$$R_{RS} = 2a_{or}b_{os}\beta_{rs} - 2\left\{\sum_{m\neq o}^{occ}\sum_{n}^{all} - \sum_{m}^{all}\sum_{n\neq o}^{occ}\right\}\frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} + \sum_{m\neq o}^{all}\frac{a_{mr}^2 b_{os}^2 \beta_{rs}^2}{E_m} + \sum_{n\neq o}^{all}\frac{a_{or}^2 b_{ns}^{r} \beta_{rs}^2}{F_n} \quad (42)$$

where a_{or}, b_{os} are the coefficients of ϕ_r, ψ_s in the NBMO's. Usually the first approximation ($R_{RS} = 2a_{or}b_{os}\beta_{rs}$) will be found sufficient.

Alternant Molecules: "Starring."—Most of the present discussion will be confined to *alternant* mesomeric systems; that is, systems where the conjugated atoms can be divided into two sets such that no two atoms of the same set (*like parity*) are directly linked. The two sets are termed *starred* and *unstarred*, respectively, the designation being arbitrary. The only types of mesomeric system excluded by this restriction are those containing odd-numbered rings. Such non-alternant compounds are difficult to analyze by methods now available, although a certain amount of information about them will be derived in the present investigation. The special properties of *alternant hydrocarbons* (AH) were first pointed out by Coulson and Rushbrooke,[10] and they have been studied further by Coulson and Longuet-Higgins.[8]

Validity of the Approximation.—The kind of accuracy to be expected in quantitative applications of the method may be indicated by an example; the calculation of the resonance energy of butadiene considered as a combination of two molecules of ethylene. If the resonance integrals of the terminal bonds in butadiene are β, and of the central bond $x\beta$, equations (16) or (17) give

$$R = \frac{1}{2}x^2\beta \quad (43)$$

Solutions of the secular equation gives

$$R = 2\beta[(x^2 + 4)^{1/2} - 2] \quad (44)$$

If $x = 1$, the values obtained are 0.5β and 0.472β, respectively; if $x < 1$, to allow for the fact that the 2:3 bond in butadiene is longer than the others, the agreement is even better.

Glossary

Alternant[10]: an alternant mesomeric system is one in which the conjugated atoms can be divided into two sets such that no two atoms of the same set (*like parity*) are directly linked. One set is termed "*starred*," the other "*unstarred*," the designation of the sets being arbitrary.

AH: an alternant hydrocarbon.

Odd, **even**: a mesomeric system is classed as odd or even according as the number of conjugated atoms in it is odd or even. An even AH is a "normal" hydrocarbon, whereas an odd AH is necessarily a radical or ion (*e.g.*, $PhCH_2^{\pm}$, $PhCH_2$).

MO, **AO**: Molecular Orbital, Atomic Orbital.

Starring: see *alternant*. If the numbers of atoms in the two sets are unequal, the more numerous set will be starred.

NBMO: Non-bonding Molecular Orbital.[9] An odd MO in an odd AH or non-Kekulé AH which has zero energy (*i.e.*, energy in this approximation identical with that of a carbon 2p AO).

Active, inactive atom[9]: an inactive atom in an odd AH is one the coefficient of whose AO vanishes in the NBMO.

CF: Canonical Form (≡ resonance structure)

Kekulé compound: a compound with at least one unexcited CF.

Isoconjugate[9]: two mesomeric compounds are termed isoconjugate if they contain similar numbers of conjugated atoms in similar arrangements, and also similar numbers of delocalized electrons (*e.g.*, benzene, pyridine, pyrimidine are isoconjugate).

Cross-conjugation: an odd mesomeric system is cross-conjugated if in the isoconjugate odd AH not all the starred atoms are active.

TS: transition state.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

A Molecular Orbital Theory of Organic Chemistry. II.[1] The Structure of Mesomeric Systems

BY M. J. S. DEWAR[2]

RECEIVED SEPTEMBER 13, 1951

The methods of Part I[1] are used to establish a series of theorems which make it possible to account for the properties of alternant hydrocarbons. In particular conditions are derived for a system to be mesomeric, and for a mesomeric system to be aromatic. The unique position of benzene and azulene as units of aromatic structures is interpreted, and the nature of degeneracy and fractional bond order is discussed. The significance of classical bond structures is considered and an explanation given for the instability of compounds for which no unexcited structures can be written. The treatment follows the lines laid down by Coulson, Longuet-Higgins and Rushbrooke,[3-5] to whom a number of the theorems are due; but most of the results are new since they are derived ultimately from theorem 13 which is novel.

Here the methods previously described[1] will be used to study mesomerism and aromaticity. The results appear as a series of formal theorems; of these the first ten have already been established by Coulson and Rushbrooke,[3] by Coulson and Longuet-Higgins,[4] and by Longuet-Higgins.[5] They are stated without proof to save continual reference to the original papers.

