D. Preparation of Uranyl Benzoylpyruvate. 1.—Using 95% aqueous ethanol solutions, 4.3 g. (0.0224 mole) of benzoylpyruvic acid was added slowly to 5.02 g. (0.01 mole) of uranyl nitrate hexahydrate. The finely divided yellow precipitate was digested for one hour on the steam-bath and filtered hot; yield 6.8 g. No solvent permitting recrystallization of this solid was found. The material darkened with apparent decomposition at 280°. The 48.7% U content of this solid showed that it had only one benzoylpyruvic acid per uranyl structure. Hence the preparation was repeated using half as much benzoylpyruvic acid: the product closely resembled the first in appearance and behavior.

Anal. Calcd. $C_{10}H_6O_6U$ anhyd.: C, 26.10; H, 1.31; U, 51.73. Found: C, 27.36; H, 1.29; U, 51.45, on correcting wet analysis for 2.98% wt. loss on drying.

2.—Acidification of an aqueous ethanol solution of the sodium uranyl benzoylpyruvate yielded a product having the same behavior and analysis as that of the direct preparation.

3.—The ethyl ester complex was boiled with water, the uranium content of the solid rising to 44.26% after 4 hours. At this time benzoylpyruvic acid was crystallized from the cooled filtrate; yield 20% predicated upon the elimination of one mole of acid from the ester complex.

E. Preparation of Bis-(ethyl Benzoylpyruvato)-dioxomolybdenum.—A mixture of 1.8 g. (0.01 mole) of molybdenum trioxide dihydrate and 7 g. (0.032 mole) of ethyl benzoylpyruvate was heated until solution of the oxide in the molten ester appeared complete (about 45 min.). A yellow solid crystallized from the hot benzene extract of the reaction mixture. This solid was unstable, changing to green on standing.

Anal. Calcd. $C_{24}H_{22}O_{10}Mo$: Mo, 16.94. Found: Mo, 16.7.

Discussion

The uranyl complexes of the methyl and ethyl esters of benzoylpyruvic acid have compositions consistent with the expectation of two β-diketone molecules per metalyl structure. The precise configuration of these compounds is, of course, not derivable from analytical evidence alone, several chelate ring formations being possible.

The uranyl compound of benzoylpyruvic acid appears to be a salt of the uranyl ion and the doubly ionized acid, this product being favored by its insolubility. The adequacy of the acid's double ionization was confirmed by conductometric titrations[7] in aqueous ethanol, of benzoylpyruvic acid and its ethyl ester with $Ba(OH)_2$, there clearly being two and one ionizable hydrogens in these materials, respectively. The analysis of the uranyl compound of sodium benzoylpyruvate definitely shows the presence of only one β-diketone per uranyl structure. Comparison of the U analysis for this preparation with the ash obtained upon its combustion appears to indicate a 1:1 atomic ratio of U and Na, but this evidence is not compelling.

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(7) We are indebted to W. L. Patchen for these measurements.

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[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

A Molecular Orbital Theory of Organic Chemistry. I. General Principles

BY M. J. S. DEWAR[1]

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By applying perturbation theory to the LCMO[12] modification of the usual semi-empirical molecular orbital treatment, a series of approximate expressions are obtained for the resonance energies bond orders and charge distributions in mesomeric systems which will later be shown to serve as a basis for a simple qualitative and semi-quantitative treatment of organic chemistry. This work is an extension of that of Coulson and Longuet-Higgins[8,9]; the extent to which it is novel is indicated.

The purpose of this series of papers is to present a general theory of organic chemistry which seems to offer important advantages over the current resonance theory.[2] The starting point for the present treatment is the familiar molecular orbital method in its original form,[3] without any of the subsequent refinements such as inclusion of non-orthogonality,[4] antisymmetrization,[5] or configurational interaction.[6] This simple version of the MO method is admittedly semi-empirical in that the basic parameters are determined from experiment rather than by *a priori* calculation, but it has proved remarkably successful in spite of its crudity. In any case the more refined treatments are far too complex for use in the present connection.

