769. *Structure and Properties of Mesomeric Systems. Part IV.* The Chemical Reactivity of Non-alternant Aza-heterocycles.*

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A perturbation method, based on the Hückel L.C.A.O. molecular-orbital theory, is used to predict that replacement of a carbon atom in a $(4\gamma + 2)$ non-alternant hydrocarbon by a nitrogen atom will have little or no effect on the orientation of ionic substitution in the molecule.

THE Hückel L.C.A.O. molecular-orbital theory[1] has had much success in interpreting the chemistry of benzenoid hydrocarbons[2] owing partly to the development of perturbation methods[2b,c] which eliminate the heavy labour involved in the formal calculations. The non-alternant hydrocarbons are now receiving much attention,[2a,3] but theoretical interpretation of their chemistry has, until recently, been hampered because the available perturbation methods are not generally applicable to them. This difficulty was overcome for many of this class by the development of alternative perturbation methods which are capable of dealing with both classes of hydrocarbon.[4] Thus the theory of the chemistry of many of the non-alternant hydrocarbons is now as easily discussed as is that of the alternant ones. The new method is based on the idea[5] that the properties of aromatic systems can be deduced from those of the corresponding cyclic polyene, the formation of the cross-links being treated as a perturbation. Thus azulene is formally obtained from *cyclo*decapentaene by cross-linking (see *J.*, 1958, 1040).

The properties of the Wheland[6] transition state can similarly be obtained from those of the corresponding open-chain polyene radical or ion. In this way, the charge distributions and localisation energies of many of the non-alternant hydrocarbons are easily obtained.[4]

We now attempt to develop these ideas further, applying them first to the replacement of a carbon atom of the mesomeric hydrocarbon by a nitrogen atom, forming a non-alternant heterocycle, and secondly to the introduction of a substituent into the hydrocarbon. The formal method of handling the first case, the aza-heterocycles, is to assign to the nitrogen atom a Coulomb integral differing from that of a carbon atom and solve the resulting secular equations.[7] For the larger hydrocarbons, however, the solution of these equations is prohibitively long, and perturbation methods are commonly employed.[8] It is then supposed that the variation of the Coulomb integral may be taken as a perturbation. This method is used here.

Substituent effects are more difficult to deal with, our general understanding of their action being far from perfect. In the following paper we divide substituent action into two effects, inductive and mesomeric; the former will be dealt with in the same way as

* Part III, *J.*, 1958, 1039.

[1] Hückel, *Z. Physik*, 1930, **60**, 423; 1931, **70**, 204; 1931, **72**, 310; 1932, **76**, 628.

[2] (*a*) Pullman and Pullman, " Les Theories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952; (*b*) Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; 1947, *A*, **192**, 16; (*c*) Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3355.

[3] Baker and McOmie, " Progress in Organic Chemistry," Butterworths Scientific Publications London, 1955, vol. 3, p. 44.

[4] Peters, *J.*, 1958, 1023, 1028, 1039.

[5] (*a*) Platt, *J. Chem. Phys.*, 1949, **17**, 484; (*b*) Dewar and Pettit, *J.*, 1954, 1617.

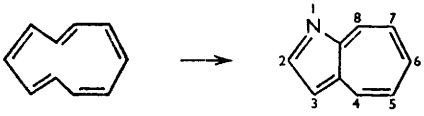
[6] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

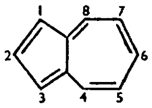
[7] (*a*) Davies, *Trans. Faraday Soc.*, 1955, **51**, 449; Burr, *J. Chem. Phys.*, 1957, **26**, 431; (*b*) Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086; Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87; Orgel, Cottrell, Dick, and Sutton, *ibid.*, 1951, **47**, 113; Nordheim and Sponer, *J. Chem. Phys.*, 1952, **20**, 285; Brown, *J.*, 1956, 272; Gyoerffy, *Compt. rend.*, 1951, **232**, 515; Chalvet and Sandorfy, *ibid.*, 1949, **228**, 566; Sandorfy, *Bull. Soc. chim. France*, 1949, **16**, 615.

[8] (*a*) Coulson and Longuet-Higgins, *J.*, 1949, 971; Jaffé, *J. Chem. Phys.*, 1952, **20**, 1554 Löwdin, *ibid.*, 1951, **19**, 1323. (*b*) Dewar and Maitlas, *J.*, 1957, 2521; Sandorfy and Yvan, *Bull. Soc. chim. France*, 1950, **17**, 131.

the introduction of the nitrogen atom, so that the methods used here can be carried over immediately for it.