In theorems 11–17 the effect of conjugation between parts R and S on the total energy of an AH RS is studied, and also its relation to the orders of the bonds linking R to S in RS. Here, as throughout this series of papers, single attachment of R to S will usually be assumed since the results can at once be generalized to cases of multiple attachment by using equation (5) of Part I.[1] The most important result of this section is that of theorem 13.

Theorems 18 and 19 relate the resonance energies of AH's differing by one carbon atom. In theorems 21–24 the nature of aromaticity is discussed and reasons given for its limitation to certain types of ring system; and in theorems 25, 26 the related problem of partial bond order is considered and reasons given for the relative constancy of bond lengths in aromatic compounds in contrast to the large difference between "single" and "double" bonds in aliphatic structures.

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[1] For Part I see THIS JOURNAL, **74**, 3341 (1952).

[2] Reilly Lecturer March–April, 1951. Present address: University of London, Queen Mary College, Mile End Road, London E.1, England.

[3] C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940).

[4] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).

[5] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265, 275, 283 (1950).

In the remaining theorems the significance of classical bond structures is discussed and reasons given for the well-known fact that no compound is stable unless at least one such structure can be written for it. A preliminary junction with resonance theory is made at this point.

Theorem 1. $\sum_m a_{mr}^2 = 1$. (This implies that the maximum charge density at any atom in a conjugated system due to the mobile electrons, is two since $q_r = 2 \sum_m^{occ} a_{mr}^2$).

Theorem 2. If the total energy of the mobile electrons is E, then $\partial E/\partial \alpha_r = q_r$, *where* α_r *is the coulomb term of atom* r.

Theorem 3. Likewise $-\partial E/\partial \beta_{rs} = 2p_{rs}$

Theorem 4. The energy levels of an even AH (i.e., an alternant hydrocarbon with an even number of conjugated atoms) occur in pairs, of energy $\pm E_m$.

Theorem 5. The coefficients of the AO's in such a pair of related MO's of an even AH are identical in absolute magnitude, and differ only in that the signs of one set of AO's of similar parity are inverted.

Theorem 6. The energy levels of an odd AH occur in pairs, as do those of an even AH; the odd NBMO left over has zero energy, and the coefficients of the unstarred AO's vanish.

Theorem 7. If the NBMO coefficients of the AO's of atoms r, s, t . . . linked to an unstarred atom p in an odd AH are a_{0r}, a_{0s}, a_{0t} . . ., *then* $\sum_r a_{0r}\beta_{pr} = 0$. This important result[5] enables one to write down the NBMO coefficients for an odd AH at sight, without solving any secular equations. It will usually be assumed that the β's are all equal, when $\sum_r a_{0r} = 0$.

Theorem 8, In a neutral AH, the charge density at each atom is unity.

Theorem 9. The resonance energy in, and bond orders of, an alternant heterocyclic compound are the same, to a first approximation, as those of the equivalent AH.

Theorem 10. $\pi_{r\cdot s} = \pi_{s\cdot r}$ *and* $\pi_{st\cdot r} = \frac{1}{2}\pi_{r\cdot st}$ where $\pi_{r,s}$ is the mutual polarizability of atoms r, s, $\pi_{st,r}$ the bond-atom polarizability between atom r and the bond between atoms s, t and $\pi_{r,st}$ the corresponding atom-bond polarizability.[6]

Theorem 11. The resonance energy of RS relative to R + S, where R and S are even, is given approximately by βp_{rs}. This result follows at once from equations (29) and (41) of Part I.[1]

Theorem 12. If R, S are both odd radicals and if their singly occupied MO's are of like energy then R_{RS} *(the resonance energy of RS relative to (R + S)) is given approximately by* $2\beta p_{rs}$. This result follows likewise from equations (11) and (42) of Part I.[1]

Theorem 13. If R, S are odd AH radicals, then R_{RS} *is given approximately by* $2a_{0r}b_{0s}\beta$. This follows at once from equation (42) of Part I[1]; the extension to the case where R, S are multiply linked is obvious.

Theorem 14. If R, S are not both odd, then R_{RS} *varies approximately as* β^2. This follows at once from equation (41) of Part I.[1]

Theorem 15. If R, S are both odd radicals, and if their singly occupied MO's have like energy, then R_{RS} *varies approximately as* β. This follows likewise from equation (42) of Part I.[2]

Theorem 16. In an even alternant compound with 2n conjugated atoms, of which not more than one is a heteroatom, there are n levels with positive, n with negative energy. Let the compound be RS, derived from an odd AH R and a heteroatom S of coulomb term α. Then the secular equation of RS is given[7] by

$$\prod_m (W - E_m)\left\{W - \alpha - \sum_m \frac{a_{mr}^2\beta^2}{W - E_m}\right\} = 0 \quad (1)$$

The roots of this equation differ from the E_m unless there is degeneracy, or unless a coefficient a_{mr} vanishes; and from theorems (4) and (5), and the discussion of degeneracy in Part I,[1] it follows that the identical roots must factorize out of equation (1) in pairs, with energies $\pm E_n$. Therefore the theorem need be proved only for the roots of the simpler equation of order $2p$

$$f(W) \equiv W - \alpha - \sum_m \frac{a_{mr}^2\beta^2}{W - E_m} = 0 \quad (2)$$

where the identical roots of (1) have been removed. Now $f(W)$ has asymptotes at $W = E_m$, and it is easily shown that

$$\frac{\partial}{\partial W} f(W) > 0 \quad (3)$$

Thus the energy levels of RS interlace with those of R; and since $(2p - 2)$ levels of R occur in pairs of energy $\pm E_m$, and the remaining level has zero energy, p roots of (2) are positive and p negative; this proves the theorem.

