770. *Structure and Properties of Mesomeric Systems. Part V.* The Effect of Substituents on the Chemical Reactivity of the* (4γ + 2) *Non-alternant Hydrocarbons.*

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By making reasonable assumptions about the parameters, one can estimate the order of magnitude of the expected substituent effects in the (4γ + 2) non-alternant hydrocarbons. The presence of one of the common substituents will probably have little or no effect on the orientation of ionic substitution in these hydrocarbons, a phenomenon which has already been discovered experimentally by Anderson and his co-workers.

IN Parts I—III a new perturbation method was developed to predict the properties of some unknown (4γ + 2) non-alternant hydrocarbons. Apart from its theoretical interest, such information is useful in synthesis, since it indicates the reaction conditions and isolation procedures which the products may survive. In Part IV these methods, extended to non-alternant aza-heterocycles, showed that the aza-azulenes should behave similarly to the parent hydrocarbon on substitution.

We now turn to substituents in (4γ + 2) non-alternant hydrocarbons. This is of practical interest since it seems that substituents might " stabilise " (reduce the reactivity) of hydrocarbons difficult of synthesis.

Previous work on substituent action has been largely concerned with predicting their directive effects in benzene,[1,2,3,4] by solution of the secular equations for a range of parameter values and comparison of the results with experiment. The major effects of substituent action in benzene can be understood. We are now primarily concerned with the order of magnitude of the substituent effects, rather than with their directive action. As the former is a relatively gross effect (whether there is any directive effect) we may hope for success with a less accurate method of calculation. This makes perturbation methods [5,6,7] possible, which avoid the solving of large secular equations. Our method is based partly on the qualitatively successful resonance theory, ascribing substituent action to inductive and mesomeric effects.[1,4,8,9] The former is treated as for the introduction of the nitrogen atom, the Coulomb integral of the carbon atom to which the substituent is attached being supposed to differ from that of a normal one. The latter is represented by the action of an idealised substituent in which all the hetero-atoms have been replaced by carbon atoms. This procedure is unsatisfactory in that it will not reproduce all the phenomena of substituent action in benzene, but it does reproduce the two major phenomena of *ortho–para*-direction with activation and *meta*-direction with deactivation. For reasons given below, this method should be adequate for the non-alternant hydrocarbons in spite of its shortcomings for benzene. As azulenes containing substituents other than alkyl can now be prepared,[10] any information would be valuable in the formidable task of their orientation.

Method.—The inductive effect being treated in the same way as the introduction of a nitrogen atom, it remains to evaluate the mesomeric effect. Both the isolated-molecule

* Part IV, preceding paper.

[1] Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086.
[2] Wheland, *ibid.*, 1942, **64**, 900.
[3] Dewar, *J.*, 1949, 463.
[4] Sandorfy, *Bull. Soc. chim. France*, 1949, **16**, 615.
[5] Jaffé, *J. Amer. Chem. Soc.*, 1955, **77**, 274.
[6] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 283.
[7] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.
[8] *Idem, ibid.*, p. 3357.
[9] Peters, *J.*, 1957, 2654.
[10] Anderson, Nelson, and Tazuma, *J. Amer. Chem. Soc.*, 1953, **75**, 4980; Anderson, Cowles, Tazuma, and Nelson, *ibid.*, 1955, **77**, 6321; Anderson, Scotoni, Cowles, and Fritz, *J. Org. Chem.*, 1957. **22**, 1193.

and the localisation approximations are used. Azulene is taken as a convenient model. Substituents are described as monatomic, diatomic, and triatomic when they contribute one (NR_2, OR), two (CO·R, CN), and three (CO_2R, NO_2*) atomic orbitals to the mesomeric system respectively. Overlap is neglected. For symbols, see the preceding paper.

Isolated-molecule Approximation.—We require the charge distribution in a cross-linked cyclic polyene carrying a group of one or more carbon atoms. Suppose atoms r and s of the cyclic polyene to be cross-linked and the attached group of carbon atoms, representing the substituent, to be joined by atom q to atom p of the cyclic polyene. Then the charge (q_t) on atom t is a function of β_{rs} and β_{pq} †