We examine the influence on the chemistry of a $(4\gamma + 2)$ non-alternant hydrocarbon of changing the Coulomb integral of one of the carbon atoms. We will be concerned largely with the aza-heterocycles derived from azulene (a useful model) although some of the larger $(4\gamma + 2)$ non-alternant hydrocarbons will be discussed briefly. No attempt is made to deal with the (4γ) non-alternant hydrocarbons, there being so little evidence against which the theory can be checked. As an example, we regard 1-aza-azulene as being formed from *cyclo*decapentaene by cross-linking and introduction of the nitrogen atom:





Method.—The two main theories of chemical reactivity, the isolated-molecule and the localisation approximations [9] are used. In the former, it is supposed that the charge distribution in the ground state determines the position of ionic attack, the atom having the largest surplus of negative (positive) charge being the preferred position of electrophilic (nucleophilic) attack. In the latter, the energies of the ground and the transition state are calculated, the difference being the activation energy. The transition state is taken [6] as the ground state with the atom undergoing substitution removed from the mesomeric system and the usual assumption is made that the π-electron energy is the only part of the activation energy to vary with the structure of the substrate. Full details of both methods have been set out elsewhere.[9] Overlap is neglected since its inclusion usually makes only minor differences.[7a, 10]

The Isolated-molecule Approximation.—Here we require the charge distribution in the ground state of the cross-linked, nitrogen-substituted, cyclic polyene. This differs from that in the cyclic polyene itself by the effects of the two perturbations. First-order perturbations being additive, we write:

$$q_t' = q_t + (\partial q_t/\partial\beta_{rs})\delta\beta_{rs} + (\partial q_t/\partial\alpha_p)\delta\alpha_p \quad . \; . \; . \; . \; . \quad (1)$$

where q_t is the charge on atom t, $\delta\beta_{rs}$ is the change in the resonance integral * of the bond between atoms r and s and $\delta\alpha_p$ is the change in the Coulomb integral * of atom p. Higher-order terms, including the first cross product, are neglected. Coulson and Longuet-Higgins's nomenclature being followed,[2b]

$$\partial q_t/\partial\beta_{rs} = \pi_{t,rs} \text{ and } \partial q_t/\partial\alpha_p = \pi_{t,p}$$

or

$$q_t' = 1 + \pi_{t,rs} \, . \, \delta\beta_{rs} + \pi_{t,p} \, . \, \delta\alpha_p \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where $\pi_{r,rs}$ and $\pi_{t,p}$ are the atom–bond and the atom–atom polarisabilities respectively. The charge distribution in the cyclic polyene itself is, of course, unity $(q_t = 1)$. If there are several cross-links and several atoms whose Coulomb integrals differ from that of a carbon atom, we have:

$$q_t' = 1 + \sum_{rs}\pi_{t,rs} \, . \, \delta\beta_{rs} + \sum_{p}\pi_{t,p} \, . \, \delta\alpha_p \quad . \; . \; . \; . \; . \; . \quad (2a)$$

These authors show that we may use these formulæ for the doubly-degenerate molecular-orbitals of the cyclic polyenes providing we use the correct zeroth-order molecular-orbitals.

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* The resonance integral β_{rs} is defined as $\int\phi_r H\phi_s d\tau$, the Coulomb integral α_p as $\int\phi_p H\phi_p d\tau$ where the ϕ's are carbon $2p$-atomic orbitals and H is the effective one-electron Hamiltonian.

[9] R. D. Brown, *Quart. Rev.*, 1952, **6**, 63.

[10] Chirgwin and Coulson, *Proc. Roy. Soc.*, 1950, *A*, **201**, 196; de Heer, *Phil. Mag.*, 1950, **41**, 370.

When $\delta\alpha_p$ is zero, we have the effect of the cross-linking alone on the charge distribution of the cyclic polyene. This has been evaluated in Part III, where a number of examples were discussed. When $\delta\beta_{rs}$ is zero, we have the effect of the change in Coulomb integral on the charge distribution of the cyclic polyene. The polarisability $\pi_{t,p}$ is given [2b] by

$$\pi_{t,p} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{jp} \cdot c_{jt} \cdot c_{kp} \cdot c_{kt}}{(e_j - e_k)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the bonding molecular-orbitals are $1 - m$, the antibonding are $(m + 1) - n$, e_j, and e_k are the energies of the jth and kth molecular-orbitals respectively and the c's are atomic-orbital coefficients whose nomenclature is derived from that of the other quantities. This expression reduces (Appendix) to

