

206. *Structure and Properties of Mesomeric Systems. Part II.* The Chemical Reactivity of Alternant and Non-alternant Hydrocarbons.*

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The chemical reactivity of the purely cyclic alternant and non-alternant hydrocarbons is examined by use of a perturbation method based on the Hückel L.C.A.O. molecular-orbital theory. Atom localisation energies for free-radical and ionic attack and bond localisation energies are obtained for the common benzenoid hydrocarbons and for the cyclic non-alternant hydrocarbons. Agreement between the perturbation localisation energies and those obtained by solution of the secular equation is generally good. The chemical reactivity of a number of complex non-alternant hydrocarbons is examined.

APPLICATION of the Hückel molecular-orbital method¹ to mesomeric hydrocarbons leads to the division of the latter into two classes, the alternant and the non-alternant hydrocarbons.² The first class, of which the common benzenoid hydrocarbons are the best known representatives, has been explored extensively, both theoretically and practically.³ The second has received relatively little attention,⁴ owing to the fact that attempts to prepare many of the simple representatives have so far failed. If suitable syntheses can be devised, however, these hydrocarbons should exhibit novel properties, and they will also provide excellent tests for theories of chemical reactivity. One feature of the non-alternant hydrocarbons, their uneven charge distribution, is particularly interesting for in this they may be regarded as intermediate between the hydrocarbons and the heterocycles, and an understanding of their chemistry may be of assistance in solving the difficult problem of the latter compounds.

Theoretical methods are also of potential value in the preparation of non-alternant hydrocarbons. Although it is often assumed that the resonance energies are important in determining the "stability"—and hence of the ability to be prepared—of a hydrocarbon, a better guide to "stability" is the chemical reactivity of the desired hydrocarbon and of the intermediates involved in its synthesis.† The major point of difference between the

* Part I, preceding paper.

† The isolation of diphenylene⁵ is then unexceptional since R. D. Brown's theoretical predictions⁶ suggest that it is of low chemical reactivity.

¹ Hückel, *Z. Physik*, (a) 1931, **70**, 204; (b) 1931, **72**, 310; (c) 1932, **76**, 628.

² (a) Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193; (b) Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; 1947, *A*, **192**, 16; (c) Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.

³ Pullman and Pullman, "Les Théories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952.

⁴ Baker and McOmie, "Progress in Organic Chemistry," Vol. 3, ch. 2, Butterworths Scientific Publications, London, 1955.

⁵ Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.

⁶ R. D. Brown, *Trans. Faraday Soc.*, 1950, **46**, 146.

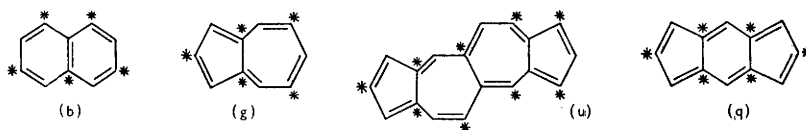
alternant and the non-alternant hydrocarbons is the fact that, in the alternant ones, the π -electron energy of activation is identical for free-radical and for ionic substitution, while this is far from being the case with the non-alternant hydrocarbons in which differences probably corresponding to many powers of ten in the rate occur in the π -electron energies of localisation and some of the non-alternant hydrocarbons may prove to be quite unstable to acid or base. An examination of the theoretical predictions of the reactivity will then provide a useful guide to the reaction conditions which can safely be used in the synthesis.

One disadvantage of the Hückel theory in its original form, particularly for the non-alternant hydrocarbons, is the amount of labour involved in the calculations. Perturbation methods are then very attractive and have the added advantage that they often provide insight into the relations between classes of hydrocarbon. Elegant perturbation methods have been used for the chemical reactivity of the alternant hydrocarbons by Dewar,⁷ but these cannot readily be extended to the non-alternant hydrocarbons and other methods have now been developed which provide a simple insight into the properties of the latter. The chemical reactivity of the alternant and non-alternant hydrocarbons is now examined by use of perturbation methods based on the Hückel L.C.A.O. molecular-orbital theory. The basis of the method is the demonstration (preceding paper) that the π energy of mesomeric hydrocarbons may be estimated by regarding them as cross-linked polyenes. When this is extended to polyene radicals, the π energy of the transition state is accessible.

The non-alternant hydrocarbons are themselves divisible into two classes, those containing only rings and those containing exocyclic bonds. Representatives of the former class are pentalene (f), azulene (g), and heptalene (h), and of the latter class fulvene, heptafulvene, and fulvalene. This geometrical difference requires that different treatments be given to the two classes and only the purely cyclic hydrocarbons will be examined here.

We are interested in substitution in, and addition to, mesomeric systems. For this reaction, Wheland's original postulate⁸ of the structure of the transition state, in which the reacting carbon atom is completely tetrahedral, is commonly used.³ Recent work⁹ has exposed the inadequacies of this model and current evidence and opinion^{10,11} are that the transition state may be anywhere between almost unchanged sp^2 and complete sp^3 , depending on the attacking species and the substrate. Experimental evidence obtained by Dewar *et al.*¹¹ shows that this variation may be accommodated by treating the resonance integral between the attached carbon atom and its neighbours as an empirical parameter.

In view of its importance to this paper, the starring process^{2,7} which distinguishes between alternant and non-alternant systems is reiterated as follows. Choose any carbon atom in a mesomeric hydrocarbon and mark it with a star. Starting from this carbon atom, star alternant carbon atoms throughout the molecule. If this process can be carried to completion, all atoms then being adjacent to atoms of the opposite kind (parity), the hydrocarbon is described as alternant. If, when the starring is complete, two adjacent carbon atoms are of the same parity, the hydrocarbon is non-alternant. Thus naphthalene (b) is alternant and azulene (g) is non-alternant.