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

together with higher terms which are neglected. The second term on the right-hand side of eqn. (1) represents the cross-linking of the cyclic polyene (Part III). The third term is a first-order perturbation expression for the charge differential produced by the idealised substituent. If the latter is represented by two carbon atoms (*i.e.*, CO·R, CN), then the perturbation vanishes, both the substituted and the unsubstituted cyclic polyene being alternant hydrocarbons. If the substituent is represented by three carbon atoms (CO_2R, NO_2), the charge developed in the ring is again zero, being confined to the terminal carbon atoms of the substituent. If the substituent is represented by a single carbon atom (*i.e.*, NR_2, OR), then there will be a charge developed in the ring, owing to the formation of a non-bonding molecular-orbital in the substituted cyclic polyene. This charge is immediately given by the well-known equation [11]

$$\sum_v c_{ov}\beta_{uv} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the summation is over all atoms (v) adjacent to atom u and c_{ov} is the coefficient at atom v of the non-bonding molecular-orbital. We take the resonance integral of the bonds in the ring as β, the standard carbon–carbon bond resonance integral when overlap is neglected. There remains the resonance integral of the bond between the substituent and the ring (β_{pq}). It is commonly agreed that this should be substantially less than β. In the case of the halogens, experimental evidence is available from the nuclear quadrupole coupling data. Howe and Goldstein [12] find that β_{C-Cl} and β_{C-Br} must be taken as approximately 0.5β and 0.4β respectively in order to reproduce the ionisation potential and the charge transfer in vinyl chloride and bromide and in chloro- and bromo-benzene. These calculations, however, include overlap. Jaffé [13] finds that values in the range 0.06—0.89β are required for the halogens and alkoxyl and amino-groups in order to reproduce the Hammett σ constants for these substituents. Sandorfy [4] estimates these resonance integrals as 0.12—0.96β for the same substituents. The present author [9] has used values of 0.2—0.4β for the monatomic substituents in order to reproduce certain ultraviolet spectral data. Another [14] finds β_{CO} in phenols to be 0.27β. As we are seeking the order of magnitude of substituent effects rather than the details of their action, we do not differentiate between the monatomic substituents, but examine a single hypothetical substituent whose resonance integral with the ring is $\beta/3$—*i.e.*, whose mesomeric constant is $\frac{1}{3}$. The conclusions depend only on the fact that β_{pq} is substantially less than β, not on its exact value.

If this value is used for β_{pq}, eqn. (2) becomes, when atom u is atom p:

$$\sum_v{}' c_{ov}\beta + c_{oq}\beta/3 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

* Attached to the ring by the centre, not by the terminal, atom.
† β_{pq} is the resonance integral of the bond between the substituent and the ring.

[11] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.
[12] Howe and Goldstein, *ibid.*, 1957, **27**, 831; 1957, **26**, 7; Goldstein, *ibid.*, 1956, **24**, 507.
[13] Jaffé, *J. Chem. Phys.*, 1952, **20**, 279.
[14] Lopex Vaquex, *Anales real soc. españ. Fis. Quim.*, 1955, **51**, 203.

The prime denotes that atom q is omitted from the summation. In this way, the mesomeric charges resulting from a monatomic substituent can be estimated for all positions of the $(4\gamma + 2)$ non-alternant hydrocarbons.

The Localisation Method.—Here we need the effect on the energy of the ground and the transition state of introducing extra carbon atoms into the mesomeric system. If the π-electron energy of the cyclic polyene is $E_{c.p.}$, the change in π-electron energy $(\delta E_{c.p.})$ on cross-linking atoms r and s and adding a new group of carbon atoms by atom q to atom p of the cyclic polyene is given by

$$\delta E_{c.p.} = (\partial E_{c.p.}/\partial\beta_{rs})\delta\beta_{rs} + (\partial E_{c.p.}/\partial\beta_{pq})\delta\beta_{pq} \quad . \quad . \quad . \quad . \quad (4)$$

plus higher terms which are neglected. The change $(\delta E_{p.r.})$ in the π-electron energy of the polyene radical on cross-linking and addition of the idealised substituent is given by

$$\delta E_{p.r.} = (\partial E_{p.r.}/\partial\beta_{rs})\delta\beta_{rs} + (\partial E_{p.r.}/\partial\beta_{pq})\delta\beta_{pq} \quad . \quad . \quad . \quad . \quad (5)$$

The localisation energy for free-radical attack $(\mathscr{E}_s)$ in the cross-linked substituted cyclic polyene is then

$$\mathscr{E}_s = E_{c.p.} + \delta E_{c.p.} - E_{p.r.} - \delta E_{p.r.} = [E_{c.p.} + (\partial E_{c.p.}/\partial\beta_{rs})\delta\beta_{rs}]$$
$$- [E_{p.r.} + (\partial E_{p.r.}/\partial\beta_{rs})\delta\beta_{rs}] + [(\partial E_{c.p.}/\partial\beta_{pq}) - (\partial E_{p.r.}/\partial\beta_{pq})]\delta\beta_{pq}$$

But from Part II (eqn. 1)

$$\mathscr{E}_a = [E_{c.p.} + (\partial E_{c.p.}/\partial\beta_{rs})\partial\beta_{rs}] - [E_{p.r.} + (\partial E_{p.r.}/\partial\beta_{rs})\delta\beta_{rs}] \quad . \quad . \quad . \quad (7)$$

where $\mathscr{E}_a$ is the atom localisation energy for free-radical substitution in the unsubstituted, cross-linked non-alternant hydrocarbon. Hence

$$\mathscr{E}_s = \mathscr{E}_a + [(\partial E_{c.p.}/\partial\beta_{pq}) - (\partial E_{p.r.}/\partial\beta_{pq})]\partial\beta_{pq} \quad . \quad . \quad . \quad . \quad (8)$$