$$\pi_{t,p} = 4 \cos (t - p)\pi \left[\sum_{j=0}^{\gamma} \frac{\chi_j^4}{2e_j} \cos^2 \left\{ 2(t - p)j\frac{\pi}{n} \right\} + 2 \sum_{j=0}^{\gamma-1} \sum_{h=j+1}^{\gamma} \frac{\chi_j^2 \chi_h^2}{e_j + e_h} \cos 2(t - p)j\frac{\pi}{n} \cdot \cos 2(t - p)h\frac{\pi}{n} \right] \quad . \quad (4)$$

where h is the bonding molecular-orbital conjugated with k. The χ's are defined below. From eqn. (4), the atom–atom polarisabilities given in Table 1 are calculated and, combining these with the atom–bond polarisabilities given in Part III, we calculated the total charge distributions in Table 2 from eqn. (2).

The Localisation Approximation.—Here we require the π-electron energy of the ground and the transition state. Taking the cyclic polyene as starting point, we need the total change in its π-electron energy ($\delta E_{\text{c.p.}}$) resulting from the change in the resonance integral ($\delta\beta_{rs}$) of the bond between atoms r and s and the change in Coulomb integral ($\delta\alpha_p$) of atom p. Expanding the π-electron energy of the cyclic polyene as a function of these two perturbations we obtain

$$\delta E_{\text{c.p.}} = (\partial E_{\text{c.p.}}/\partial\beta_{rs})\delta\beta_{rs} + (\partial E_{\text{c.p.}}/\partial\alpha_p)\delta\alpha_p \quad . \quad . \quad . \quad . \quad . \quad (5)$$

to the first approximation. Higher terms, including the first cross product, are neglected and the two perturbations are additive. The change ($\delta E_{\text{p.r.}}$) in the π-electron energy of the polyene radical ($E_{\text{p.r.}}$) under the same two perturbations is similarly

$$\delta E_{\text{p.r.}} = (\partial E_{\text{p.r.}}/\partial\beta_{rs})\delta\beta_{rs} + (\partial E_{\text{p.r.}}/\partial\alpha_p)\delta\alpha_p \quad . \quad . \quad . \quad . \quad (6)$$

The atom localisation energies for free-radical substitution ($\mathcal{E}_{\text{h}}$) in the cross-linked, nitrogen-substituted cyclic polyene are then

$$\mathcal{E}_{\text{h}} = E_{\text{c.p.}} + \delta E_{\text{c.p.}} - E_{\text{p.r.}} - \delta E_{\text{p.r.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathcal{E}_{\text{h}} = [E_{\text{c.p.}} + (\partial E_{\text{c.p.}}/\partial\beta_{rs})\delta\beta_{rs} + (\partial E_{\text{c.p.}}/\partial\alpha_p)\delta\alpha_p] - [E_{\text{p.r.}} + (\partial E_{\text{p.r.}}/\partial\beta_{rs})\delta\beta_{rs} + (\delta E_{\text{p.r.}}/\delta\alpha_p)\delta\alpha_p] \quad . \quad . \quad . \quad (8)$$

But from Part II (eqn. 1):

$$\mathcal{E}_{\text{a}} = [E_{\text{c.p.}} + (\partial E_{\text{c.p.}}/\partial\beta_{rs})\delta\beta_{rs}] - [E_{\text{p.r.}} + (\partial E_{\text{p.r.}}/\partial\beta_{rs})\delta\beta_{rs}] \quad . \quad . \quad (9)$$

where $\mathcal{E}_{\text{a}}$ is the atom localisation energy for free-radical substitution in the cross-linked hydrocarbon. Hence

$$\mathcal{E}_{\text{h}} = \mathcal{E}_{\text{a}} + [(\partial E_{\text{c.p.}}/\partial\alpha_p) - (\partial E_{\text{p.r.}}/\partial\alpha_p)]\delta\alpha_p \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It remains to evaluate the two terms in the bracket in eqn. (10). The second of these is immediately given, in free-radical substitution, by

$$\delta E_{\text{p.r.}}/\delta\alpha_p = q_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

To evaluate the first, the first-order perturbation of degenerate systems must be considered.