From approximate solutions of the MO equations, obtained by perturbation methods, it will prove possible on the one hand to derive qualitative relationships between molecular structure and physicochemical properties, and on the other to calculate in a very simple manner various molecular quantities (energies, charge distributions, etc.) of importance in chemistry. These calculations naturally share in the semi-empirical nature of the MO method in the form used here, but at least the results will all be obtained by rigorous reasoning within a framework of clearly stated approximations, and no appeal will be made to the kind of intuitive arguments on which the resonance theory[7] is based.

It should be emphasized at the outset that the general plan behind this treatment is not new, and

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

(3) For a recent account of the method and references see A. Pullman and B. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson, Paris, 1952.

(4) *Cf.* G. W. Wheland, THIS JOURNAL, **63**, 2025 (1941).

(5) M. Goeppert Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(6) D. P. Craig, *Proc. Roy. Soc. (London)*, **A200**, 474 (1950).

(7) This criticism applies to the resonance theory, not to the valence bond method which is a valuable and correct method of approximation. The connection between the two is by no means rigorous.

that perturbation methods have been applied to the MO theory in this connection by Coulson and Longuet-Higgins[8] and by Longuet-Higgins[9] following a preliminary investigation into certain principles of MO theory by Coulson and Rushbrooke.[10] These authors obtained a number of important relations between structure and molecular properties which form the basis of the present treatment; but one vital link was missing and without it the analysis could be applied only to certain very limited problems. The relations which they obtained referred only to structural changes which left the conjugated system of a molecule qualitatively unchanged; that is, changes involving only alterations in the electronegativities of the constituent atoms. The majority of chemical problems involve, however, an understanding of other types of structural alteration; in particular the effects of electromeric substituents and comparisons between structures of different types.

The structural changes considered by Coulson and Longuet-Higgins[8,9] can be represented in MO terminology as changes in the coulomb integrals of atoms in mesomeric systems. By regarding these changes as perturbations and applying perturbation theory, corresponding changes in energy, etc., could be calculated. In order to study the relations between conjugated systems of different sizes some analogous method is needed for calculating the changes in energy, etc., when two isolated mesomeric systems combine to form one larger one. For instance in the study of aromatic substitution by Wheland's[11] method it is necessary to calculate the energy difference between the initial aromatic compound with N conjugated atoms and a transition state with only $(N - 1)$. Again, the effect of an electromeric substituent with M conjugated atoms on the properties of the aromatic compound involves differences in energy, etc., between the parent compound with N conjugated atoms and its derivative with $(N + M)$.

The necessary technique has now been provided by applying perturbation methods to a modification[12] of the usual MO method wherein the MO's of a mesomeric system RS are written as linear combinations not of atomic orbitals (AO's), but of MO's of parts R, S into which RS can in principle be subdivided. Instead of calculating the coefficients of these MO's in the MO's of RS by the usual variation procedure,[12] they will be found to a sufficient approximation by regarding formation of the bonds linking R to S in RS as a perturbation and applying perturbation theory.

Such techniques have been used already in the study of light absorption,[13] but in Part I of this series the treatment will be extended considerably; in particular it will be shown that in certain cases there can be a first-order perturbational energy-difference between (R + S) and RS, it having been assumed previously that the first order perturbations always vanish.[8] These cases are especially important since first order perturbations can be calculated much more simply than those of higher order.

In Parts II–V a series of theorems will be established, which, together with those known already from the work of Coulson and Longuet-Higgins,[8,9] will serve as a basis for a general theory of organic chemistry. The treatment is deliberately formal to emphasize that it is rigorous within its own limitations—which as already indicated are severe. The mathematical treatment is given in small print since it will seldom enter the subsequent applications of the theoretical structure to specific problems. One such application, to reactions of aromatic compounds, is discussed in Part VI by way of illustration. Other applications, in particular to the study of light absorption, will be described elsewhere.