Now the first-order perturbation term $\partial E_{c.p.}/\partial\beta_{pq}$ is zero. This is easily shown by writing the molecular-orbitals of the cyclic polyene as ψ_h and the molecular (atomic) orbitals of the substituent as ψ_s and then we have for the energies $(e_{c.p.}')$ of the perturbed molecular-orbitals of the cyclic polyene [7]

$$e_{c.p.}' = e_{c.p.} + \int\psi_h H'\psi_h d\tau \quad . \quad . \quad . \quad . \quad . \quad (9)$$

with a similar expression for the energies of the perturbed molecular-orbitals of the substituent. Expanding the molecular-orbitals into their constituent atomic orbitals (ϕ's), we have

$$\psi_h{}^a = \sum_n c_{an}\phi_h{}^n \qquad \psi_s{}^b = \sum_m c_{bm}\phi_s{}^m$$

and if it is assumed that the only non-vanishing term is $\int\phi_h{}^p H' \phi_s{}^q d\tau$ the first-order perturbation vanishes.

The second term in eqn. (8) is also a first-order perturbation expression, describing the interaction between the substituent and the residual molecule. If the substituent is represented by two carbon atoms (CO·R, CN), there is only accidental degeneracy between doubly-filled molecular-orbitals, and the situation is the same as in the cyclic polyene—the perturbation vanishes. For triatomic and monatomic substituents, there is degeneracy between the non-bonding molecular-orbital of the polyene radical and the zero-energy atomic (molecular) orbital of the idealised substituent. In this case [7]

$$e_{p.r.}{}^{0\prime} = e_{p.r.}{}^0 + c_{op} \cdot c_{oq} \cdot \beta_{pq} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $e_{\text{p.r.}}^{0\prime}$ is the energy of the perturbed non-bonding molecular-orbital of the polyene radical and c_{op} and c_{oq} are the atomic orbital coefficients of the non-bonding molecular-orbitals of the polyene radical and the substituent respectively. For triatomic substituents, $c_{oq} = 0$ and the perturbation vanishes. For monatomic substituents, $c_{oq} = 1$, $\beta_{pq} = \beta/3$, and eqn. (10) becomes

$$e_{\text{p.r.}}^{0\prime} = e_{\text{p.r.}}^{0} + c_{op} \cdot \beta/3 \quad\quad\quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now if p is unstarred,[6,7] $c_{op} = 0$ and the perturbation vanishes. If p is starred, $c_{op} \neq 0$ and there is a first-order correction to the energy unless both non-bonding molecular-orbitals are doubly occupied. The common monatomic substituents all contribute two electrons to the mesomeric system, so that in nucleophilic substitution there is again no correction to the energy. In electrophilic substitution there is a decrease in the π-electron energy of the polyene radical which is given by

$$\delta E_{\text{p.r.}}/\delta\beta_{pq} = 2c_{op}/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or

$$\mathscr{E}_{\text{s}}^{+} = \mathscr{E}_{\text{a}}^{+} - 2c_{op}\beta/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Results.—In the Table the charge distribution and localisation energies of azulenes carrying a single monatomic substituent of inductive constant $+1\cdot0$ and mesomeric constant $\frac{1}{3}$ are reported, calculated from eqns. (3) and (13) and data in the preceding paper. The charge distribution and localisation energies of azulene are taken from Parts II and III.

Distribution of charge $(1 - q_t)$ and localisation energies (units of β) for electrophilic $(\mathscr{E}_{\text{s}}^{+})$ and nucleophilic $(\mathscr{E}_{\text{s}}^{-})$ processes for azulene and azulenes substituted with a single monatomic substituent at the position denoted by **X.**

[Standard numbering: see preceding paper.]