With the exception of the lowest bonding and the highest anti-bonding, the molecular-orbitals [ψ(cos),ψ(sin)] of the cyclic polyene (C_nH_n) occur in doubly-degenerate pairs

$$\left.\begin{aligned}\psi_j\,(\cos) &= \sum_{a=1}^{n} \chi_j \cos\left[\left(2aj\frac{\pi}{n}\right) + \zeta_j\right]\phi_a \\ \psi_j\,(\sin) &= \sum_{a=1}^{n} \chi_j \sin\left[\left(2aj\frac{\pi}{n}\right) + \zeta_j\right]\phi_a\end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (12)$$

where χ_j is the normalising factor, equal to $(1/n)^{\frac{1}{2}}$ for the non-degenerate orbitals and to $(2/n)^{\frac{1}{2}}$ for the doubly-degenerate; ϕ_a is a carbon $2p$-atomic orbital; j is a quantum number and ζ is a phase factor chosen arbitrarily in the cyclic polyenes themselves. The perturbation, the change in the Hamiltonian operator, being denoted by H′, the usual second-order determinant is

$$\begin{vmatrix} H_{11}^{(1)} - \delta e_j & H_{12}^{(1)} \\ H_{21}^{(1)} & H_{22}^{(1)} - \delta e_j \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

where
$$H_{11}^{(1)} = \int \psi_j\,(\sin)\,H'\psi_j\,(\sin)\,d\tau \qquad H_{22}^{(1)} = \int \psi_j\,(\cos)\,H'\psi_j\,(\cos)\,d\tau$$

$$H_{12}^{(1)} = H_{21}^{(1)} = \int \psi_j\,(\sin)\,H'\psi_j\,(\cos)\,d\tau$$

and δe_j is the first-order correction to the energy of the jth molecular-orbital. Now by Dewar and Pettit's method,[5b] the secular determinant can be solved and the phase factor ζ determined by choosing ζ so that the off-diagonal elements $H_{12}^{(1)}$ vanish:

$$H_{12}^{(1)} = \int \sum_{a=1}^{n} \chi_j \cos\left[\left(2aj\frac{\pi}{n}\right) + \zeta_j\right] \sum_{a=1}^{n} \sin\left[\left(2aj\frac{\pi}{n}\right) + \zeta_j\right] \phi_a H'\phi_a d\tau = 0 \ . \qquad (14)$$

If the only non-vanishing matrix element is $\int \phi_p H'_p d\tau = \delta\alpha_p$, we have

$$\cos\left(2pj\frac{\pi}{n} + \zeta_j\right).\sin\left(2pj\frac{\pi}{n} + \zeta_j\right).\delta\alpha_p = 0 \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

$$\sin\left(4pj\frac{\pi}{n} + 2\zeta_j\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

$$\sin\left(4pj\frac{\pi}{n}\right).\cos\,(2\zeta_j) + \cos\left(4pj\frac{\pi}{n}\right).\sin\,(2\zeta_j) = 0 \quad . \quad . \quad . \quad . \qquad (17)$$

$$\tan\,(2\zeta_j) = -\tan\left(4pj\frac{\pi}{n}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

whose primitive solution is

$$\zeta_j = 2\,pj\pi/n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

For several cross-links, ζ is given by

$$\tan\ (2\zeta) = -\sum \sin\,(4pj\pi/n)/\sum \cos\,(4pj\pi/n) \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

the summations being taken over the cross-links. The energies of the perturbed molecular-orbitals are

$$\begin{aligned}\delta e_j\,(\sin) &= \int \psi_j\,(\sin)\,H'\psi_j\,(\sin)\,d\tau \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21) \\ &= \sum_{a=1}^{n} \sum_{a=1}^{n} \chi_j^2 \sin^2\left(2aj\frac{\pi}{n} + \zeta_j\right).\delta\alpha_a \quad . \quad . \quad . \qquad (22) \\ &= \chi_j^2 \sin^2\left(2pj\frac{\pi}{n} + \zeta_j\right)\delta\alpha_p \quad . \quad . \quad . \quad . \quad . \qquad (23)\end{aligned}$$

and
$$\delta e_j\,(\cos) = \chi_j^2 \cos^2\left(2pj\frac{\pi}{n} + \zeta_j\right)\delta\alpha_p \quad . \quad . \quad . \quad . \quad . \qquad (24)$$

Equations (23) and (24) confirm that the degeneracy does not affect the result, since for non-degenerate molecular-orbitals we have immediately

$$\delta e_j = c_{jp}^2 \,.\, \delta\alpha_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Accordingly, we can write

$$\delta E_{\text{c. p.}}/\delta\alpha_p = q_p = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

the charge density in the cyclic polyene being unity. In free-radical substitution, the charge density in the polyene radical is also unity, so that from equations (10), (11), and (26)

$$\mathscr{E}_{\text{h}} = \mathscr{E}_{\text{a}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Replacement of a carbon atom in a non-alternant hydrocarbon by a nitrogen atom thus has no effect on the free-radical reactivity. No doubt this conclusion oversimplifies the true position, but it shows that in the non-alternant hydrocarbons, as in benzene,[11] free-radical reactivity is only slightly affected by the introduction of a nitrogen atom.