One possible source of error should be noted. It is true for the simpler hydrocarbons that an odd-numbered ring is the result of cross-linking atoms of like parity, while an even-numbered ring is formed by cross-linking atoms of opposite parity. This result is

⁷ Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.*

⁸ Wheland, *ibid.*, 1942, **64**, 900.

⁹ Melander, *Arkiv Kemi*, 1950, 213.

¹⁰ Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

¹¹ Dewar, Mole, and Warford, *J.*, 1956, 3581, and refs. therein.

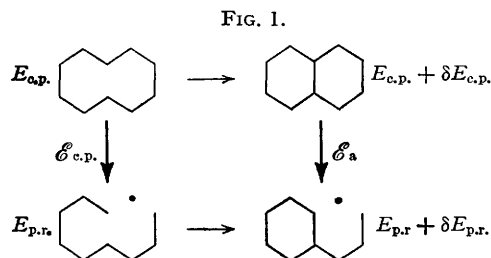
not general if more than two rings are present. In the hydrocarbon (u) for example, the fact that all rings are odd numbered may suggest that all cross-links are between atoms of like parity, but the starring exposes the fallacy. Conversely, in hydrocarbon (q) the presence of a six-membered ring suggests that a cross-link between atoms of opposite parity is present, but starring shows that this is not so. The difficulty only arises when odd-numbered rings are present and one ring is interposed between two others, but it must be emphasised that the nature of the cross-links, and not the odd or even number of the rings, is the important property.

Method.—Considering free-radical reactivity first, we require the difference between the total electron energy of the ground state and that of the transition state. Making the usual assumption that the only part of the total electron energy which varies with the structure of the hydrocarbon is the π -electron energy, we require the difference between the π -electron energy of the ground and the transition state. It is advantageous if this can be estimated directly, as in Dewar's method,⁷ but for the non-alternant hydrocarbons it is necessary to obtain the π energies individually. The π energy of the ground state is obtained by Dewar and Pettit's cyclic-polyene method,¹² the aromatic hydrocarbon being formally obtained from the corresponding cyclic polyene by the formation of cross-links. The π energy of the ground state is then that of the cyclic polyene ($E_{c.p.}$) plus the change in energy on cross-linking ($\delta E_{c.p.}$). The π energy of the transition state is obtained by extending the method used in the preceding paper to polyene radicals, the latter being cross-linked to build up this state. The π energy of the transition state is then that of the linear polyene radical ($E_{p.r.}$) plus the energy change on cross-linking ($\delta E_{p.r.}$). The atom localisation energy (\mathcal{E}_a) * of the cross-linked hydrocarbon is then

$$\mathcal{E}_a = E_{c.p.} + \delta E_{c.p.} - E_{p.r.} - \delta E_{p.r.} \quad \dots \quad (1)$$

$$\mathcal{E}_a = \mathcal{E}_{c.p.} + \delta E_{c.p.} - \delta E_{p.r.} \quad \dots \quad (2)$$

where $\mathcal{E}_{c.p.}$ is the atom localisation energy of the cyclic polyene. Equations (1) and (2) can be illustrated diagrammatically, position 1 of naphthalene being used as an example, as in Fig. 1. Ionic localisation energies follow simply from this treatment and bond localisation energies are obtained analogously. The three terms on the right-hand side of eqn. (2) are now calculated in turn.



(a) *The change in π -electron energy of a cyclic polyene on cross-linking.* The energy (e_j) of the j th molecular-orbital (ψ_j) of a cyclic polyene (C_nH_n) is given,¹ in the usual Hückel approximation, by

$$e_j = 2\beta \cos(2j\pi/n) \dots j = 0, \pm 1, \pm 2, \dots + n/2 \quad \dots \quad (3)$$

The Coulomb integral of a normal carbon atom is taken as zero, thus fixing the energy zero.† Overlap is neglected and β is the standard carbon-carbon bond resonance integral.

* As defined here, \mathcal{E} is a negative energy quantity—a positive numeric times β , itself a negative energy quantity.

† The sign convention used here is the opposite of that used by Hückel¹ and by Dewar and Pettit¹² and conforms to that used by Coulson and Longuet-Higgins.^{2b}

¹² Dewar and Pettit, *J.*, 1954, 1617.

The molecular orbitals occur in degenerate pairs, except for the lowest bonding and the highest antibonding, which are not degenerate. The real molecular orbitals are given^{1,12,13} by

$$\begin{aligned}\psi_j(\cos) &= \sum_{a=1}^n \chi_j \cos [(2aj\pi/n) + \epsilon_j] \phi_a \\ \psi_j(\sin) &= \sum_{a=1}^n \chi_j \sin [(2aj\pi/n) + \epsilon_j] \phi_a\end{aligned} \quad \dots \dots \dots (4)$$

where χ , a normalising factor, is $(1/n)^{1/2}$ for the non-degenerate orbitals and $(2/n)^{1/2}$ for the doubly degenerate. The ϕ 's are carbon $2p$ atomic orbitals and ϵ_j is a phase factor.* In favourable cases, correct choice of numbering will cause the phase factor to vanish.

