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

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

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

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

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

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

$$\simeq a_{ot}^2\left\{1 + \frac{\alpha}{2a_{or}\beta}\right\} \qquad (5)$$

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

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

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

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

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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).

and since $E_m < 0$ for occupied MO's, q_t decreases with decreasing α, *i.e.*, with increasing electron affinity of S. This proves the theorem.

Definitions of Substituents. An *electromeric substituent* is a substituent which can conjugate with a suitable adjacent mesomeric system. A *simple nucleophilic electromeric* ($-E$) *substituent* consists of an atom with a pair of unshared *p* (or potentially *p*) electrons; *e.g.*, HO-, O^--, R_2N-, Cl-. A *simple electrophilic electromeric* ($+E$) *substituent* contains the grouping —X=Y, or —X≡Y, where Y is a heteroatom and X may be carbon or another heteroatom; *e.g.*, —CR=O, —C≡N, $-\overset{+}{N}\equiv N$. Hydrocarbon radicals (*e.g.*, vinyl, phenyl) are classed as $\pm E$ substituents.

Theorem 37. In an odd AH anion or cation the charge is confined to starred atoms, being given approximately by a_{0r}^2. This important result, due to Longuet-Higgins,[5] follows from theorems 6 and 8 of Part II.[2]

Theorem 38. A $-E$ substituent at an unstarred position in an even AH raises the charge density at all starred positions and lowers that at all unstarred positions, the former effect predominating. If the AH is R and the substituent S, RS is equivalent to an odd AH anion RS′, in which the charge is confined to starred positions (theorem 37). Replacing S′ by S lowers the charge density at all positions in R (theorem 36). The latter effect is, however, only a small perturbation effect and therefore less than the former. Thus the substituent produces large negative charges at the starred positions in R, and smaller positive charges at the unstarred positions.

(This "law of alternating polarity" was first derived in a more qualitative form by Coulson and Longuet-Higgins.[4])

Theorem 39. A $+E$ substituent at an unstarred position in an even AH lowers the charge density at all positions, the effect being greater at starred positions. If the AH is R, the substituent S, then RS is derived from an even AH RS′ by replacing an unstarred carbon by a heteroatom. Theorem 34 states that the main effect will be a decrease in charge density at the starred atoms in RS′. However the inductive effect of the heteroatom will induce a positive charge on the adjacent starred carbon atom and so raise its electron affinity; this brings about a second order decrease in charge density at the unstarred atoms in RS.

Theorem 40. A $+E$ substituent at an active position stabilizes an odd AH anion more efficiently, and an odd AH cation less efficiently, than it stabilizes a neutral AH radical. Let the AH be R, the substituent S, and the analogous $\pm E$ substituent be S′. Then RS′ is an odd AH, and the heteroatom of S occupies a starred position in it. Let the coefficient of the NBMO of RS there be a_{0s}.

Then the resonance energies of $(RS')^+$, (RS') and $(RS')^-$ are identical since the three compounds differ only in the number of electrons that occupy the NBMO. From theorem 2,[2] the resonance energies of the cation $(RS)^+$, (R^+), of the radical (RS), $(R^\cdot)$, and the anion $(RS)^-$, (R^-), are related by

$$R^+ = R^\cdot + a_{0s}^2\alpha$$
$$R^- = R^\cdot - a_{0s}^2\alpha \qquad (9)$$

Since $\alpha < 0$, the anion is stabilized more, and the cation less, than is the neutral radical.

Theorem 41. A $-E$ substituent at an active position stabilizes an odd AH cation R^+ much more efficiently, and an odd AH anion R^- much less efficiently than it stabilizes the neutral odd AH radical R. Let the odd AH be R and the substituent, of Coulomb term α, be S. Then the resonance energy of RS (relative to R + S) is given[1] by

$$R_{RS} = -2\sum_{m\neq o}^{\text{unocc}} \frac{a_{mr}^2\beta^2}{\alpha - E_m} - \frac{(2-n)a_{0r}^2\beta^2}{\alpha} \qquad (10)$$

where n is the number of electrons in the NBMO of R ($n = 0$ for R^+, $n = 1$ for R, $n = 2$ for R^-). The first sum in (10) is a second-order perturbation energy which will be close to that for the resonance energy of R′S, where R′ is an AH similar to R but even. The quantity $a_{0r}^2\beta^2/\alpha$ in the last term of (10) will be large. Hence if R is an anion (R^-), the resonance energy of RS will be close to that for RS′. But if R is a radical, the stabilization by the substituent will be much larger, and if R is a cation, larger still.