Posn. (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
$\mathscr{E}_{\text{s}}^{+}$	1·92	2·32	1·92	2·72	2·32	2·72	2·32	2·72
$\mathscr{E}_{\text{s}}^{-}$	2·72	2·32	2·72	1·92	2·32	1·92	2·32	1·92
Charge	**X**	−0·090	−0·141	+0·206	+0·052	+0·187	+0·052	+0·207
$\mathscr{E}_{\text{s}}^{+}$	**X**	2·22	2·06	2·86	2·22	2·86	2·22	2·86
$\mathscr{E}_{\text{s}}^{-}$	**X**	2·12	2·58	1·78	2·12	1·78	2·12	1·78
Charge	−0·219	**X**	−0·219	+0·200	+0·058	+0·181	+0·058	+0·200
$\mathscr{E}_{\text{s}}^{+}$	1·82	**X**	1·82	2·62	2·46	2·62	2·46	2·62
$\mathscr{E}_{\text{s}}^{-}$	2·52	**X**	2·52	1·72	2·18	1·72	2·18	1·72
Charge	−0·142	−0·019	−0·141	**X**	−0·019	+0·188	+0·052	+0·206
$\mathscr{E}_{\text{s}}^{+}$	2·06	2·22	2·06	**X**	2·22	2·86	2·22	2·86
$\mathscr{E}_{\text{s}}^{-}$	2·58	2·12	2·58	**X**	2·12	1·78	2·12	1·78
Charge	−0·095	−0·013	−0·148	+0·129	**X**	+0·110	+0·059	+0·200
$\mathscr{E}_{\text{s}}^{+}$	1·82	2·46	1·82	2·62	**X**	2·62	2·46	2·62
$\mathscr{E}_{\text{s}}^{-}$	2·52	2·18	2·52	1·72	**X**	1·72	2·18	1·72
Charge	−0·142	−0·019	−0·142	+0·207	−0·019	**X**	−0·019	+0·207
$\mathscr{E}_{\text{s}}^{+}$	2·06	2·22	2·06	2·86	2·22	**X**	2·22	2·86
$\mathscr{E}_{\text{s}}^{-}$	2·58	2·12	2·58	1·78	2·12	**X**	2·12	1·78

DISCUSSION

The diatomic and triatomic substituents have, in this approximation, no mesomeric effect either on the charge distribution or on the localisation energies, so that their action is purely inductive. In Table 2 of the preceding paper the charge distribution and localisation energies of an azulene molecule which carries a single substituent whose inductive constant is $+1\cdot0$ were reported. We now require the inductive constants of the diatomic and triatomic substituents. An attempt has been made [9] to estimate these from the σ constants of the Hammett $\rho\sigma$ equation, the results suggesting that the inductive

constants of all of the common substituents are in the range -0.1 to $+1.0$. Since a substituent whose inductive constant is at the upper limit of this range has only a minor effect on the charge distribution and localisation energies of azulene, we conclude that these substituents are unlikely to affect the orientation of ionic substitution in azulene.

The monatomic substituents are more complex. They have both inductive and mesomeric effects, usually in opposition. When one quite outweighs the other no difficulty arises, but when they are fairly evenly balanced—as with the halogens—it is not surprising that the crude Hückel method does not satisfactorily predict the small difference between two large quantities. Nevertheless, the figures in the Table show that, unless the method is completely misleading, these substituents also have only minor effects on the charge distribution and localisation energies of azulene. That is, the orientation of ionic substitution in a monosubstituted azulene will be the same as in the parent hydrocarbon and no directive effect analogous to that found in benzene is to be expected.

This conclusion agrees exactly with the known experimental facts. Anderson and his co-workers [10] prepared a number of mono- and di-substituted azulenes from azulene itself, introducing the substituents by substitutions which would be expected to be electrophilic. They state that the presence of one substituent does not affect the position of substitution for the second entering group, in agreement with the present conclusions. This is true for all of the substituents which they studied, regardless of their directive effect in benzene. Specifically, these workers found that 1-nitro-, 1-halogeno-, 1-acetamido-, 1-acetyl- and 1-methoxycarbonyl-azulene all undergo electrophilic substitutions such as nitration, acetylation, halogenation, and Friedel–Crafts benzylation in the 3-position. Furthermore, disubstitution often accompanies monosubstitution, showing that the presence of a substituent in the 1-position does not drastically deactivate the 3-position. Again, they have reported no instance of appreciable quantities of tri- or poly-substitution, showing that the two substituents in the 1- and the 3-position do not have any profound influence on the remaining positions. All this evidence is in line with the theory.

Returning to the predictions, we can say that the main conclusion will apply to all of the $(4\gamma + 2)$ non-alternant hydrocarbons having charge and localisation energy differentials comparable with those in azulene, a condition which is fulfilled by all those discussed in Parts II and III. This conclusion might be invalidated by a substituent whose inductive or mesomeric constant is much greater than the values used in this paper, but from experiment it seems unlikely that this will apply to common substituents.

The rate of substitution will be affected by the substituent, but it seems unlikely that the present crude method will suffice to predict this more subtle phenomenon with any accuracy. It is always possible that the mechanisms which operate in the benzenoid hydrocarbons will not always operate in non-alternant systems. If this is so, we may expect discrepancies between theory and experiment which will be useful in detecting these mechanistic changes.

The possibility that substituents could be used to " stabilise " non-alternant hydrocarbons which have proved difficult to prepare has clearly not been realised, the substituents having only minor effects on the chemical reactivity.