Now Dewar and Pettit show¹² that the formation of a cross-link between atoms r and s of a cyclic polyene results in a change (δe_j) in the energy of the j th molecular orbital of

$$\begin{aligned}\delta e_j(\cos) &= \chi_j^2 \beta \{ \cos [2j(r-s)\pi/n] + \cos [(2j(r+s)\pi/n) + 2\epsilon_j] \} \\ \delta e_j(\sin) &= \chi_j^2 \beta \{ \cos [2j(r-s)\pi/n] - \cos [(2j(r+s)\pi/n) + 2\epsilon_j] \}\end{aligned} \quad \dots \dots \dots (5)$$

The resulting change in the total π -electron energy ($\delta E_{c.p.}$)[†] of the cyclic polyene depends on the value of n , $(4\gamma + 2)$ or (4γ) , γ being a positive integer.

(1) When $n = (4\gamma + 2)$, *e.g.*, naphthalene or azulene, the cyclic polyene has no non-bonding molecular orbitals and summation of (5) gives

$$\delta E_{c.p.}(4\gamma + 2) = \frac{4\beta}{n} + \frac{8\beta}{n} \sum_{j=1}^{\gamma} \cos [2j(r-s)\pi/n] \quad \dots \dots \dots (6)$$

The factor of $4\beta/n$ appearing in eqn. (6) is from the lowest bonding molecular orbital, whose phase factor is zero. Summing, we have

$$\delta E_{c.p.}(4\gamma + 2) = \frac{4\beta}{n} \left\{ \frac{\sin [(r-s)\pi/2]}{\sin [(r-s)\pi/n]} \right\} \quad \dots \dots \dots (7)$$

and since first-order perturbations are additive, the effect of several cross-links is given by

$$\delta E_{c.p.}(4\gamma + 2) = \frac{4\beta}{n} \sum_{\text{cross}}^{\text{links}} \left\{ \frac{\sin [(r-s)\pi/2]}{\sin [(r-s)\pi/n]} \right\} \quad \dots \dots \dots (8)$$

When atoms of like parity are linked, $(r-s)/2$ is an integer and $\delta E_{c.p.}(4\gamma + 2)$ is zero. The π -electron energy of a $(4\gamma + 2)$ cyclic polyene is thus unchanged when cross-links are formed between atoms of like parity, while the effect of cross-linking atoms of opposite parity is given by eqn. (8).

(2) When $n = (4\gamma)$, *e.g.*, pentalene or heptalene, the cyclic polyene has two non-bonding molecular orbitals containing two electrons. These orbitals being omitted for the moment, the change in the π -electron energy [$\delta E_{c.p.}'(4\gamma)$] on cross-linking is

$$\delta E_{c.p.}'(4\gamma) = \frac{4\beta}{n} + \frac{8\beta}{n} \sum_{j=1}^{\gamma-1} \{ \cos [2(r-s)j\pi/n] \} \quad \dots \dots \dots (9)$$

$$= \frac{4\beta}{n} \left\{ \sin \left[(r-s) \frac{\pi}{2} \right] \cot \left[(r-s) \frac{\pi}{n} \right] - \cos \left[(r-s) \frac{\pi}{2} \right] \right\} \quad (10)$$

* The phase factor is fully discussed by Dewar and Pettit.¹² It is given by

$$\tan (2\epsilon_j) = - \sum_{\text{cross}}^{\text{links}} \sin [2j(r+s)\pi/n] / \left(\sum_{\text{cross}}^{\text{links}} \cos [2j(r+s)\pi/n] \right), r \text{ and } s \text{ being the cross-linked atoms.}$$

† Unless the contrary is stated, throughout this paper we deal with the total π -electron energy, not with the total energy of the occupied M.O.s.

¹³ Moffitt, *J. Chem. Phys.*, 1954, **22**, 323.

When atoms of like parity are linked, $(r - s)/2$ is an integer and the first term in the braces vanishes. When several cross-links are formed

$$\delta E_{c.p.}'(4\gamma) = \frac{4\beta}{n} \sum_{\text{cross}}^{\text{links}} \left\{ \sin \left[(r - s) \frac{\pi}{2} \right] \cot \left[(r - s) \frac{\pi}{n} \right] - \cos \left[(r - s) \frac{\pi}{2} \right] \right\} \quad (11)$$

The change in the π energy of the cosine wave function non-bonding molecular orbital [$\delta e_{c.p.}^{\circ}(\cos)$] is *

$$\delta e_{c.p.}^{\circ}(\cos) = \frac{2\beta}{n} \left\{ \cos \left[(r - s) \frac{\pi}{2} \right] + \cos \left[(r + s) \frac{\pi}{2} + 2\epsilon^{\circ} \right] \right\} \quad (12)$$

and for several cross-links

$$\delta e_{c.p.}^{\circ}(\cos) = \frac{2\beta}{n} \sum_{\text{cross}}^{\text{links}} \left\{ \cos \left[(r - s) \frac{\pi}{2} \right] + \cos \left[(r + s) \frac{\pi}{2} + 2\epsilon^{\circ} \right] \right\} \quad (13)$$

Similarly, for the sine wave function non-bonding molecular orbital

$$\delta e_{c.p.}^{\circ}(\sin) = \frac{2\beta}{n} \sum_{\text{cross}}^{\text{links}} \left\{ \cos (r - s) \frac{\pi}{2} - \cos \left[(r + s) \frac{\pi}{2} + 2\epsilon^{\circ} \right] \right\} \quad (14)$$

The pair of electrons which originally occupied the non-bonding molecular orbitals now inhabit whichever of the perturbed non-bonding molecular orbitals is of lower energy. The total change in the π -electron energy of the (4γ) cyclic polyene [$\delta E_{c.p.}(4\gamma)$] on the formation of several cross-links is found by eqns. (11) and (13) or (14) to be

$$\delta E_{c.p.}(4\gamma) = \frac{4\beta}{n} \left\{ \sum_{\text{cross}}^{\text{links}} \sin (r - s) \frac{\pi}{2} \cos (r - s) \frac{\pi}{n} \pm \sum_{\text{cross}}^{\text{links}} \cos \left[(r + s) \frac{\pi}{2} + 2\epsilon^{\circ} \right] \right\} \quad (15)$$

the plus sign being taken when the perturbed non-bonding molecular orbital having a cosine wave function is of lower energy and the minus sign if the reverse is the case.

