{r<d}{\overset{*}{\Sigma}\,\overset{*}{\Sigma}} a_{mr}a_{md} + \underset{t<u}{\overset{0}{\Sigma}\,\overset{0}{\Sigma}} (-a_{mt})(-a_{mu})\right\} \quad . \; . \; . \quad (4)$$

where β' is the resonance integral between *meta*-atoms. Hence

$$\Delta E_{m^+} = \Delta E_{m^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The total energy change $E_{\text{occ.}}$ for all the occupied molecular orbitals is given by

$$\begin{aligned}\Delta E &= 2\underset{m}{\Sigma}\Delta E_{m^+}\\ &= \underset{m}{\Sigma}\Delta E_{m^+} + \underset{m}{\Sigma}\Delta E_{m^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)\end{aligned}$$

So ΔE is equal to the sum of the corrections to all the energy levels, bonding and antibonding. But the complete secular determinant is of the form

$$\begin{vmatrix} W & \beta_{12} & \beta_{13} & \cdot\;\cdot\;\cdot\;\cdot & \beta_{1n}\\ \beta_{21} & W & \beta_{23} & \cdot\;\cdot\;\cdot\;\cdot & \beta_{2n}\\ \beta_{31} & \beta_{32} & W & \cdot\;\cdot\;\cdot\;\cdot & \beta_{3n}\\ \cdot & \cdot & \cdot & & \cdot\\ \cdot & \cdot & \cdot & & \cdot\\ \cdot & \cdot & \cdot & & \cdot\\ \cdot & \cdot & \cdot & & \cdot\\ \beta_{n1} & \beta_{n2} & \beta_{n3} & \cdot\;\cdot\;\cdot\;\cdot & W \end{vmatrix} = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where β_{vs} is the resonance integral between atoms v and s and no such integrals are neglected. Expanding this determinant, one obtains an equation for W in which the coefficient of W^{n-1} vanishes. Hence the sum of the roots is zero. Therefore the sum of all the energy levels vanishes; since this is true whatever the values of the β_{vs}, it must be true both for the set of levels found with neglect of *meta*-interaction, and for the set found including *meta*-interaction. Consequently, the sum of all the corrections for *meta*-interaction vanishes, and so therefore does ΔE [equation (6)]. This proves the theorem for even alternant hydrocarbons. The proof for odd alternant hydrocarbons radicals is precisely similar; the equation corresponding to equation (6) is then

$$\begin{aligned}\Delta E &= 2\underset{m\neq 0}{\Sigma}\,\Delta E_{m^+} + \Delta E_0\\ &= \underset{m\neq 0}{\Sigma}\,\Delta E_{m^+} + \Delta E_0 + \underset{m\neq 0}{\Sigma}\,\Delta E_{m^-} \quad . \; . \; . \; . \; . \; . \; . \quad (8)\end{aligned}$$

where ΔE_0 is the energy of the singly occupied (" non-bonding ") molecular orbital. The last line of (8) shows that ΔE is again equal to the sum of the corrections to all the molecular orbitals for *meta*-interaction, and the same argument shows that this sum must vanish.

These results can at once be extended to isoconjugate heterocyclic systems since, to a first approximation, the charge densities at the individual atoms are unaffected by changes in their coulomb terms (cf. Coulson and Longuet-Higgins, *loc. cit.*; the changes in charge density are second-order effects).

(2) *Inclusion of* meta-*interactions in an odd alternant hydrocarbon raises the energy of the non-bonding molecular orbital* (*and so makes it antibonding*). Let the carbon atoms, at most three in number, attached to an inactive atom r, be s, t, u. With the usual assumption that resonance integrals between adjacent carbon atoms are similar ($=\beta$), the non-bonding molecular orbital coefficients a_{0s}, a_{0t}, a_{0u} at atoms s, t, u are related (Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265) by

$$a_{0s} + a_{0t} + a_{0u} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

To a first approximation, *meta*-interactions in this molecular orbital will occur only between active atoms, since the molecular orbital will be unchanged to a first approximation. The total energy E_{stu} for interactions between atom s, t, u, will then be given by

$$E_{stu} = -2\beta'(a_{0s}a_{0t} + a_{0t}a_{0u} + a_{0u}a_{0s}) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where β' is the resonance integral between *meta*-carbon atoms. Combining equations (9) and (10), we have

$$\begin{aligned} E_{stu} &= -2\beta'\{a_{0s}a_{0t} - (a_{0s} + a_{0t})(a_{0s} + a_{0t})\} \\ &= 2\beta'\{a_{0s}^2 + a_{0s}a_{0t} + a_{0t}^2\} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11) \end{aligned}$$

Since the whole change in the energy of the molecular orbital is a sum of terms similar to E_{stu}, and since these are all positive, the *meta*-interactions must raise the energy of the molecular orbital.

(3) *Charge distribution in alternant hydrocarbons should be altered by* meta-*interactions.* The charge density at atom r is related to the resonance integral β_{st} of the bond s–t by the expression $\pi_{r,st} = \partial q_r/\partial\beta_{st}$ (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, **191**, *A*, 39) or equivalently $\delta q_r = \pi_{r,st}\delta\beta_{st}$. Coulson and Longuet-Higgins showed by a perturbation treatment that

$$\pi_{r,st} = 4\sum_{j=1}^{m}\ \sum_{k=m+1}^{n} \frac{a_{jr}\,a_{kr}\,(a_{js}a_{kt} + a_{jt}\,a_{ks})}{\varepsilon_j - \varepsilon_k}$$

there being m occupied levels, and ε_i being the energy of the ith molecular orbital.

Consider a pair of levels ε_u and ε_v in an alternant hydrocarbon. Two cases arise:

(*a*) If atoms s and t are of opposite parity, so that $c_{sj} = -c_{tj}$, then on summation over occupied and unoccupied levels the sign of the numerator is invariant whilst that of the denominator changes. Hence, on summing over all such pairs, the value of $\pi_{r,st}$ is seen to be zero.

(*b*) If atoms s and t are of same parity, both the numerator and denominator change sign, and hence $\pi_{r,st}$ is no longer zero.

Consequently, changes in the resonance integrals of bonds between atoms of like parity do alter the charge distribution in alternant hydrocarbons, whereas changes in resonance integrals of bonds between atoms of opposite parity leave that charge distribution unchanged to a first approximation (Coulson and Longuet-Higgins, *loc. cit.*). Since *meta*-interactions can be regarded as being due to an increase in resonance integrals of bonds between atoms (*meta*) of like parity from zero to some finite value, they should in general alter the charge distribution.

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