It can be shown that the same result will usually hold for systems with more than one heteroatom, unless the ratio of their number to that of carbon atoms is high or their electron affinities great.

Theorem 17. $R_{RS} > 0$. This follows at once from theorem 16 and equations (41) and (42) of Part I,[1] if RS contains not more than one heteroatom, for all the terms in the expressions for R_{RS} are then positive. The extension to cases with several heteroatoms is less definite but it can be made in first approximation by invoking theorem 9.

Theorem 18. The difference in total mobile electron energy between an even AH with n conjugated atoms, and the odd AH with (n + 1) conjugated atoms formed from it by attaching a carbon atom to it at one point, is of order β, *but somewhat less than* β. Let the even AH be R, the atom S. Then the energy difference is given by (*cf.* equation (32) of Part I[1])

$$\begin{aligned} E &= -2\sum_m^{occ} \frac{a_{mr}^2\beta^2}{E_m} - \sum_m^{all} \frac{a_{mr}^2\beta^2}{E_m} \\ &= -2\sum_m^{occ} \frac{a_{mr}^2\beta^2}{E_m} \end{aligned} \quad (4)$$

since RS is an AH (*cf.* theorems 4, 5). The charge density at atom *r* is given by theorem 1

$$q_r = 2\sum_m^{occ} a_{mr}^2 = 1 \quad (5)$$

To a first approximation

$$E \leqq -2\sum_m^{occ} \frac{a_{mr}^2\beta^2}{\bar{E}_m} \leqq -\frac{\beta^2}{\bar{E}_m} \quad (6)$$

where $\bar{E}_m$ is the mean value of E_m. Now if the resonance energy of R were zero, $\bar{E}_m$ would equal $-\beta$. The actual resonance energy is positive (theorem 17), but small compared with the total π-electron energy since it represents only a small perturbation of the total π-electron energy. Hence E_m is slightly less than $-\beta$, and so ΔE is slightly less than β, but of the same order of magnitude.

Theorem 19. Likewise addition of one carbon to an odd AH, giving an even AH with one more conjugated atom, lowers the total π*-electron energy by somewhat more than* β. Let the odd AH be RS, derived from an even AH R and an atom S. Let addition of a further atom T give the even AH RST. From theorem 17, the resonance energy of RST relative to (R + ST) *i.e.*, (R + ethylene), is positive. The difference in π-electron energy between R and RST is therefore greater than 2β (though only slightly greater, since the difference is a second-order perturbation). But from theorem 18, the difference in π-electron energy between R and RS is somewhat less than β. Hence the difference in π-electron energy between RS and RST is somewhat greater than β.

Theorem 20. The difference in total π*-electron energy between an odd AH R and an even AH RS formed by adding one atom S, is given by* $2\beta\sum a_{0r}$ *where S is attached to R at atoms r.* This follows from Theorem 13. It is an important result since the NBMO coefficients of an odd AH can be calculated so simply (theorem 7), and since energy differences of this type govern the rates of many reactions.

---

(6) These coefficients are defined[4] by

$$\pi_{rs} = \partial q_r/\partial \alpha_s;\ \pi_{st,r} = \partial p_{st}/\partial \alpha_r;\ \pi_{r,st} = \partial q_r/\partial \beta_{st}$$

They indicate the variation in properties of the molecule with the resonance integrals of bonds and coulomb terms of atoms in it.

(7) M. J. S. Dewar, *Proc. Camb. Phil. Soc.*, **45**, 639 (1949).

Theorem 21. Even alternant compounds containing six-membered mesomeric rings are more stable than corresponding open-chain compounds by approximately β per ring. Consider the corresponding AH RS, derived from an odd AH radical R and an atom S, where S forms part of the ring. From theorem 20

$$R_{\mathrm{RS}} = 2\beta(a_{\mathrm{or}} + a_{\mathrm{ot}}) \qquad (7)$$

where atom S is attached to atoms r, t. Now two open-chain compounds (RS)′, (RS)″ can be derived by attaching atom S to atom r only, or to atom t only; the corresponding resonance energies are

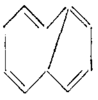
$$R'_{\mathrm{RS}} = 2\beta(a_{\mathrm{or}}) \qquad (8)$$

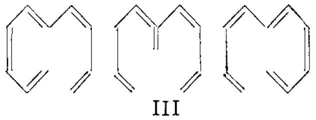
$$R''_{\mathrm{RS}} = 2\beta(a_{\mathrm{ot}}) \qquad (9)$$

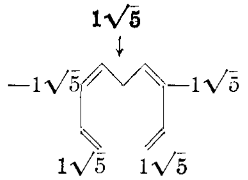
and from theorem 19, both R'_{RS} and R''_{RS} are of order β. Hence from equations (7–9), R_{RS} is greater than R'_{RS} or R''_{RS} by approximately β, which proves the theorem for the monocyclic case. The argument can be extended in a similar manner to polycyclic compounds. For an illustrative example see Theorem 23.