(b) *The change in the π -electron energy of a linear polyene radical on cross-linking.* In the preceding paper, the effect of the formation of cross-links on the π -electron energy of a linear polyene was examined. Now the energy and wave functions of the polyene radical molecular orbitals are given by the same formulæ as are those of a linear polyene¹⁴ but the presence of the singly-occupied non-bonding molecular orbital prevents the immediate carrying over of the polyene results to the polyene radical. For this reason, and also because the behaviour of the non-bonding molecular orbital on cross-linking determines the ionic reactivity, this molecular orbital is treated separately from the remaining bonding orbitals.

Consider a polyene radical $(C_{n-1}H_{n+1})$. The change in the π energy ($\delta E_{p.r.}'$) of the electrons of the bonding, doubly-occupied molecular orbitals on cross-linking atoms r and s follows in a similar manner to eqn. (9) of the preceding paper

$$\delta E_{p.r.}' = \frac{2\beta}{n} \left\{ \frac{\sin [(r - s)(n - 1)\pi/2n]}{\sin [(r - s)\pi/2n]} - \frac{\sin [(r + s)(n - 1)\pi/2n]}{\sin [(r + s)\pi/2n]} \right\} \quad (16)$$

Expanding the $(n - 1)$ terms of the numerators, we have

$$\delta E_{p.r.}' = \frac{2\beta}{n} \left\{ \sin [(r - s)\pi/2] \cot [(r - s)\pi/2n] - \sin [(r + s)\pi/2] \cot [(r + s)\pi/2n] \right\} \\ - \frac{2\beta}{n} \left\{ \cos [(r - s)\pi/2] - \cos [(r + s)\pi/2] \right\} \quad (17)$$

* ϵ° is the phase factor for the non-bonding molecular orbitals.

¹⁴ Coulson, *Proc. Roy. Soc.*, 1938, A, **164**, 393.

Now consider the change in the π energy ($\delta e_{p.r.}^\circ$) of the non-bonding molecular orbital. From eqn. (4) of the preceding paper, it is given by

$$\delta e_{p.r.}^\circ = \frac{4\beta}{n} \sin(rj\pi/n) \cdot \sin(sj\pi/n) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and since $j = n/2$ for this orbital

$$\delta e_{p.r.}^\circ = \frac{2\beta}{n} \left\{ \cos[(r-s)\pi/2] - \cos[(r+s)\pi/2] \right\} \quad . \quad . \quad . \quad . \quad (19)$$

Hence the total change in the π energy of a linear polyene on cross-linking atoms r and s is

$$\delta E_{p.r.} = (2\beta/n) \left\{ \sin[(r-s)\pi/2] \cot[(r-s)\pi/2n] - \sin[(r+s)\pi/2] \cot[(r+s)\pi/2n] \right\} \quad (20)$$

When atoms of like parity are linked, both $(r-s)/2$ and $(r+s)/2$ are integers, both terms in the braces in eqn. (20) vanish and there is no change in the total π -electron energy of a linear polyene radical on the formation of such cross-links. There is, however, a change in the energy of the non-bonding molecular orbital. When atoms of opposite parity are cross-linked, there is a change in the total π -electron energy, but there is no change in the energy of the non-bonding molecular orbital. These results are in agreement with those of the exact method. The formation of several cross-links is dealt with in the usual way, eqn. (20) being summed over the cross-links.

(c) *The atom localisation energies of a cyclic polyene.* These are easily found. The π -electron energy ($E_{c.p.}$) of a cyclic polyene (C_nH_n) depends on the value of n , $(4\gamma + 2)$, or (4γ) .

$$E_{c.p.}(4\gamma + 2) = 4\beta + 8\beta \sum_{j=1}^{\gamma} \cos(2j\pi/n) \quad . \quad . \quad . \quad . \quad (21)$$

$$= 4\beta \operatorname{cosec}(\pi/n) \quad . \quad . \quad . \quad . \quad (22)$$

and

$$E_{c.p.}(4\gamma) = 4\beta + 8\beta \sum_{j=1}^{\gamma-1} \cos(2j\pi/n) \quad . \quad . \quad . \quad . \quad (23)$$

$$= 4\beta \cot(\pi/n) \quad . \quad . \quad . \quad . \quad (24)$$

The transition state is a polyene radical, whose π -electron energy is

$$E_{p.r.} = 4\beta \sum_{j=1}^{(n/2)-1} \cos(j\pi/n) \quad . \quad . \quad . \quad . \quad (25)$$

$$= 2\beta [\cot(\pi/2n) - 1] \quad . \quad . \quad . \quad . \quad (26)$$

The atom localisation energies (\mathcal{E}) for free radical substitution are then

$$\mathcal{E}_{c.p.}(4\gamma + 2) = 4\beta \operatorname{cosec}(\pi/n) - 2\beta \cot(\pi/2n) + 2\beta \quad . \quad . \quad . \quad (27)$$

$$\mathcal{E}_{c.p.}(4\gamma) = 4\beta \cot(\pi/n) - 2\beta \cot(\pi/2n) + 2\beta \quad . \quad . \quad . \quad (28)$$