The present treatment involves an unfamiliar terminology and a glossary is accordingly given at the end of this paper.

Assumptions and Terminology.—The treatment is derived from the LCAO MO method in its original form[3] with neglect of overlap integrals, and of resonance integrals between non-adjacent AO's. In this paper the possibility of resonance integrals varying will be recognized, but in most subsequent applications it will be assumed that they are all equal; this will be a sufficient approximation for the present purpose, and variation of the resonance integrals can easily be introduced later when necessary. Energies are reckoned relative to that of carbon 2p atomic orbitals, a MO with negative energy implying that an electron in it is more tightly bound than an electron in a carbon 2p AO. The resonance integral β is taken to be a positive quantity. The coulomb term α likewise compares the energy of an electron in an AO with that of an electron in a carbon 2p AO; that is, it represents the difference between the coulomb integral of a given atom and that of carbon, the sign being such that negative α corresponds to an atom of electronegativity greater than that of carbon.

Union of two mesomeric systems implies merging of the delocalized electrons; the incidental formation of any necessary σ-bonds is not discussed. Thus two benzyl radicals will unite in the present sense not to bibenzyl but to stilbene.

Symbols

Φ_m = mth MO of R
Ψ_n = nth MO of S
E_m, F_n = energies of Φ_m, Ψ_n
ϕ_i, ψ_j = AO's of atom i in R, atom j in S.
a_{mi}, b_{nj} = coefficients of ϕ_i, ψ_j in Φ_m, Ψ_n, respectively.
Ξ_p = pth MO of RS
G_p = energy of Ξ_p
A_{pi} = coefficient of AO of atom i in Ξ_p
β_{ij} = resonance integral between atoms i, j
β = resonance integral between adjacent atoms when it is assumed that all such integrals are equal.
α_k = coulomb term of atom k
q_k = total mobile electron charge density at atom k
p_{ij} = mobile bond order of bond between adjacent atoms i, j
a_{or}, b_{os} = NBMO coefficients in R, S when they are odd AH's

Basic Equations.—The problem is to calculate the difference in total π-electron energy between two separated mesomeric systems R, S and one RS formed by their union. The π-MO's of R, S are Φ_m, Ψ_n ($m, n = 1, 2, \ldots$) where

$$\Phi_m = \sum_r a_{mr}\phi_r; \quad \Psi_n = \sum_s b_{ns}\psi_s \qquad (1)$$

The energies of the MO's are given by

$$\int \Phi_m^* H^R \Phi_m d\tau = E_m; \quad \int \Psi_n^* H^S \Psi_n d\tau = F_n \qquad (2)$$

(8) 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).

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

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

(11) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).

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

(13) M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950); F. A. Matsen, THIS JOURNAL, **72**, 5243 (1950).

where H^R, H^S are the Hamiltonian operators for R, S. The Hamiltonian operator for RS, H^{RS}, is then

$$H^{RS} = H^R + H^S + P \tag{3}$$

where the perturbation P represents formation of the bonds between R and S in RS, the required matrix elements are

$$\begin{aligned} S_{mn} &= \int \Phi_m^* \Phi_n d\tau \quad P_{mn} = \int \Phi_m^* P \Phi_n d\tau \\ S_m^n &= \int \Phi_m^* \Psi_n d\tau \quad P_m^n = \int \Phi_m^* P \Phi \Psi_n d\tau \\ S^{mn} &= \int \Psi_m^* \Psi_n d\tau \quad P^{mn} = \int \Psi_m^* P \Psi_n d\tau \end{aligned} \tag{4}$$

It was shown previously[12] that their values are

$$\begin{aligned} S_{mn} &= S^{mn} = \delta_{mn}; \; S_m^n = 0 \\ P_{mn} &= P^{mn} = 0; \; P_m^n = \sum_{r,s} a_{mr} b_{ns} \beta_{rs} \end{aligned} \tag{5}$$

where the sum extends over pairs of atoms r in R, s in S which are directly linked in RS. It will be assumed as a rule in what follows that attachment is at one point only, so that the sum in (5) can be replaced by a single term $a_{mr} \cdot b_{ns}\beta_{rs}$. The generalization to cases of multiple attachment will be self-evident.