Theorem 42. A $+E$ substituent in an even AH, or at an inactive position in an odd AH, has about the same stabilizing effect as an analogous $\pm E$ substituent. This follows at once from equations (9) since the charge densities at all positions in an even AH, or at inactive positions in an odd AH (ion or radical), are unity.

Theorem 43. If RS is an even AH, formed by combination of an odd AH R with an atom S, then the resonance energies of RS relative to (R + S) is the same (R_0) no matter whether R is an ion or radical. If, however, an active atom t in R is replaced by a heteroatom of coulomb term α, the relative resonance energies for the cases where R is an anion (R^-), a radical($R^\cdot$) or a cation (R^+) are given approximately by

$$R^\cdot = R_0$$
$$R^- = R_0 + a_{0t}^2\alpha$$
$$R^+ = R_0 - a_{0t}^2\alpha \qquad (11)$$

This result follows from theorems 2 and 9 of Part II, since the charge densities at atom t in the ions are $(1 \pm a_{0t}^2)$.

Theorem 44. The effect in theorem 43 of replacing carbon t by a heteroatom is similar to the effect of attaching a $+E$ atom substituent to atom t. This follows from equations (9) and (11), since from theorem 7 of Part II,[2] the squared coefficients a_{0s}^2 in (9) and a_{0t}^2 in (11) are similar.

Theorem 45. The specific stabilizing effect of a $-E$ substituent on an odd AH ion or radical is greater, the less the charge density at the point of attachment. This result follows at once from theorem 41 and equation (10). The relative effects of a $-E$ substituent on the stabilities of various odd AH ions can be calculated semi-quantitatively from equation (10); thus the stabilizing effect on an odd AH cation is proportional to a_{0r}^2, to a first approximation.

Theorem 46. To a first approximation, the resonance energy R_{RST} of RST relative to (R + S + T) is the sum of the resonance energies of RS relative to (R + S)(R_{RS}), and of ST relative to (S + T) (R_{ST}), if R, S, T are neutral AH's and at least two are even. Let R be attached to S through atom r in R to atom s in S; and S to T through atom u in S to atom v in T; and let the energy levels of R, S, T be E_m, F_n, G_p, respectively. Then from equation (41) of Part I,[1]

$$\begin{aligned} R_{RST} &= -2\left\{\sum_m^{\text{occ}}\sum_n^{\text{unocc}} - \sum_m^{\text{unocc}}\sum_n^{\text{occ}}\right\}\frac{a_{mr}^2 b_{ns}^2\beta^2}{E_m - F_n} \\ &\quad -2\left\{\sum_n^{\text{occ}}\sum_p^{\text{unocc}} - \sum_n^{\text{unocc}}\sum_p^{\text{occ}}\right\}\frac{b_{nu}^2 c_{pv}^2\beta^2}{F_n - G_p} \\ &= R_{RS} + R_{ST} \end{aligned} \qquad (12)$$

It is easily seen that this result is unaffected by degeneracy unless two of the groups R, S, T are odd.

Definitions.—Two groups R, T are said to *conjugate mutually* through a mesomeric system S if in the notation of theorem 46, $R_{RST} > R_{RS} + R_{ST}$.

An odd alternant system is said to be *cross conjugated* if the active segment in it does not cover all the conjugated atoms.

Theorem 47. Two $+E$ substituents cannot conjugate mutually, nor can two $-E$ substituents. The first part of the theorem can be proved in exactly the same way as theorem 46. The second part follows from the proof of theorem 44, which implies that if the $-E$ substituents are R, T and the intermediate AH S, then the resonance energies of RS relative to (R + S), and of RST relative to (R + ST) are similar.

Theorem 48. If R is an even alternant system and S a $-E$ group, the charge density at S in RS is less, the greater the R–S bond order and the greater the resonance energy of RS relative to (R + S). This result follows at once as a first approximation from the expressions for bond order, charge density and resonance energy (equations 33, 39, 40, 41 of Part I[1]). An example is provided by aromatic amines where the charge density at the amino group should be less, the more strongly it is conjugated with the ring.