After some manipulation, these reduce to

$$\mathcal{E}_{c.p.}(4\gamma + 2) = 2\beta[1 + \tan(\pi/2n)] \quad . \quad . \quad . \quad . \quad (29)$$

$$\mathcal{E}_{c.p.}(4\gamma) = 2\beta[1 - \tan(\pi/2n)] \quad . \quad . \quad . \quad . \quad (30)$$

This completes the evaluation of the three terms on the right-hand side of eqn. (2) and we can now obtain the atom localisation energies for free radical substitution for all of the

purely cyclic alternant and non-alternant hydrocarbons. Collecting these terms together, we have

$$\mathcal{E}_a(4\gamma + 2) = 2\beta[1 + \tan(\pi/2n)] + \frac{4\beta}{n} \left\{ \sum_{\text{cross}}^{\text{links}} \frac{\sin[(r-s)\pi/2]}{\sin[(r-s)\pi/n]} \right\} - \frac{2\beta}{n} \left\{ \sum_{\text{cross}}^{\text{links}} \sin[(r-s)\pi/2] \cot[(r-s)\pi/2n] - \sin[(r+s)\pi/2] \cot[(r+s)\pi/2n] \right\} \quad (31)$$

$$\mathcal{E}_a(4\gamma) = 2\beta[1 - \tan(\pi/2n)] + \frac{4\beta}{n} \left\{ \sum_{\text{cross}}^{\text{links}} \sin\left[\left(r-s\right)\frac{\pi}{2}\right] \cot\left[\left(r-s\right)\frac{\pi}{n}\right] \pm \sum_{\text{cross}}^{\text{links}} \cos\left[\left(r+s\right)\frac{\pi}{2} + 2\varepsilon^\circ\right] \right\} - \frac{2\beta}{n} \left(\sum_{\text{cross}}^{\text{links}} \left\{ \sin\left[\left(r-s\right)\frac{\pi}{2}\right] \cot\left[\left(r-s\right)\frac{\pi}{2n}\right] - \sin\left[\left(r+s\right)\frac{\pi}{2}\right] \cot\left[\left(r+s\right)\frac{\pi}{2n}\right] \right\} \right) \quad (32)$$

In eqns. (31) and (32), the first summation(s) on the right-hand side refers to the ground state, the second to the cross-linked radical of the transition state.

The free-radical localisation energies calculated from eqns. (31) and (32) are reported in Tables 1, 2, and 3, together with those obtained by solution of the secular equations [$\mathcal{E}_a(\text{s.e.})$]. In the evaluation of these equations, it often turns out that the non-alternant hydrocarbons are more easily calculated than are the alternants.

TABLE 1. Atom localisation energies of alternant hydrocarbons.

Hydrocarbon	Position	Localisation energy (units of β)	
		\mathcal{E}_a	$\mathcal{E}_a(\text{s.e.})^{16}$
Benzene (a)	—	2.54	2.54
Naphthalene (b)	1	2.42	2.30
	2	2.55	2.48
Anthracene (c)	1	2.44	2.25
	2	2.57	2.40
	9	2.12	2.01
Phenanthrene (d)	1	2.51	2.30
	2	2.57	2.50
	3	2.51	2.41
	4	2.58	2.39
	9	2.33	2.30
Naphthacene (e)	5	2.07	1.93

TABLE 2. Atom localisation energies of non-alternant hydrocarbons (units of β).

Hydrocarbon	Position	Localisation energy ⁶					
		Radical		Nucleophilic		Electrophilic	
		\mathcal{E}_a	$\mathcal{E}_a(\text{s.e.})$	\mathcal{E}_a	$\mathcal{E}_a(\text{s.e.})$	\mathcal{E}_a	$\mathcal{E}_a(\text{s.e.})$
Pentalene (f)	1	2.10	1.96	1.60	1.54	2.60	2.38
	2	2.10	2.03	2.10	2.03	2.10	2.03
Azulene (g) *	1	2.32	2.26	2.72	2.60	1.92	1.92
	2	2.32	2.36	2.32	2.36	2.32	2.36
	4	2.32	2.24	1.92	1.93	2.72	2.55
	5	2.32	2.34	2.32	2.34	2.32	2.34
	6	2.32	2.36	1.92	1.99	2.72	2.73
Heptalene (h)	1	2.07	1.93	2.40	2.19	1.74	1.66
	2	2.07	2.03	2.07	2.03	2.07	2.03
	3	2.07	2.03	2.40	2.36	1.74	1.71

* The azulene figures [$\mathcal{E}_a(\text{s.e.})$] were personally communicated by Dr. R. D. Brown.

Ionic Substitution.—In proposing a model for the transition state of ionic substitution, Wheland assumed ⁸ that the molecular orbitals of the residual molecule * are occupied by one more (nucleophilic) or by one less (electrophilic) electron than in free-radical

* The residual molecule is the parent hydrocarbon with the carbon atom undergoing substitution removed.

TABLE 3. Atom localisation energies [\mathcal{E}_a (s.e.) followed by \mathcal{E}_a] of benzannulated azulenes (units of β) for radical, electrophilic, and nucleophilic substitution.