Consider now the energy levels of RS. Consider the MO Ξ_m of RS, of energy G_m, corresponding to the MO Φ_m of the unperturbed system (R + S). Consider first the case where there is no degeneracy (*i.e.*, all the E_m and F_n are different). Then first order perturbation theory gives for Ξ_m and G_m

$$\Xi_m = \Phi_m - \sum_{u \neq m} \frac{p_{mu}\Phi_u}{E_m - E_u} - \sum_n \frac{p_m^n \Psi_n}{E_m - F_n} \tag{6}$$

$$= \Phi_m - \sum_n \frac{a_{mr} b_{ns} \beta_{rs}}{E_m - F_n} \Psi_n \tag{7}$$

$$G_m = E_m + P_{mm} = E_m \tag{8}$$

using equations (5). The first order expression for the MO is sufficient for the present purpose, but obviously the energy must be calculated to a higher approximation. Second order perturbation theory gives

$$\begin{aligned} G_m &= E_m + \sum_{u \neq m} \frac{P_{mu}^2}{E_m - E_u} + \sum_n \frac{(P_m^n)^2}{E_m - F_n} \\ &= E_m + \sum_n \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} \end{aligned} \tag{9}$$

Similar expressions can be written for the MO Ξ_n corresponding to the MO Ψ_n of S

$$\begin{aligned} \Xi_n &= \Psi_n - \sum_m \frac{a_{mr} b_{ns} \beta_{rs}}{F_n - E_m} \Phi_m \\ G_n &= F_n + \sum_m \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{F_n - E_m} \end{aligned} \tag{10}$$

Suppose now that R has a degenerate level E_u, corresponding to the y MO's Φ_u^x ($x = 1, 2, \ldots, y$). The secular equation for RS can be reduced[12] to the form

$$(W - E_u)^{y-1} \left\{ \Pi_m (W - E_m) \Pi_n (W - F_n) \left[1 - \sum_m \sum_n \frac{c_{mr}^2 b_{ns}^2 \beta_{rs}^2}{(W - E_m)(W - F_n)} \right] \right\} = 0 \tag{11}$$

where

$$\begin{aligned} c_{mr} &= a_{mr} \; (m \neq u) \\ c_{ur} &= \left[\sum_x (a_{ur}^x)^2 \right]^{1/2} \end{aligned} \tag{12}$$

If there were no degeneracy, the secular equation for RS would be[4]

$$\Pi_m (W - E_m) \Pi_n (W - F_n) \left\{ 1 - \sum_m \sum_n \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{(W - E_m)(W - F_n)} \right\} = 0 \tag{13}$$

Comparison with (11) shows that in the degenerate case the set of MO's Φ_u^x has been replaced by linear combinations (as is always allowable for degenerate levels) such that in the modified MO's the coefficients C_{ur} of the AO ϕ_r are given by

$$\begin{aligned} c_{ur}^x &= 0 \; (x = 1, 2 \ldots (y - 1)) \\ c_{ur}^y &= \left[\sum_x (a_{ur}^x)^2 \right]^{1/2} \end{aligned} \tag{14}$$

Thus the second order perturbation values for the y levels G_u^x of RS corresponding to the levels E_u of R are

$$\begin{aligned} G_u^x &= E_u \; (x = 1, 2 \ldots (y - 1)) \\ G_u^y &= E_u + \sum_n \frac{\left[\sum_x (a_{ur}^x)^2 \right] b_{ns}^2 \beta_{rs}^2}{E_u - F_n} \end{aligned} \tag{15}$$

The corresponding MO's Ξ_u^x are

$$\begin{aligned} \Xi_u^x &= (\Phi_u^x) \; (x = 1, 2 \ldots (y - 1)) \\ \Xi_u^y &= (\Phi_u^y) - \sum_n \frac{\left[\sum_x (a_{ur}^x)^2 \right]^{1/2}}{E_u - F_n} b_{ns} \beta_{rs} \Psi_n \end{aligned} \tag{16}$$