Theorem 49. A $+E$ substituent R can conjugate mutually with a $-E$ substituent T if they are attached to atoms of unlike parity in an even AH S: provided that if the equivalent AH R′ST is cross-conjugated, R′ is attached to the starred segment of ST. This result follows at once from theorems 43 and 44; the charge displacements in S brought about by conjugation with T lead to a first-order difference in conjugation energy between RST and RS

$$R_{RST} \simeq R_{RS} - a_{0s}^2\alpha \qquad (13)$$

where a_{0s} is the coefficient of the NBMO of the odd AH

ST at the point, S, of attachment of the $+E$ substituent R. If, however, RST is cross-conjugated so that a_{0s} vanishes, so too does the *mutual conjugation energy*, M, which can be defined by

$$M = R_{\mathrm{RST}} - R_{\mathrm{RS}} - R_{\mathrm{ST}} \tag{14}$$

Definitions.—The *$+E$ activity* of a $+E$ substituent R is defined to be a measure of the difference in stability between RS^- and $R'S^-$, where S^- is an odd AH anion, R being attached at an active atom, and R′ is the $\pm E$ (hydrocarbon) group equivalent to R. Likewise the *$-E$ activity* of a group T is defined to be a measure of the difference in resonance energy between R^+T, R^+ being an odd AH cation, and R′T, R′ being the corresponding neutral radical.

Theorem 50. The $+E$-activity of a simple $+E$ group is greater, the greater the electron affinity of the heteroatom in it; and the $-E$-activity of a simple $-E$ group is less, the greater the electron affinity of its heteroatom. The first part of the theorem follows from theorem 44 and equation (11). The second part follows from equation (10), since $E_m > 0$ for unoccupied MO's.

Theorem 51. The charge displacements in an even AH S due to a $+E$ substituent R, are greater, the greater the $+E$ activity of the substituent. This follows at once from theorem 39 and equation (5); the greater $|\alpha|$, the greater the charge displacements.

Theorem 52. If S is an even AH, and T a $-E$ substituent, the charge densities at the atoms of S in ST are less, the less the $-E$ activity of T. This follows at once from theorems 36 and 50.

Theorem 53. The mutual conjugation energy of RST is greater, the greater the $+E$ activity of R or the $-E$ activity of T. From theorem 52, the charge density in ST at the point of attachment of R is greater, the greater the $-E$ activity of T; and the method of proof of theorem 49 shows that the mutual conjugation energy is proportional to this charge density, and also to the $+E$ activity of R.

Definitions.—The results on mutual conjugation energies suggest an extended definition of electromeric substituents; *a $+E$ substituent is any group which can conjugate mutually with a simple $-E$ substituent, and a $-E$ substituent one which can conjugate mutually with a simple $+E$ substituent.* From theorem 49, it follows that a $+E$ substituent is a $\pm E$ substituent in which one or more atoms of opposite parity to that by which the substituent is attached to the rest of the molecule have been replaced by heteroatoms; while a $-E$ substituent is a substituent iso-π-electronic with an odd AH anion and attached through an active atom.

A *neutralized system* is defined as one in which a $+E$ and a $-E$ substituent conjugate mutually; or, more generally, a system iso-π-electronic with an odd AH anion in which there are two or more starred heteroatoms.

From the definitions of $+E$, $-E$ substituents and from theorems 41, 44, 49, a measure of activity can be defined. Thus if R is a $+E$ substituent, R′ the corresponding $\pm E$ substituent, and if the coefficients of the NBMO of the odd AH $R'CH_2$, at the positions of the heteroatoms r in R are a_{0r}, then the relative $+E$ activity ϵ of the substituent is defined to be

$$\epsilon = -\sum_r a_{0r}^2 \alpha_r \tag{15}$$

where α_r is the coulomb term of atom r in R. Likewise if T is a $-E$ substituent and T′ the equivalent odd AH anion, and if the NBMO coefficient of atom t in T′ is b_{0t}, the relative $-E$ activity ν of T is defined by

$$\nu = \sum_r b_{0t}^2 \alpha_t \tag{16}$$

In each case the activity is relative to that of an equivalent $\pm E$ (hydrocarbon) substituent; and as usual in the present investigation, the results are limited to alternant systems.