Theorem 22. A non-alternant even AH with one odd-numbered ring has approximately the same resonance energy as an AH derived from it by opening the ring. The proof follows the same lines as that of theorem 21; but here atom S (in the odd-numbered ring) is attached to atoms (r, t) of opposite parity. Hence either a_{or} or a_{ot} vanishes. Also RS can be converted to a classical AH by breaking the bond between S and that atom r or t whose coefficient vanishes in the zero MO of R. From equations (7–9), it follows that such a change leaves the energy unchanged in first approximation.

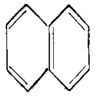
Theorem 23. Azulenes should be semi-aromatic, having resonance energies intermediate between corresponding decapentaene and naphthalene derivatives. Consider azulene (I) itself. Azulene can be derived from a carbon atom and a nonatetraenyl radical (II); as also can the three analogous decapentaenes (III), and naphthalene (IV). The NBMO coefficients of (II) can be calculated by using theorem 7 and are given in (II)


I


III



II


IV

The approximate differences in π-electron energy between (I), (III) and (IV) can be calculated from theorem 20

$$\mathrm{III} = 2\beta\sqrt{5}$$

$$\mathrm{I} = 4\beta\sqrt{5}$$

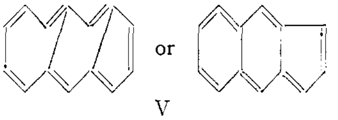
$$\mathrm{IV} = 6\beta\sqrt{5} \qquad (10)$$

Hence azulene is approximately half-way between naphthalene and decapentaene in stability. The proof can be extended to any azulene derivative, containing no other odd rings, since in each case removal of one azulene bridge carbon leaves an AH radical, and in reconstructing azulene from it, only two of the NBMO coefficients at the points of attachment are non-vanishing, whereas all three are non-vanishing in the isomeric naphthalene.

Theorem 24. Azulene and benzene are the fundamental units of even aromatic systems. Consider first a cyclic AH RS with $2n$ atoms in the ring. Removal of one atom S from the ring leaves an open-chain AH radical R, in which the NBMO coefficients are alternately $\pm n^{1/2}$ (theorem 7). The energy of the cyclic AH is then given relative to R by

$$R_{\mathrm{RS}} = 2\beta(n^{1/2} + (-1)^n n^{1/2}) \qquad (11)$$

If n is even, R_{RS} vanishes; if n is odd, R_{RS} is approximately double the value R'_{RS}, of an analogous open chain polyene. Thus aromatic character is confined to compounds with 6-, 10-, 14- . . . numbered rings; and since the resonance energy can be large only if the rings are approximately planar and symmetrical, steric factors tend to limit aromatic properties to six-rings. The same argument can be applied in the bicyclic non-alternant series to show that azulene occupies a unique position. (It corresponds actually to the case of a simple 10-ring, the *trans*-annular bond not contributing to the stability, but assisting with the stereochemical difficulties. Similar behavior may be anticipated in higher members of the series, *e.g.* (V), but the tendency to isomerize to 6-ring derivatives should become progressively greater, and the effective stability progressively less. Thus isomerization of (V) to anthracene should be about twice as exothermic as isomerization of azulene to naphthalene).



V

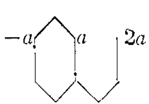
Theorem 25. The bond-orders in an open-chain polyene alternate, the structure corresponding qualitatively to the classical representation. Let the polyene be RST, where S is a carbon atom linked to polyene fragments R, T. Let R be singly linked to S in the classical representation of RST; then R is an even AH. Likewise if T is doubly linked to S in the classical representation, T is an odd AH. To a first approximation (first-order perturbation theory)

$$p_{\mathrm{rs}} = 0$$

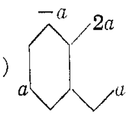
$$p_{\mathrm{rt}} = a_{\mathrm{ot}} \qquad (12)$$

where a_{ot} is the coefficient of the NBMO of T at the point of attachment of R. The second-order perturbation terms should be less than these first order ones; therefore the classical "double" bond ST has a higher order than the "single" bond RS. The argument can be applied successively to each atom in the polyene, thus proving that the "double" bonds have uniformly higher orders than the "single" ones.

Theorem 26. Bond orders in aromatic compounds alternate less than those in polyenes. This can be proved by the same argument used in proving theorem 25; here there is a first-order perturbation contribution to each bond. The relative bond orders can be found approximately by the NBMO method outlined above. The radicals (VI) and (VII) have the indicated NBMO coefficients; hence the 1:2 bond in naphthalene has approximately twice the order of the 1:9 or 2:3 bonds.