It is in ionic reactivity that the effect of the nitrogen atom is more pronounced, both in the alternant and in the non-alternant systems. In this case, the non-bonding molecular-orbital of the polyene radical is no longer singly occupied but is doubly occupied (nucleophilic) or is unoccupied (electrophilic). The resulting modification of the localisation energies of the cross-linked hydrocarbon has been dealt with in Part II. The charge on atom p in the polyene radical is given by

$$q_p = (1 \mp c_{op}^2) = \delta E_{\text{p.r.}}/\delta\alpha_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where c_{op} is the coefficient at atom p of the non-bonding molecular-orbital of the polyene radical. The minus sign is taken in electrophilic, and the plus sign in nucleophilic, substitution. Now the non-bonding molecular-orbital coefficients are immediately given [12] by

$$\sum_s c_{op} \,.\, \beta_{rs} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

followed by normalisation. The summation in equation (29) is over all atoms (s) adjacent to atom r. The resonance integral β_{rs} is taken as the standard resonance integral β. The ionic localisation energies are then from eqn. (10)

$$\mathscr{E}_{\text{h}}^+ = \mathscr{E}_{\text{a}}^+ + [1 - (1 - c_{op}^2)]\delta\alpha_p = \mathscr{E}_{\text{a}}^+ + c_{op}^2 \,.\, \delta\alpha_p \quad . \quad . \quad . \quad (30)$$

$$\mathscr{E}_{\text{h}}^- = \mathscr{E}_{\text{a}}^- + [1 - (1 + c_{op}^2)]\delta\alpha_p = \mathscr{E}_{\text{a}}^- - c_{op}^2 \,.\, \delta\alpha_p \quad . \quad . \quad . \quad (31)$$

The localisation energies $\mathscr{E}_{\text{h}}^+$ and $\mathscr{E}_{\text{h}}^-$ refer to electrophilic and to nucleophilic attack respectively; $\mathscr{E}_{\text{a}}^+$ and $\mathscr{E}_{\text{a}}^-$ are the same quantities in the parent hydrocarbon. From eqns. (30) and (31) and the values of $\mathscr{E}_{\text{a}}^+$ and $\mathscr{E}_{\text{a}}^-$ given in Part II, the results reported in Table 2 are calculated.

As in all work of this kind, there remains the problem of the numerical value of the Coulomb integral of the nitrogen atom (α_{N}). If we write $\alpha_{\text{N}} = \alpha_{\text{C}} + h\beta$ or $\delta\alpha_{\text{N}} = h\beta$, we must assign a value to the parameter h. The sum of experience so far[7,8,13] suggests that h is in the range $+0{\cdot}5$ to $+1{\cdot}0$, but slightly different values will no doubt be required in different situations to absorb the error inherent in the Hückel method. Fortunately the exact value of h in this range is not critical for this work, and we have taken $h = 1{\cdot}0$ to avoid underestimating the effect of the nitrogen atom. It is also necessary to allow for the change in the Coulomb integral (α_{C}') of the carbon atoms adjacent to the nitrogen atom. This is the so-called σ inductive effect. We write $\alpha_{\text{C}}' = \alpha_{\text{C}} + k\beta$ and take k as

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[11] Hey and Williams, *Discuss. Faraday Soc.*, 1953, **14**, 216.

[12] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.

[13] R. D. Brown and Penfold, *Trans. Faraday Soc.*, 1957, **53**, 397.

1/3.[8b,14] Only immediate neighbours are considered, and again the results do not depend critically on the choice of this parameter. The resonance integral of the bond between a a carbon and a nitrogen atom is taken as 1·0β.

Results.—The atom–atom polarisabilities ($\pi_{t,p}$) for the 10- and the 14-atom cyclic polyenes are recorded in Table 1. In Table 2, the charge distributions and localisation energies for the aza-azulenes are reported. The figures for azulene itself are taken from Parts II and III.