Theorem 54. In the neutralized system RST, R is more negative than in RS and T more positive than in ST. The mutual conjugation energy arises from the fact that R is more negative in RST than in RS, as has already been shown (*cf.* theorem 49). Also R is attached to an active atom in ST; the heteroatoms in R therefore occupy active positions in RST. Hence from theorem 36, the charge density at T in RST is less than in R′ST, R′ being the hydrocarbon equivalent of R; and since the charge densities at T will be similar in R′ST and ST, the charge density at T in RST is less than in ST–*i.e.*, in the former, T is more positive.

Theorem 55. The neutralized system RST behaves as a $+E$ substituent if attached to another molecule through an unstarred atom in S, but as a $-E$ substituent if it is attached through a starred atom. An equivalent statement is that a $-E$ group can conjugate mutually with more than one suitably placed $+E$ group, and a $+E$ group with more than one suitably placed $-E$ group; and this can be proved by arguments exactly similar to that used in proving theorem 49.

Theorem 56. The $+E$ activity of the neutralized group RST is less than that of RS, and the $-E$ activity of RST less than that of ST. Mutual conjugation raises the charge density of R and lowers that of T in RST. The increased charge density at the heteroatoms of R lowers their electron affinity, and so lowers the $+E$ activity of the group; while the decreased charge density at the heteroatoms of T increases their electron affinity, and decreases the $-E$ activity of the group.

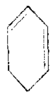
Theorem 57. The resonance energy of an odd alternant anion RS^- relative to $(R + S^-)$, S being an atom, is less, the greater the electron affinity of S. Let R be an even AH, S the atom of coulomb term α. Then the resonance energy of RS relative to $(R + S^-)$ is given[1] by

$$R_{\mathrm{RS}} = -2 \sum_m^{\mathrm{unocc}} \frac{a_{m\mathrm{r}}^2 \beta^2}{\alpha - E_m} \tag{17}$$

Since $E_m > 0$ for unoccupied orbitals, and $\alpha < 0$ for the usual heteroatoms, R_{RS} is less the more negative α—*i.e.*, the greater the electron affinity of S.

Discussion

The results of this section are best illustrated by example. Consider benzene(I) as an example of an even AH, and consider the effects of (a) replacing an unstarred carbon by nitrogen to give pyridine (II): (b) introducing a $+E$ substituent, say NO_2 to give nitrobenzene (III): (c) introducing the basic $-E$ substituent, $-CH_2^-$ to give the benzyl anion (IV); and (d) introducing a typical heteroatomic $-E$ substituent, *e.g.*, NH_2 to give aniline (V).



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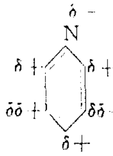

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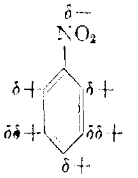

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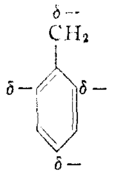

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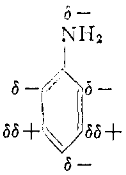

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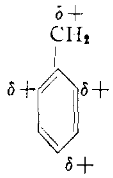
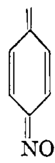


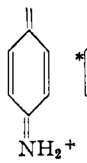
VI

In (a) and (b), the charge density should be lowered at all positions, but much more so in the positions (o:p) of opposite parity to the carbon atom replaced by N or substituted by NO_2. In (c), the formal negative charge is confined to the starred atoms in the odd AH benzyl system; while (d) differs from (c) in that a smaller general charge migration takes place from all positions in the ring to the substituent, leaving second-order positive charges in the meta positions. These conclusions clearly agree qualitatively with those of current theory. (See II–V; $\delta\delta\pm$ implies a second-order positive or negative charge.)

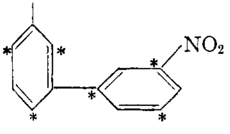
Another set of results concerns the ability of electromeric substituents to stabilize odd AH ions, such as the benzyl ions (IV) and (VI). Here $+E$ substituents stabilize the anions (*e.g.*, IV) more efficiently, and the cations (*e.g.*, VI) less efficiently than do analogous $\pm E$ (hydrocarbon) substituents (such a pair being the $+E$ formyl group and the isoelectronic $\pm E$ vinyl group), the effect being much more marked if the substituent is attached to an active atom. $-E$ substituents (*e.g.*, NH_2) show exactly the opposite effect. These conclusions also agree with resonance theory, it being possible to write unexcited ionic resonance structures (*e.g.*, VII, VIII) only if the substituent is attached to an active carbon atom.