1: 2-Benzazulene (i)												
Position	3		4		5		6		7		8	
Radical	1.53	2.17	1.39	2.27	—	2.33	1.50	2.33	1.40	2.27	1.56	2.40
Electro	1.14	1.89	1.56	2.55	—	2.33	1.72	2.62	1.40	2.27	1.83	2.69
Nucleo	1.93	2.46	1.22	1.98	—	2.33	1.29	2.05	1.40	2.27	1.28	2.12
4: 5-Benzazulene (j)												
	1		2		3		6		7		8	
Radical	1.54	2.33	—	2.27	1.63	2.40	1.39	2.17	1.72	2.40	1.38	2.27
Electro	1.35	2.05	—	2.27	1.39	2.12	1.74	2.46	1.72	2.40	1.75	2.55
Nucleo	1.74	2.62	—	2.27	1.87	2.69	1.03	1.89	1.72	2.40	1.01	1.98
5: 6-Benzazulene (k)												
	1		2		3		4		7		8	
Radical	1.60	2.33	1.70	2.33	1.52	2.27	1.34	2.17	1.48	2.17	1.50	2.40
Electro	1.36	2.05	1.70	2.33	1.33	1.98	1.65	2.46	1.48	2.17	1.64	2.69
Nucleo	1.83	2.62	1.70	2.33	1.71	2.55	1.04	1.89	1.48	2.17	1.36	2.12

\mathcal{E}_a (s.e.) are taken from ref. 15 and include overlap, while \mathcal{E}_a neglect overlap.

The sign convention for ionic reactivity used in ref. 15 is the opposite of that used here.

substitution. With this assumption, consider the effect on the terms in eqn. (2) on changing from free-radical to ionic substitution. Clearly, $E_{c.p.}$, $E_{p.r.}$, and $\delta E_{c.p.}$ are unchanged and $\delta E_{p.r.}$ is also unchanged if the non-bonding molecular orbital of the polyene radical is unchanged in energy on cross-linking, *i.e.*, if alternant rings are formed [eqn. (19)]. This conclusion agrees with that from the exact method. If non-alternant rings are formed, this orbital may be changed in energy and the total π -electron energy of the transition state may be affected by the number of electrons occupying this orbital. This result brings out clearly the underlying reason for the difference in ionic reactivity between alternant and non-alternant hydrocarbons.

We need consider, then, only cross-links between atoms of like parity and we require the change in energy of the non-bonding molecular orbital of the polyene radical on cross-linking. This can now be written [eqn. (19)]

$$\delta e_{p.r.}^{\circ} = \frac{2\beta}{n} [(-1)^{(r-s)/2} - (-1)^{(r+s)/2}] \quad . \quad . \quad . \quad (33)$$

If more than one cross-link is formed, eqn. (33) is summed over these cross-links in the usual way. Hence

$$\mathcal{E}_a^{-} = \mathcal{E}_a - \delta e_{p.r.}^{\circ} = \mathcal{E}_a - \frac{2\beta}{n} \sum_{\text{cross}} [(-1)^{(r-s)/2} - (-1)^{(r+s)/2}] \quad . \quad . \quad . \quad (34)$$

$$\mathcal{E}_a^{+} = \mathcal{E}_a + \delta e_{p.r.}^{\circ} = \mathcal{E}_a + \frac{2\beta}{n} \sum_{\text{cross}} [(-1)^{(r-s)/2} - (-1)^{(r+s)/2}] \quad . \quad . \quad . \quad (35)$$

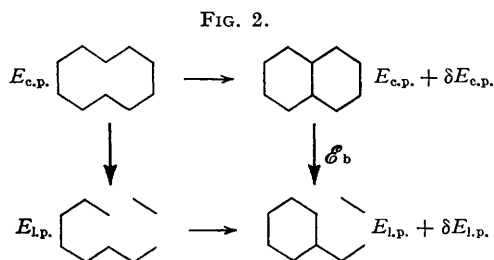
where \mathcal{E}_a^{-} and \mathcal{E}_a^{+} are the atom localisation energies for nucleophilic and electrophilic substitution respectively. Using equations (34) and (35), we have calculated the ionic localisation energies of some cyclic non-alternant hydrocarbons (Tables 2 and 3).

Bond Localisation Energies.—In this reaction, the transition state is a polyene, cross-linked at one or more points. The π -electron energy of the ground state of a cyclic polyene and the change in energy have been given [eqns. (8), (15), (22), (24)]. The π -electron energy of a linear polyene and the change in energy on cross-linking have been given in the preceding paper [eqns. (9) and (11)]. From these equations, the bond localisation energies (\mathcal{E}_b) of the cross-linked hydrocarbons are

$$\mathcal{E}_b(4\gamma + 2) = 4\beta \operatorname{cosec}(\pi/n) - 2\beta \operatorname{cosec}[\pi/2(n-1)] + \delta E_{c.p.} - \delta E_{l.p.} \quad . \quad . \quad (36)$$

$$\mathcal{E}_b(4\gamma) = 4\beta \cot(\pi/n) - 2\beta \operatorname{cosec}[\pi/2(n-1)] + \delta E_{c.p.} - \delta E_{l.p.} \quad . \quad . \quad (37)$$

These equations can be illustrated, the 1 : 2-bond of naphthalene being used as an example, as in Fig. 2.



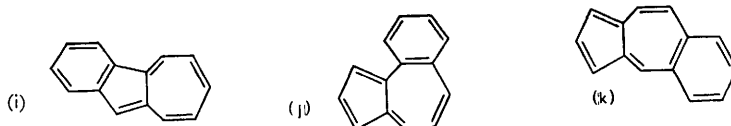
In Table 4, the perturbation (\mathcal{E}_b) and secular equation [\mathcal{E}_b (s.e.)] bond localisation energies for the simple non-alternant hydrocarbons are reported.

TABLE 4. Bond localisation energies for the simple cyclic non-alternant hydrocarbons (units of β).