If equation (9) had been applied ignoring the degeneracy, the energy levels $(G_u^x)'$ would have been given by

$$(G_u^x)' = E_u + \sum_n \frac{(a_{ur}^x)^2 b_{ns} \beta_{rs}^2}{E_u - F_n} \tag{17}$$

From equations (15) and (17)

$$\sum_x G_u^x = \sum_x (G_u^x)' \tag{18}$$

Thus so long as the whole set of perturbed levels is full, which is nearly always the case in practice, the degeneracy can be neglected, since the energies given by equations (15) and (17) agree. The same is true for total charge densities, etc., and indeed in all applications required in the present investigation; so degeneracy of this kind rarely needs to be considered explicitly.

If, however, there is degeneracy between a level E_u and R and a level F_v in S, a different situation arises. This time the correct zeroth order MO's of RS will be linear combinations of the MO's, Φ_u, Ψ_v, and such a combination gives rise to a first order perturbation energy. This fact will be of fundamental importance in the present treatment. By applying the usual variation method, the correct zeroth order combinations Ξ_u^+, Ξ_u^- are found to be

$$\begin{aligned} \Xi_u^+ &= \frac{1}{\sqrt{2}} (\Phi_u + \Psi_v) \\ \Xi_u^- &= \frac{1}{\sqrt{2}} (\Phi_u - \Psi_v) \end{aligned} \tag{19}$$

The first-order perturbation energies G_u^+, and G_u^- are then

$$\begin{aligned} G_u^+ &= E_u - a_{ur} b_{vs} \beta_{rs} \\ G_u^- &= E_u + a_{ur} b_{vs} \beta_{rs} \end{aligned} \tag{20}$$

The first-order perturbed MO's are

$$\begin{aligned} \Xi_u^+ &= \frac{1}{\sqrt{2}} \left\{ \Phi_u + \Psi_v - \sum_{n \neq v} \frac{a_{ur} b_{ns} \beta_{rs}}{E_u - F_n} \Psi_n - \sum_{m \neq u} \frac{a_{mr} b_{vs} \beta_{rs}}{E_u - E_m} \Phi_m \right\} \\ \Xi_u^- &= \frac{1}{\sqrt{2}} \left\{ \Phi_n - \Psi_u - \sum_{n \neq v} \frac{a_{ur} b_{ns} \beta_{rs}}{E_u - F_n} \Psi_n - \sum_{m \neq u} \frac{a_{mr} b_{vs} \beta_{rs}}{E_u - E_m} \Phi_m \right\} \end{aligned} \tag{21}$$

The second-order perturbed energies are

$$\begin{aligned} G_u^+ &= E_u - a_{ur} b_{vs} \beta_{rs} + \frac{1}{2} \left\{ \sum_{n \neq v} \frac{a_{ur}^2 b_{ns}^2 \beta_{rs}^2}{E_u - F_n} + \sum_{m \neq u} \frac{a_{mr}^2 b_{vs}^2 \beta_{rs}^2}{E_u - E_m} \right\} \\ G_u^- &= E_u + a_{ur} b_{vs} \beta_{rs} + \frac{1}{2} \left\{ \sum_{n \neq v} \frac{a_{ur}^2 b_{ns}^2 \beta_{rs}^2}{E_u - F_n} + \sum_{m \neq u} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_u - E_m} \right\} \end{aligned} \tag{22}$$

Application of the crude theory, simply neglecting terms with vanishing denominators, would give

$$(G_u^+)' = E_u + \sum_{n \neq v} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_u - F_n}$$
$$(G_u^-)' = E_u + \sum_{m \neq u} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_u - E_m} \tag{23}$$

From equations (21) and (23)

$$G_u^+ + G_u^- = (G_u^+)' + (G_u^-)' \tag{24}$$

Here again the degeneracy can be neglected if both the perturbed MO's are filled in RS. But many cases of importance will arise where this is not the case; and as a rule the first order approximations (20) may then be used since the second order terms should be of a smaller order of magnitude.