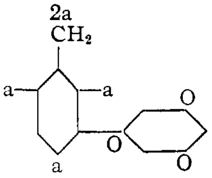
VII



VIII



IX



X

From this follows the rule for mutual conjugation of substituents, mutual conjugation being the condition in which the resonance energy of an even AH is increased more by attaching two substituents than one would anticipate from additivity of their individual effects. The previous correspondence with resonance theory ensures that here too both treatments should lead to similar conclusions. Thus mutual conjugation occurs only when the two substituents are of opposite types (one $+E$, one $-E$) and when they are attached to positions of opposite parity (*e.g.*, *o* or *p* in benzene; *cf.* (I)).

This rule for mutual conjugation is necessary but not sufficient. If the $-E$ substituent is S and the even AH R, then RS will be isoelectronic with an odd AH anion RS′; if the NBMO does not cover all the active atoms in this, RS′ is cross-conjugated and attachment of a $+E$ group at inactive starred atoms in RS′, or at equivalent atoms in RS, will not lead to mutual conjugation. This effect is seen well in 3-nitro-3′-aminobiphenyl (IX); the NO_2 and NH_2 groups are attached to atoms of opposite parity in biphenyl, but the NO_2 is attached to an atom inactive in the analogous *m*-biphenylmethyl anion (X) (the NBMO coefficients are as indicated). The resonance theory leads to similar conclusions, the condition for mutual conjugation given here being equivalent to the condition that an unexcited structure $S^+{=}R{=}T^-$ can be written. It follows that both treatments lead to similar conclusions concerning the qualitative charge distributions in neutralized, or mutually conjugated, systems; and both to similar general definitions of $+E$ and $-E$ substituents.

The present treatment differs from resonance theory, however, in the possibility it offers of estimating all these effects semi-quantitatively within its limitations.[1] The introduction of ionic structures in resonance theory rests almost entirely on qualitative reasoning and intuition, and their importance cannot be estimated in any given case except by appeal to experiment. Some such applications of the present treatment to the prediction of $+E$ and $-E$ activity of substituents are indicated above; others will appear in subsequent papers of this series when definite chemical problems are studied.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

A Molecular Orbital Theory of Organic Chemistry. IV.[1] Free Radicals

BY M. J. S. DEWAR[2]

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The methods of the preceding papers[1] are applied to the study of free radicals. Their reactivity and their stabilization by substituents are discussed.

Free radical chemistry has proved something of a stumbling block to existing qualitative theories, since the latter were designed mainly to analyze charge distributions in even systems. The extension to radicals has involved an unusually large proportion of *ad hoc* explanations. Here the methods previously used[1] will be applied to the study of radicals and the effect of substituents, etc., on their stability. The notation used is that of Parts (I)–(III),[1] and the discussion will be limited to alternant Kekulé radicals.

Theorem 58. The total π-electron energy of two odd AH radicals is normally greater than that of the two even AH's obtained by transfer of one active atom (*i.e.*, the even AH's are the more stable). This result follows at once from theorems 18 and 19 of Part (II).[1] The rise in energy on separating the active carbon from one radical is $< \beta$, and the decrease in energy when that atom is added to the other radical is $> \beta$.

Theorem 59. Combination of an odd AH radical RS, S being an atom, with another radical T to give R–S–T, is more exothermic if S is active. The atom S passes over to sp^3 hybridization in the reaction and is so removed from conjugation with R. If S is active in RS, then R is a normal even AH or a pair of such AH's; if S is inactive, R is either a non-Kekulé AH, or a pair of odd AH radicals. From theorem 29 of Part (II),[1] a non-Kekulé AH is less stable than a Kekulé isomer; and from theorem 58, two odd AH radicals are less stable than an isomeric pair of even Kekulé AH's. Hence the most exothermic modes of addition of T will be those where S is active.

Theorem 60. An odd alternant radical is stabilized by an increase in electron affinity of any atom in it. Let the odd radical be RS, derived from an even AH R and an atom S coulomb term α. Then the resonance energy R_{RS} of RS relative to (R + S), is given[1] by

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[1] For parts (I), (II) and (III) of this series see THIS JOURNAL, **74**, **3341**, **3345**, **3350** (**1952**).

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