Hydrocarbon	Pentalene		Heptalene			Azulene				
	1 : 2	1 : 7	1 : 2	2 : 3	1 : 11	1 : 2	4 : 5	5 : 6	1 : 9	8 : 9
\mathcal{E}_b (s.e.)	0.99	1.47	1.04	1.14	1.56	1.37	1.31	1.42	1.85	1.85
\mathcal{E}_b	1.17	1.17	1.20	1.20	1.20	1.43	1.43	1.43	1.43	1.43

\mathcal{E}_b (s.e.) for pentalene and heptalene are taken from ref. 6. The azulene figures were obtained from published data³ on the residual molecule or calculated.

An excellent opportunity of testing the perturbation method on more complex non-alternant hydrocarbons is available from the work of Simon, Naville, Susler, and Heilbronner.¹⁵ These workers, in attempting to correlate the observed basicities of azulene and the benzannelated azulenes, have reported free-radical and ionic localisation energies for most positions in 1 : 2-, 4 : 5-, and 5 : 6-benzazulene (i, j, and k respectively). The perturbation method has been applied to these compounds and both sets of results are reported in Table 3.



DISCUSSION

The perturbation method is first tested on the alternant benzenoid hydrocarbons in Table 1. The perturbation localisation energies reproduce those obtained by solution of the secular equations with satisfactory accuracy and if the perturbation figures are reduced by 0.1β , the agreement is good.

Now consider the atom localisation energies for free-radical substitution in the simple cyclic non-alternant hydrocarbons (Table 2). A particularly simple situation arises when n is $(4\gamma + 2)$, the atom localisation energies for free-radical substitution being those of the corresponding cyclic polyene. Since the localisation energies of the latter hydrocarbons lie in the range 2.32β ($n = 10$) to 2.0β ($n = \infty$), this is also the range of the localisation energies for free-radical reaction of the cross-linked hydrocarbons.

Turning to the specific calculations in Table 2, we find that the agreement between the perturbation localisation energies and those from the secular equations is clear. One shortcoming of the perturbation results is the prediction that all positions in any one simple cyclic non-alternant hydrocarbon are of equal free-radical reactivity. This is an oversimplification but, compared with the very large range of ionic localisation energies, the free-radical localisation energies of these hydrocarbons do approximate to this result.

¹⁵ Simon, Naville, Susler, and Heilbronner, *Helv. Chim. Acta*, 1956, **39**, 1107.

It will be most interesting to discover whether the differences, predicted by the Hückel theory, in the free-radical reactivity of the various positions in, say, azulene are borne out in practice as the self-consistency of the method is lost in non-alternant hydrocarbons.^{2a,17}

Ionic Reactivity.—It is in this type of reactivity that there is a clear distinction between the alternant and the non-alternant hydrocarbons, the non-alternant ones having an extremely large range of ionic localisation energies. Dewar and his co-workers¹¹ found a rate variation for nitration of the benzenoid hydrocarbons which would lead to rate differences of the order of 10^{15} for some of the non-alternant hydrocarbons discussed in this paper. Only experiment can decide whether changes of mechanism will accompany such large rate differences.

Assuming for the moment that no mechanistic changes occur, we can speculate on the effect of such differences on the chemical properties of these hydrocarbons. From general experience, an electrophilic localisation energy of 2.0β (e.g., anthracene) is sufficiently high for the hydrocarbon to be quite stable under ordinary acidic conditions.¹⁸ By "ordinary conditions" is meant, for example, those of acid-catalysed elimination of HX in the formation of a double bond. When the electrophilic localisation energy falls to 1.9β (e.g., azulene and the benzannelated azulenes¹⁵), the hydrocarbon is detectably basic. In heptalene, the electrophilic localisation energy of 1.6 — 1.7β is perhaps sufficiently low for the hydrocarbon to undergo cationic polymerisation during the synthetic operation mentioned above. Preparation of this hydrocarbon would then best be attempted in the absence of strong acids.

There is less information to guide us in considering the allowable limits of nucleophilic localisation energies. The common benzenoid hydrocarbons (nucleophilic localisation energies of greater than 2.0β) are quite stable to the common bases. In pentalene, however, the localisation energy for nucleophilic attack in the 1 position is 1.6β and this may be sufficiently low for anionic polymerisation to occur fairly easily. The preparation of this hydrocarbon would then best be attempted in the absence of strong base.

Such considerations as have been put forward in the last paragraphs are necessarily vague at present, there being little relevant experimentation to guide them. The details of reaction conditions will be of major importance, but where there is a free choice of using either acidic or basic reaction conditions, the uncertainty as to the stability of the product can be reduced by an examination of the theoretical predictions.

The results obtained from the benzazulenes (Table 3) are particularly encouraging, the agreement between the results of the perturbation method and those from the solution of the secular equations being excellent. The disparity in absolute magnitude is due to overlap's being neglected in the perturbation calculations while it is included in the reported results.¹⁵ Clearly the perturbation method picks out the position of protonation as accurately as does the exact method, and there is also good agreement with regard to nucleophilic localisation energies. As with the simple non-alternant hydrocarbons, there is not complete agreement in the radical localisation energies but the differences are small.

Bond Localisation Energies.—The bond localisation energies calculated by the perturbation method are in reasonable agreement with those obtained by solution of the secular equations (Table 4). In particular, the higher bond localisation energy of azulene than pentalene and heptalene is brought out well. Bonds having a carbon atom common to two rings have much higher secular-equation localisation energies than those calculated by the perturbation method, but as such bonds are the least reactive in the molecule, inability to deal with them is not important for studies of chemical reactivity. The remaining bonds in any one simple cyclic non-alternant hydrocarbon are predicted to be of the same localisation energy and, from the exact calculations, this is a reasonable approximation.