TABLE 1.

$C_{10}H_{10}$	$\pi_{1,1}$	$\pi_{1,2}$	$\pi_{1,3}$	$\pi_{1,4}$	$\pi_{1,5}$	$\pi_{1,6}$		
	+0·437	−0·145	+0·028	−0·072	+0·002	−0·063		
$C_{14}H_{14}$	$\pi_{1,1}$	$\pi_{1,2}$	$\pi_{1,3}$	$\pi_{1,4}$	$\pi_{1,5}$	$\pi_{1,6}$	$\pi_{1,7}$	$\pi_{1,8}$
	+0·455	−0·141	+0·039	−0·063	+0·008	−0·048	+0·001	−0·045

TABLE 2. *Distribution of charge* $(1 - q_t)$ *and ionic localisation energies* ($\mathcal{E}_h^+$, $\mathcal{E}_h^-$) (*in units of* β) *of azulene and the aza-azulenes. For this paper we revert to standard chemical numbering as shown on p.* 3764.

Atom (t)	1	2	3	4	5	6	7	8
Charge ...	−0·185	−0·056	−0·185	+0·163	+0·015	+0·144	+0·015	+0·163
$\mathcal{E}_h^+$	1·92	2·32	1·92	2·72	2·32	2·72	2·32	2·72
$\mathcal{E}_h^-$	2·72	2·32	2·72	1·92	2·32	1·92	2·32	1·92
Charge ...	**N**	−0·065	−0·141	+0·206	+0·077	+0·187	+0·077	+0·206
Charge	**N**	*+0·069*	*−0·151*	*+0·145*	*+0·055*	*+0·130*	*+0·061*	*+0·168*
$\mathcal{E}_h^+$	**N**	2·52	2·06	2·86	2·52	2·86	2·52	2·86
$\mathcal{E}_h^-$	**N**	2·12	2·58	1·78	2·12	1·78	2·12	1·78
Charge ...	−0·194	**N**	−0·194	+0·225	+0·058	+0·206	+0·058	+0·225
Charge	*−0·038*	**N**	*−0·038*	*+0·186*	*+0·013*	*+0·168*	*+0·013*	*+0·186*
$\mathcal{E}_h^+$	2·12	**N**	2·12	2·92	2·46	2·92	2·46	2·92
$\mathcal{E}_h^-$	2·52	**N**	2·52	1·72	2·18	1·72	2·18	1·72
Charge ...	−0·142	+0·006	−0·141	**N**	+0·006	+0·188	+0·077	+0·206
$\mathcal{E}_h^+$	2·06	2·52	2·06	**N**	2·52	2·86	2·52	2·86
$\mathcal{E}_h^-$	2·58	2·12	2·58	**N**	2·12	1·78	2·12	1·78
Charge ...	−0·124	−0·013	−0·123	+0·154	**N**	+0·135	+0·059	+0·225
$\mathcal{E}_h^+$	2·12	2·46	2·12	2·92	**N**	2·92	2·46	2·92
$\mathcal{E}_h^-$	2·52	2·18	2·52	1·72	**N**	1·72	2·18	1·72
Charge ...	−0·142	+0·006	−0·142	+0·207	+0·006	**N**	+0·006	+0·207
Charge	*−0·173*	*+0·005*	*−0·173*	*+0·133*	*+0·155*	**N**	*+0·155*	*+0·133*
$\mathcal{E}_h^+$	2·06	2·52	2·06	2·86	2·52	**N**	2·52	2·86
$\mathcal{E}_h^-$	2·58	2·12	2·58	1·78	2·12	**N**	2·12	1·78

DISCUSSION

Kon[15] has solved the secular equations for 1-, 2-, and 6-aza-azulene, taking $h = 1$ as in the present paper, but neglecting the σ inductive effect—*i.e.*, taking $k = 0$. The resulting charge distribution is given in *italics* in Table 2. The agreement between these figures and the present results is good, except for the positions adjacent to the nitrogen atoms and here Kon's neglect * of the σ inductive effect must give too low a charge density. Further theoretical data on the charge distribution or localisation energies of the aza-azulenes are not available, and there is little experimental evidence against which the theory can be checked, although 1-aza-azulene has been prepared[16] and several derivatives of the aza-azulenes are known.[17,18]

In the results of the perturbation method, there is generally good agreement between the two methods of predicting the chemical reactivity and this agreement reinforces our confidence in these predictions. The charge distribution and localisation energies in

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* In his " correction 1."