$(a = 11^{-1/2})$
VI



$(a = 8^{-1/2})$
VII

The values of bond orders so calculated are only very approximate since the second-order perturbation contributions are appreciable; particularly in large molecules.

Kekulé Forms.—It has long been known that as a rule compounds are stable only if classical structures can be written for them in which all the bonds are real (*i.e.*, join atoms which are at approximately their normal bond-length apart). Thus *o*- and *p*-benzoquinone are well known, but the *m*-isomer has never been prepared. The special importance of such Kekulé forms, as they may be termed, may now be investigated, since the MO theory does not directly ascribe importance to classical bond structures. Compounds for which one or more Kekulé forms may be written will be called Kekulé compounds, those with no Kekulé forms, non-Kekulé compounds. In each lowest-excited canonical form (CF) for a non-Kekulé compound, two or more atoms will be linked by virtual bonds. Such atoms will be called *active* (*cf.* Longuet-Higgins[5]). Consider one CF of an alternant non-Kekulé compound, and consider a starred[3] active atom in it. Other similar CF's can then be obtained by allylic shifts of the active atom; *e.g.*

$$>\overset{*}{C}_A-\overset{|}{C}=C_B< \longleftrightarrow >C_A=\overset{|}{C}-\overset{*}{C}_B<$$

The path over which the activity of the starred atom can be transferred may be termed a *starred segment* of the molecule; likewise an unstarred active atom will define an *unstarred segment*.

Theorem 27. A non-Kekulé AH with m active atoms has m MO's of zero energy. This theorem is due to Longuet-Higgins[5]; the proof given here provides a clearer insight into the phenomenon. Consider first the case where the active atoms $A_1, A_2 \ldots A_m$ are all starred. Consider the residue R left when the active atoms are removed from the system; R is then by definition an even Kekulé AH. Consider the odd AH radical RA_1; this will have a NBMO covering only starred atoms (A_1 being starred). Now regenerate the original AH by adding the atoms ($A_2 \ldots A_m$). Since these are attached to unstarred atoms in RA_1, where the coefficients of the NBMO in RA_1 vanish, they do not affect that MO (*cf.* Part I[1]). Likewise the NBMO's of RA_2, RA_3, RA_m survive intact in the parent AH, which therefore contains *m* independent NBMO's.

Now consider the case where there are both starred and unstarred active atoms present. It is evident that no starred segment of the AH can contain an unstarred active atom; otherwise a starred active atom could be brought next to it by allylic shifts, and an extra real bond then formed—in contradiction to hypothesis. It is also evident that a starred segment can be attached to the rest of the molecule only through unstarred atoms; otherwise the active atoms could be transferred outside the active segment by allylic shifts. Let the starred segment contain *r* active atoms and consider the starred segment in isolation. It will contain *r* NBMO's with density vanishing at unstarred atoms. Since the rest of the molecule is attached to it only at unstarred atoms, these NBMO's must survive intact in the whole molecule. The same argument applies to each of the other segments, starred or unstarred, so that the whole molecule, with *m* active atoms, must have *m* NBMO's.

Theorem 28. A non-Kekulé AH is a polyradical. This, as Longuet-Higgins[5] has pointed out, is an immediate corollary of theorem 27 and Hund's rule.

Theorem 29. A non-Kekulé AH is less stable than a Kekulé isomer. Consider a non-Kekulé AH RA, A being an active (starred) atom. Since the NBMO's of R have zero density at the point of attachment of A, R and RA have similar π-electron energies in the approximation of first-order perturbation theory (theorem 13). Consider an isomer R′A, where A is attached at an active atom in R; if the coefficients of the NBMOs of R at this atom are a_{01}, a_{01} . . . a_{0r}, then the π-electron energy difference A between RA and R′A, will be given by (theorem 13)

$$\Delta R = -2\beta \sum_r a_{0r} \qquad (13)$$

to a first approximation. Also R′A evidently contains two active atoms less than does RA. Continuing this argument, the most stable isomers of RA will be those with the fewest active atoms—*i.e.*, the Kekulé isomers.

Theorem 30. If an AH has n starred atoms and m unstarred atoms ($n > m$), at least ($n - m$) atoms are active. This is an evident corollary from the method of proof of theorem 27.

Theorem 31. Theorem 29 holds also for heteroatomic alternant systems. This follows from theorem 9. Theorems 27 and 28 do not hold for heteroatomic systems, so this result alone accounts for the instability of non-Kekulé heteroatomic compounds.

Theorem 32. At least two unexcited CF's can be written for an aromatic AH. This follows from the method of proof used in theorem 21; the two unexcited CF's correspond to the open-chain compounds (RS)′ and (RS)″.