The bond order p_{rs} of the bond between atoms r, s in RS is defined by

$$p_{rs} = \sum_m A_{mr} B_{ms} \cdot n_m \tag{25}$$

where A_{mr}, B_{ms} are the coefficients of the AO's ϕ_r, Ψ_s in the MO Ξ_m of RS, and n_m is the number of electrons in that MO. In the absence of degeneracy, for the MO corresponding to Ξ_m, equation (7) gives

$$A_{mr} = a_{mr}$$
$$B_{ns} = -\sum_n b_{ns} \left\{ \sum_n \frac{a_{mr} b_{ns} \beta_{rs}}{E_m - F_n} \right\}$$
$$= -\sum_n \frac{a_{mr} b_{ns}^2 \beta_{rs}}{E_m - F_n} \tag{26}$$

Likewise for the MO Ξ_n corresponding to Ψ_n, equation (10) gives

$$A_{mr} = -\sum_m \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}}{F_n - E_m}$$
$$B_{ns} = b_{ns} \tag{27}$$

From equations (25), (26) and (27)

$$p_{rs} = -\sum_m \sum_n \frac{n_m a_{mr}^2 b_{ns}^2 \beta_{rs}}{E_m - F_n} - \sum_m \sum_n \frac{n_n a_{mr}^2 b_{ns}^2 \beta_{rs}}{F_n - E_m} \tag{28}$$

If the MO's in RS are either doubly occupied or empty, this can be put in the simpler form

$$p_{rs} = -2 \left\{ \sum_m^{occ} \sum_n^{unocc} - \sum_m^{unocc} \sum_n^{occ} \right\} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}}{E_m - F_n} \tag{29}$$

where $\sum^{occ}$ implies summation over occupied MO's, $\sum^{unocc}$ summation over unoccupied MO's. The same expression holds if levels in R, or levels in S, are degenerate, provided that all the corresponding perturbed MO's are filled in RS. If a level E_u of R and a level F_v of S coincide, however, the bond order of the rs bond is easily shown to be, in zeroth approximation

$$p_{rs} = a_{ur} b_{vs} \tag{30}$$

The higher approximation is given by

$$p_{rs} = a_{ur} b_{vs} - 2^{1/2} \left\{ \sum_{n \neq v} \frac{a_{ur} b_{ns} \beta_{rs}}{E_u - F_n} + \sum_{m \neq u} \frac{a_{mr}^2 b_{vs}^2 \beta_{rs}}{F_v - E_m} \right\} \tag{31}$$

A special case of importance is that in which S is a single atom (or a group in which that atom is attached to substituents only by σ-bonds: *e.g.*, MeO). If the coulomb term of the atom is α, and if no energy level of R coincides with α, the approximate MO's and energies of RS are given (*cf.* equations (7)–(10) by

$$\Xi_m = \Phi_m - \frac{a_{mr} \beta_{rs}}{E_m - \alpha} \psi$$
$$\Xi_s = \psi - \sum_m \frac{a_{mr} \beta_{rs}}{\alpha - E_m} \Phi_m \tag{32}$$
$$G_m = E_m - \frac{a_{mr}^2 \beta_{rs}^2}{E_m - \alpha}$$
$$G_s = \alpha - \frac{a_{mr}^2 \beta_{rs}^2}{\alpha - E_m}$$

The rS bond order is likewise given by

$$p_{rs} = -2 \sum_m^{occ} \frac{a_{mr}^2 \beta_{rs}}{E_m - \alpha} - 2 \sum_m^{all} \frac{a_{mr}^2 \beta_{rs}}{\alpha - E_m}$$
$$= 2 \sum_m^{unocc} \frac{a_{mr}^2 \beta_{rs}}{E_m - \alpha} \tag{33}$$