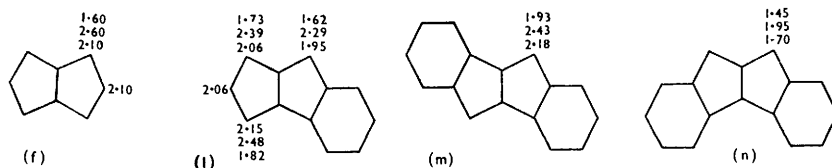
¹⁶ Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.

¹⁷ Coulson and Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 54.

¹⁸ Gold and Tye, *J.*, 1952, 2172.

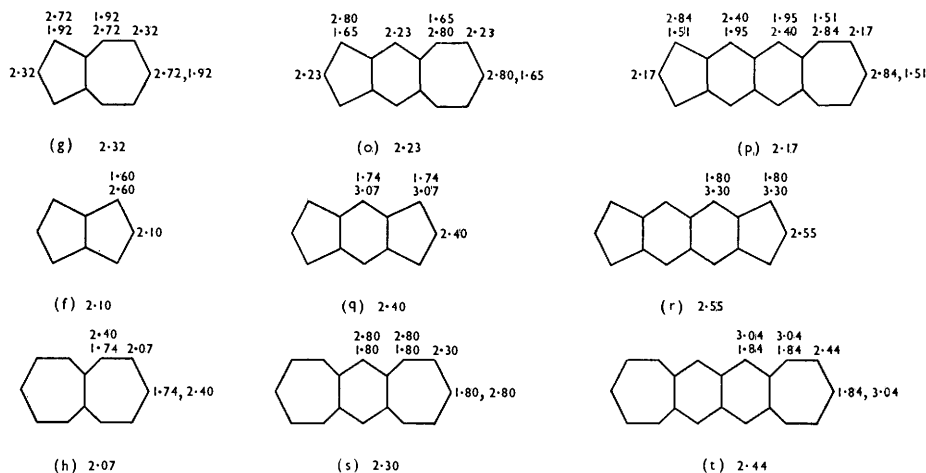
To illustrate the use of the perturbation method, the effect of benzannelation and benzinterposition on the free-radical and ionic reactivity of azulene, pentalene and, in part, heptalene has been examined. The monobenzazulenes have already been dealt with in Table 3; the predicted chemical reactivity of the benzannelated pentalenes is shown in Fig. 3, where the numerals represent, in order from the ring outward, radical, electrophilic, and nucleophilic reactivity.

FIG. 3.



Dibenzopentalene (m) is of particular interest as experimental data are available for it and, at the same time, the same workers using similar synthetic methods were unable to obtain pentalene itself.¹⁹ The theoretical predictions are that monobenzannelation has little effect on the reactivity and that dibenzannelation [in the sense of (m)] has little effect on the free-radical reactivity but does decrease the nucleophilic reactivity substantially. Possibly this reduction in reactivity towards bases is

FIG. 4.



sufficient to allow the benzannelated compound to be isolated, while the simple hydrocarbon is too reactive in this respect. It would also be predicted from the theory that the dibenzopentalene (m) is not basic* and this agrees with the experimental observation that it does not dissolve in orthophosphoric acid, in which azulene and the benzannelated azulenes are soluble. The observation¹⁹ that dibenzopentalene (m) is destroyed by concentrated sulphuric acid and is polymerised by concentrated hydrochloric acid suggests that these two acids are not acting as simple protonating media, but have other modes of chemical reactivity here. In fact, the situation suggests an interesting possibility which could arise with some of the non-alternant hydrocarbons. Consider a hydrocarbon which has little reactivity towards electrophils, but is reactive towards bases. It then becomes possible for reaction with, say, hydrochloric acid to occur by the chlorine anion's attacking

* A position with an electrophilic localisation energy of some 1.9—2.0 β or lower being assumed to be required for basicity.

¹⁹ Blood and Linstead, *J.*, 1952, 2255, 2263.

first. Such mechanistic variations are to be expected with some non-alternant hydrocarbons. The effect of dibenzannelation of pentalene in the sense of (n) is markedly to increase the free-radical and the ionic reactivity.

The effect of benzinterposition on azulene, pentalene, and heptalene is shown in Fig. 4. The numeral closer to the ring represents electrophilic reactivity, that further out the nucleophilic reactivity. Where they are the same, only one is quoted. The numeral beside the identifying letter is the radical reactivity for all positions.

In azulene, benzinterposition (o) and (p) does not change the predicted orientation of substitution but the free-radical reactivity is increased slightly and the ionic reactivity is increased substantially. When two benzene rings are interposed (p), both the electrophilic and the nucleophilic reactivities are reduced to 1.51β at different positions. Preparation of this hydrocarbon would then best be attempted in the absence of both strong acid and strong base.

In pentalene and heptalene, benzinterposition does not change the predicted orientation of substitution, but now the ionic reactivity is decreased. Both mono- and di-benzinterposed pentalenes should be quite stable to simple protonating media but, as the dibenzopentalene data¹⁹ show, caution is required in assuming that the common mineral acids do not react in other ways with these very reactive hydrocarbons. Conversely, the mono- and di-benzinterposed heptalenes should be quite stable to bases but should be quite basic.

The author is indebted to Dr. R. D. Brown for the azulene figures (Table 2) and to Professor M. J. S. Dewar for advice.

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