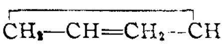
Theorem 33. Symmetrical monocyclic AH's with 4n conjugated atoms are biradicals. This follows from the method of proof of theorem 24; if the AH RS, with 4*n* atoms is dissected into an odd AH R and one atom S, the NBMO of R survives in RS. Since NBMO's in an even AH can occur only in pairs (theorem 4), RS contains at least two NBMO's and is therefore a biradical. This theorem is not of much importance since cyclobutadiene does not seem to exist as a stable entity, and since the higher members of the series are prevented by stereochemical factors from adopting symmetrical coplanar structures.

Discussion

This set of theorems provides a satisfactory basis for the discussion of mesomerism, and one free from certain difficulties and inconsistencies of the current VB approach.

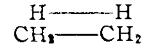
From theorem 9, due to Coulson and Longuet-Higgins,[4] the structure and resonance energy of a heteroatomic systems is similar in first approximation to that of an analogous hydrocarbon. From theorem 17, it follows that a set of *n* atoms form a conjugated system if AO's on those atoms mutually overlap; and from theorem 16, the system will be most stable if the *n* AO's contain *n* electrons, or if *n* is odd and they contain ($n \pm 1$) electrons. From theorems 14 and 15, the resonance energy will be greater, the greater the resonance integrals between the AO's; this accounts at once for the fact that conjugation is important only if the AO's are *p* or *d*AO's, and if the AO's overlap well (so that in the usual systems with *p* AO's, the component atoms should be approximately coplanar).

These rules for mesomerism are more precise than those given by resonance theory.[8] Thus they account at once for the difference between butadiene and ethane; whereas in resonance theory, excited CF's such as (VIII) must be invoked to explain the mesomerism of butadiene, and yet analogous excited CF's such as (IX) can be also written for the non-mesomeric ethane.



$$CH_2-CH=CH_2 \cdots CH_2$$

VIII



$$\overset{H \text{———} H}{CH_2\text{———}CH_2}$$

IX

(Indeed, more such singly excited CF's can be written for *n*-butane than for butadiene, although the resonance energy of the latter is much the greater.)

The neutrality and zero dipole moments of AH's are explained at once[4] by theorem 8; the theorem does not apply to non-alternant hydrocarbons such as fulvene or azulene, and these are now known to have appreciable dipole moments. It does not seem possible to account for this difference in any convincing way on the basis of resonance theory, but the moments have been interpreted theoretically[9] by use of the MO method.

It has been commonly suggested that the MO method does not adequately account for the success of classical valency structures in representing the properties of simple molecules. This contention is met by the results of theorems 27–31, which indicate the importance of such structures, and indicate that compounds with no unexcited CF's should be relatively unstable (*e.g.*, *m*-quinones).

Theorems 21–24 account for the special and specific stabilities shown by aromatic and pseudoaromatic structures, and for the lesser stability of the latter (*e.g.*, azulene) compared with the former. Also the fact that open-chain polyenes can be represented approximately by single valence bond

(8) *Cf.* G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

(9) *Cf.* G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

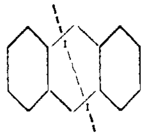
structures, whereas aromatic and pseudoaromatic compounds cannot, is explained by theorems 25 and 26.

The large stabilities of odd AH radicals is interpreted well by theorems 18 and 19; there is no great difference in the average π-electron energy per conjugated atom between odd and even AH's.

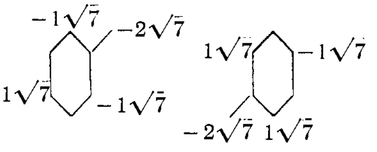
The analysis also provides some useful semi-quantitative methods for estimating the energy differences between odd AH's and even AH's derived from them by addition or subtraction of carbon atoms, and between AH's and fragments obtained by their dissection (theorems 7, 11, 12, 13, 20). These methods will later prove of fundamental importance in the interpretation of chemical reactivity and light absorption. The resonance theory provides no analogous techniques. Admittedly attempts have often been made to correlate the stability of molecules with the numbers of unexcited CF's that can be written for them, but this procedure has no basis in VB theory; and A. and B. Pullman[10] have shown that the assumption that unexcited CF's always make the major contribution to the ground state of a molecule is itself quite incorrect. (The problem will be discussed in detail elsewhere.)

The present treatment does show, however, that at least $(r + 1)$ unexcited CF's can be written for any aromatic compound with r six-rings (theorem 32); but it does not follow that an AH for which two or more unexcited CF's can be written will show aromatic properties (*cf.* the $4n$-membered cyclic polyenes which should show little extra stability over open-chain analogs). However, the arguments used to prove theorems 25 and 26 do imply that alternation of bond orders should be small in compounds for which two or more unexcited CF's can be written; and that such a compound should not be represented accurately by a unique classical bond structure. The present picture of mesomeric molecules thus fits in well with the current resonance interpretation, but it is more complete as well as being better based in theory.