[14] Jaffé, *J. Chem. Phys.*, 1953, **21**, 415.

[15] Kon, *Sci. Reports Tohoku Univ.*, 1954, **38**, 67.

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[18] Nozoe, Mukai, and Murata, *J. Amer. Chem. Soc.*, 1954, **76**, 3352.

Table 2 immediately establish the important point that, insofar as ionic substitution is concerned, the chemistry of azulene is qualitatively unaffected by the introduction of the nitrogen atom. That is, the predicted orientation of ionic attack is the same in the heterocycle as in the parent hydrocarbon, and this result is quite different from that in the alternant systems.[8b] The effect of the nitrogen atom is the same, in this approximation, in both classes of hydrocarbon, but the large variations in reactivity between the different positions in the non-alternant systems mask the directive effect of the nitrogen atom. It is clear from Table 2 that a very unreasonable choice of *h* or *k* would be required to invalidate this conclusion.

While the orientation of ionic attack should be the same in the heterocycle as in the parent hydrocarbon, the rate of attack will, of course, be affected but one cannot be certain that the crude perturbation method will correctly predict this more subtle effect. It is clear from the figures that all the aza-azulenes differ from azulene itself in much the same way. The effect of the nitrogen atom in all but one of the aza-azulenes is to reduce the electron surplus on atoms 1 and 3 and to increase the electron deficit on 4, 6, and 8. Furthermore, the electrophilic localisation energies of the 1- and the 3-position are increased while the nucleophilic localisation energies of atoms 4, 6, and 8 are reduced. So if the perturbation method is sufficiently accurate for this purpose, we may expect, in general, reduced electrophilic reactivity in positions 1 and 3 and increased nucleophilic reactivity at positions 4, 6, and 8. There is a little confirmatory evidence here, 1 : 3-diaza-azulene being resistant to electrophilic attack.[18]

The general conclusion requires qualification. First, the nitrogen atom will have its own intrinsic properties—protonation, quaternisation, etc. Secondly, the assumption of the Wheland transition state is apparently not valid for all processes which might be expected to be electrophilic substitutions.[19] Thirdly, the true transition state occurs earlier in the molecular act than the point represented by the Wheland transition state.[8b] Fourthly, there is not complete quantitative agreement between the localisation and the static methods, but this is commonly the case in the non-alternant systems.[20] Fifthly, in electrophilic substitution in acid media, the nitrogen atom is protonated and then *h* may be rather larger than unity.[8b, 21] Detailed experimental investigation of these reactions will be required before the importance of these points can be assessed.

With regard to the larger C_{14} hydrocarbons discussed in Parts II and III, the derived aza-heterocycles should behave in much the same way as the aza-azulenes, the polarisabilities in Table 1 showing that the differences between the different positions in the hydrocarbons are much larger than the effects of the nitrogen atom. It seems likely that this conclusion will apply to most of the $(4\gamma + 2)$ non-alternant hydrocarbons.

It has been supposed thus far that the change in Coulomb integral of the carbon atom is due to its replacement with a nitrogen atom. As discussed earlier, the inductive effect of substituents may also be represented in this way, but the values of the parameters *h* and *k* may require revision (see following paper).

APPENDIX

It is required to obtain eqn. (4) from eqn. (3).

We have
$$\pi_{t,p} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{tj} \, . \, c_{pj} \, . \, c_{tk} \, . \, c_{pk}}{(e_j - e_k)} \quad . \; . \; . \; . \; . \; . \quad \text{(as 3)}$$

Consider the term from a bonding cosine wave function molecular-orbital (ψ_j cos) with an antibonding cosine wave function orbital [ψ_k (cos)]. This is
$$\frac{\chi_j^2 \chi_k^2}{(e_j - e_k)} \cos\left(2tj\frac{\pi}{n} + \zeta_j\right) \cos\left(2pj\frac{\pi}{n} + \zeta_j\right) \cos\left(2tk\frac{\pi}{n} + \zeta_k\right) \cos\left(2pk\frac{\pi}{n} + \zeta_k\right)$$

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[19] Dewar and Maitlas, *J.*, 1957, 944.

[20] R. D. Brown, *Trans. Faraday Soc.*, 1949, **45**, 296; 1950, **46**, 146.