An especially important case arises where $\alpha = 0$, and where R also has a non-bonding[9] molecular orbital (NBMO) of zero energy; in this degenerate case, the energies of the perturbed NBMO's are given by

$$G_o^{\pm} = \mp a_{or} \beta_{rs} + \frac{1}{2} \sum_{m \neq o} \frac{a_{mr}^2 \beta_{rs}^2}{E_m} \tag{34}$$

and the perturbed MO's by

$$\Xi_o^{\pm} = \frac{1}{\sqrt{2}} \left(\Phi_o \pm \psi \mp \sum_{m \neq o} \frac{a_{mr} \beta_{rs}}{E_m} \Phi_m \right) \tag{35}$$

Charge densities will be required in the subsequent discussion only for the case where S is monatomic. The charge density q_t at atom t in RS, is defined by

$$q_t = 2 \sum_m^{occ} A_{mt}^2 \tag{36}$$

Since the coefficient A_{mt} enters this expression as a square, the MO's given by equation (32) are not sufficiently accurate and must be normalized (the first-order perturbation theory gives MO's normalized only to terms involving first powers of the coefficients). Thus

$$\Xi_m = \left\{ \Phi_m - \frac{a_{mr} \beta_{rs} \psi}{E_m - \alpha} \right\} \left\{ 1 + \frac{a_{mr}^2 \beta_{rs}^2}{(E_m - \alpha)^2} \right\}^{-1/2}$$
$$\Xi_s = \left\{ \psi - \sum_m \frac{a_{mr} \beta_{rs}}{\alpha - E_m} \Phi_m \right\} \left\{ 1 + \sum_m \frac{a_{mr}^2 \beta_{rs}^2}{(\alpha - E_m)^2} \right\}^{-1/2} \tag{37}$$

If atom t is in the portion R of RS, and if $m = s$

$$A_{mt}^2 = a_{mt}^2 \left\{ 1 + \frac{a_{mr}^2 \beta_{rs}^2}{(E_m - \alpha)^2} \right\}^{-1}$$
$$\simeq a_{mt}^2 \left\{ 1 - \frac{a_{mr}^2 \beta_{rs}^2}{(E_m - \alpha)^2} \right\} \tag{38}$$

from equations (37). Likewise

$$A_{ms}^2 \simeq \frac{a_{mr}^2 \beta_{rs}^2}{(E_m - \alpha)^2} \tag{39}$$

For the MO Ξ_s

$$A_{st}^2 = a_{mt}^2 \sum_m^{all} \frac{a_{mr}^2 \beta_{rs}^2}{(E_m - \alpha)^2}$$
$$A_{ss}^2 = 1 - \sum_m^{all} \frac{a_{mr}^2 \beta_{rs}^2}{(E_m - \alpha)^2} \tag{40}$$

The resonance energy R_{RS} of RS relative to (R + S) is defined as the difference in π-electron energy between (R + S) and (RS). Expressions for resonance energies can be written down at once from the equations given above. Thus if R, S are both polyatomic and there is no degeneracy

$$R_{RS} = 2 \sum_m^{occ} E_m + 2 \sum_n^{occ} F_n - \left\{ 2 \sum_m^{occ} E_m + 2 \sum_n^{occ} F_n + 2 \sum_m^{occ} \sum_n^{all} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} + 2 \sum_m^{all} \sum_n^{occ} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{F_n - E_m} \right\}$$

from equations (9) and (10), hence

$$R_{RS} = -2 \left\{ \sum_m^{occ} \sum_n^{unocc} - \sum_m^{unocc} \sum_n^{occ} \right\} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} \tag{41}$$

This expression also applies in the case of degeneracy provided that all the degenerate orbitals are filled, if terms with vanishing denominators are omitted. The only other case of importance is that in which both R and S have a NBMO and the pair of NBMO's contains but two electrons. In this case the resonance energy is easily seen from equations (9), (10) and (22) to be

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

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

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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.

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

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