The resonance energies of aromatic compounds can be calculated approximately by using theorem 13, if π-electron energies of radicals obtained by its fragmentation are known. Thus anthracene (X) can be derived from the union of two benzyl radicals (XI); the NBMO coefficients of the latter are indicated in (XI)



X



XI

The π-electron energy of benzyl is easily calculated to be 8.72β. The π-electron energy ϵ of (X) should then be given by

$$\epsilon = 2 \times 8.72\beta + 2\beta\left(\frac{2}{7} + \frac{2}{7}\right) = 18.58\beta \qquad (14)$$

Subtracting the energy of one unexcited CF (14β), the calculated resonance energy R is 4.58β, in fair agreement with the accurate MO value (5.31β[11]). The values calculated by this method should be too low, since the higher order perturbation energies are neglected; but there is an excellent linear correlation between the approximate and exact values (Fig. 1).

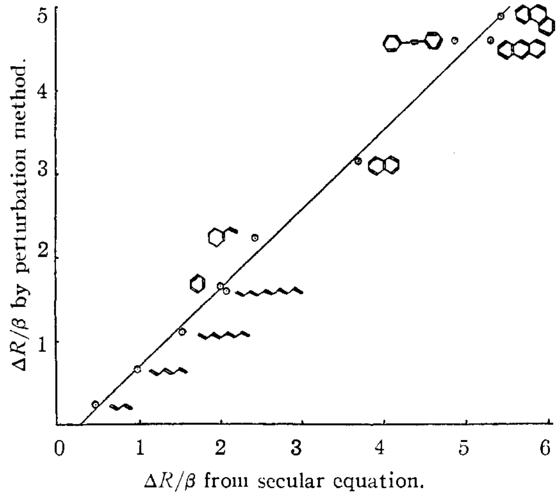
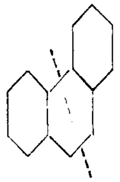


Fig 1.

Although more exact empirical methods are available for estimating such resonance energies without great computational labor,[12] the present treatment may be useful for rough calculations. For instance it explains in a simple way why the linear polyacenes are less stable than the isomeric polyphenes; thus in the formation of phenanthrene (**XII**) from (XI), the first-order perturbation energy is greater by $\beta/7$ than in the formation of (X) from (XI); and it can be shown that a similar relation holds generally between isomeric acenes and phenes.



XII

One further point may be emphasized. It has commonly been asserted on the basis of resonance theory that mesomerism requires almost perfect coplanarity of the conjugated system. This is quite incorrect; theorems 14 and 15 show that the resonance energy of RS relative to (R + S), although greatest when the system is coplanar, varies only as $\cos\theta$ or $\cos^2\theta$ where θ is the angle through which S is twisted out of coplanarity with R; since the resonance integral β_{RS} is given approximately by

$$\beta^{\theta}_{RS} \cong \beta^{0}_{RS}\cos\theta \qquad (14)$$

where β^{θ}_{RS} is the value of β_{RS} for an angle of twist θ. This factor becomes important in the triarylmethyl radicals which are very far from coplanar; current calculations of their resonance energies are undoubtedly incorrect (they assume coplanarity of the molecule, which is impossible for steric reasons),

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[10] A. Pullman and B. Pullman, *Experientia*, **2A**, 364 (1946); *cf.* A. Pullman, Thesis, Paris, 1946.

[11] G. W. Wheland, THIS JOURNAL, **63**, 2025 (1941).

[12] R. D. Brown, *Trans. Faraday Soc.*, **46**, 1013 (1950).

but so too is the argument that the resonance energies of such non-coplanar compounds must be small and their stabilities due solely to steric factors. This point will be discussed in more detail elsewhere.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

A Molecular Orbital Theory of Organic Chemistry. III.[1,2] Charge Displacements and Electromeric Substituents

BY M. J. S. DEWAR[3]

RECEIVED SEPTEMBER 13, 1951

The methods of the preceding papers[1,2] are used to analyze the displacements of charge in an AH when one or more carbon atoms are replaced by heteroatoms, or when electromeric substituents are introduced. The effects of heteroatoms had been considered previously by Coulson and Longuet-Higgins,[4,5] but here they will be studied by an alternative and more accurate method. Conditions are found for two electromeric substituents to conjugate with one another through an intermediate mesomeric system. The results of this treatment agree qualitatively with those of current theory, but the possibility now appears of estimating various effects semi-quantitatively within the limitations[1] of the present methods.

The next step in the program is to analyze the nature, causes and effects of charge displacements in conjugated systems due to the presence of heteroatoms and electromeric substituents. Considerable progress has been made already in the analysis of changes in an AH caused by replacing one or more carbon atoms by heteroatoms, by Coulson and Longuet-Higgins[4] and by Longuet-Higgins.[5] In particular they were able to derive the classical "law of alternating polarity" for such systems. Here the same general problem is considered to a higher approximation by using the new relations given in Parts I[1] and II.[2] It will also prove possible to discuss the effects of electromeric substituents which lay outside the scope of the previous treatment. These two topics are discussed in theorems 34–39 and 40–45, respectively. Theorem 37 is due to Longuet-Higgins.[5]

In theorems 46–49 the ability of two groups to conjugate with each other ("mutual conjugation") through an intermediate mesomeric system is considered, and as a result rules (theorems 50–53) are found for describing the relative activities of electromeric substituents semi-quantitatively (this problem will be discussed further in Part VI).