[21] R. D. Brown, *Austral. J. Chem.*, 1956, **9**, 83.

and there is a second term from the same bonding orbital [$\psi_j(\cos)$] with the antibonding sine wave function molecular-orbital [$\psi_k(\sin)$]—

$$\frac{\chi_j^2\chi_k^2}{(e_j - e_k)} \cos\left(2tj\frac{\pi}{n} + \zeta_j\right) \cos\left(2pj\frac{\pi}{n} + \zeta_j\right) \sin\left(2tk\frac{\pi}{n} + \zeta_k\right) \sin\left(2pk\frac{\pi}{n} + \zeta_k\right)$$

From the sum of these two terms

$$\frac{\chi_j^2\chi_k^2}{(e_j - e_k)} \cos\left(2tj\frac{\pi}{n} + \zeta_j\right) \cos\left(2pj\frac{\pi}{n} + \zeta_j\right) \cos\left(2(t - p)k\frac{\pi}{n}\right) \quad . \quad . \quad (33)$$

there is another pair of terms from the bonding molecular-orbital having a sine wave function [$\psi_j(\sin)$] with the same antibonding orbitals.

Summation of these two terms gives

$$\frac{\chi_j^2\chi_k^2}{(e_j - e_k)} \sin\left(2tj\frac{\pi}{n} + \zeta_j\right) \sin\left(2pj\frac{\pi}{n} + \zeta_j\right) \cos\left(2(t - p)k\frac{\pi}{n}\right) \quad . \quad . \quad (34)$$

Summing (33) and (34) and then summing over the totality of the molecular-orbitals, we obtain

$$\pi_{t,p} = 4 \sum_{j=0}^{\gamma} \sum_{k=\gamma+1}^{2\gamma+1} \frac{\chi_j^2\chi_k^2}{(e_j - e_k)} \cos 2(t - p)j\frac{\pi}{n} \,.\, \cos 2(t - p)k\frac{\pi}{n} \quad . \quad . \quad (35)$$

The non-degenerate lowest bonding and highest antibonding molecular-orbitals are included in this summation as explained in Part III, Appendix 1.

When j and k are conjugate molecular-orbitals, *i.e.*, $k = [(2\gamma + 1) - j]$ and $e_k = - e_j$, the term within the summation sign is

$$\frac{\chi_j^4}{2e_j} \cos (t - p)\pi \,.\, \cos^2\left\{2(t - p)j\frac{\pi}{n}\right\}$$

The total contribution to $\pi_{t,p}$ from such terms is

$$4 \sum_{j=0}^{\gamma} \frac{\chi_j^4}{2e_j} \cos (t - p)\pi \,.\, \cos^2\left\{2(t - p)j\frac{\pi}{n}\right\} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The remaining terms are from the non-conjugate molecular-orbitals. Let the kth antibonding molecular-orbital be conjugate with the hth bonding molecular-orbital. Then $k = \{(2\gamma + 1) - h\}$, $e_k = -e_h$, and the term within the summation is

$$\frac{\chi_j^2\chi_h^2}{(e_j + e_h)} \cos (t - p)\pi \,.\, \cos 2(t - p)j\frac{\pi}{n} \,.\, \cos 2(t - p)h\frac{\pi}{n}$$

and there is another term from the bonding molecular-orbital (h) with the antibonding when $k = [(2\gamma + 1) - j]$, $e_k = -e_j$. This term is

$$\frac{\chi_j^2\chi_h^2}{(e_j + e_h)} \cos (t - p) \,.\, \cos 2(t - p)j\frac{\pi}{n} \,.\, \cos 2(t - p)h\frac{\pi}{n}$$

The sum of such terms is

$$8 \sum_{j=0}^{\gamma-1} \sum_{h=j+1}^{\gamma} \frac{\chi_j^2\chi_h^2}{(e_j + e_h)} \cos (t - p)\pi \,.\, \cos 2(t - p)j\frac{\pi}{n} \,.\, \cos 2(t - p)h\frac{\pi}{n} \quad . \quad (37)$$

Combining (36) and (37), we have

$$\pi_{t,p} = 4 \cos (t - p)\pi \left[\sum_{j=0}^{\gamma} \frac{\chi_j^2}{2e_j} \cos^2\left(2(t - p)j\frac{\pi}{n}\right) + 2 \sum_{j=0}^{\gamma-1} \sum_{h=j+1}^{\gamma} \frac{\chi_j^2\chi_h^2}{(e_j + e_h)} \cos 2(t - p)j\frac{\pi}{n} \,.\, \cos 2(t - p)h\frac{\pi}{n}\right] \quad . \quad (4)$$

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