Qualitatively, the present treatment will be found to give conclusions similar to those reached by current theory.

Theorem 34. The main effect of an increase in electron affinity of an unstarred atom in an even AH is to decrease the charge densities at all starred atoms. Let the AH be RS, derived from an odd AH R and an atom S of coulomb term α. If $|\alpha|$ is small, there will be a zeroth order perturbation of the AO ψ of S and the NBMO Φ_o of R. This effect will be larger than any due to higher perturbations; and so a first approximation to the change in charge density with α may be found from 2 consideration of the corresponding change in the pair of MO's arising from ψ and Φ_o.

The secular equation for the perturbed energies is

$$\begin{vmatrix} w & a_{or}\beta \\ a_{or}\beta & w - \alpha \end{vmatrix} = w^2 - \alpha w - a_{or}^2\beta^2 = 0 \qquad (1)$$

with the solutions

$$W = \frac{1}{2}(\alpha \pm (\alpha^2 + 4a_{or}^2\beta^2)^{1/2}) \qquad (2)$$

Of these the lower level alone will be occupied in RS. The coefficients b_s of ψ, b_o of Φ_o, in this MO are given by

$$b_o = \frac{2a_{or}\beta}{[2\alpha^2 + 8a_{or}^2\beta^2 + 2\alpha(\alpha^2 + 4a_{or}^2\beta^2)^{1/2}]^{1/2}}$$

$$b_s = \frac{(\alpha^2 + 4a_{or}^2\beta^2)^{1/2} - \alpha}{[2\alpha^2 + 8a_{or}^2\beta^2 - 2\alpha(\alpha^2 + 4a_{or}^2\beta^2)^{1/2}]^{1/2}} \qquad (3)$$

The NBMO Φ_o covers only starred atoms in R, *i.e.*, atoms in RS of opposite parity to S. Hence the perturbation leaves the charge densities of unstarred atoms in RS unchanged to a first approximation.

If atom t is a starred atom in RS, the coefficient of ϕ_t in the NBMO being a_{ot}, then the coefficient of ϕ_t in the perturbed MO is given approximately by

$$a_{ot}b_o = \frac{2a_{or}^2a_{ot}\beta}{[2\alpha^2 + 8a_{or}^2\beta^2 - 2\alpha(\alpha^2 + 4a_{or}^2\beta^2)^{1/2}]^{1/2}} \qquad (4)$$

The corresponding charge density at t due to occupation of this MO by two electrons in RS, is then

$$q_{ot} = \frac{8a_{or}^2a_{ot}^2\beta^2}{2\alpha^2 + 8a_{or}^2\beta^2 - 2\alpha(\alpha^2 + 4a_{or}^2\beta^2)^{1/2}}$$
$$\simeq a_{ot}^2\left\{1 + \frac{\alpha}{2a_{or}\beta}\right\} \qquad (5)$$

if α is small. Hence q_{ot} decreases as α decreases, which proves the theorem, since a decrease in α implies an increase in the electron affinity of S.

Theorem 35. If in the even AH RS, atom S is attached to atom r in R, the mutual polarizability of atoms S, t is given approximately by $a_{ot}^2/2a_{or}$. This result follows at once from equation (5) and the definition[4] of mutual polarizability

$$\pi_{s,t} = \pi_{t,s} = \partial q_t/\partial\alpha_s \simeq a_{ot}^2/2a_{or}\beta \qquad (6)$$

Theorem 36. Increasing the electron affinity of a starred atom in an odd AH lowers the charge densities at all other positions by comparable amounts. Let the odd AH be RS, derived from an even AH R and the atom S of coulomb term α (α small). From equations (38) and (40) of Part I[1], the charge density at atom t is given by

$$q_t = \sum_m^{\text{occ}} 2a_{mt}^2\left(1 - \frac{a_{mr}^2\beta^2}{(E_m - \alpha)^2}\right) + n_s\sum_m^{\text{all}}\frac{a_{mr}^2a_{mt}^2\beta^2}{(E_m - \alpha)^2} \qquad (7)$$

where n_s is the number of electrons in the NBMO of RS. Now since R is an AH, the levels E_m occur in pairs, $\pm E_m$, with the same values for the squared coefficients a_{mr}^2, a_{mt}^2. Hence if α is small, the last term in (7) will be approximately constant. Therefore

$$q_t - \text{constant} \simeq -\sum^{\text{occ}}\frac{2a_{mt}^2a_{mr}^2\beta^2}{(E_m - \alpha)^2} \qquad (8)$$

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(1) For Part I see THIS JOURNAL, **74**, 3341 (1952).

(2) For Part II see *ibid.*, **74**, 3345 (1952).

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(4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447, 456 (1948), **A195**, 188 (1948).

(5) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265, 275, 283 (1950).