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Ground States of σ-Bonded Molecules. I.
A Semiempirical SCF MO Treatment of Hydrocarbons[1]

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Abstract: In a recent series of papers[3] it was shown that the heats of formation of conjugated molecules can be calculated with surprising accuracy by the Pople SCF MO method, the σ bonds being treated as localized. Here we describe an extension of the method to include all the valence electrons in a molecule, using procedures similar to those suggested by Pople, Santry, and Segal[4] and by Klopman.[5] Preliminary calculations for a number of hydrocarbons are reported; the agreement between the calculated and observed heats of formation is already very satisfactory, implying that this approach should ultimately give results of sufficient accuracy to be of value in predicting the structures and reactivities of molecules.

In a recent series of papers[3] it was shown that the heats of formation from atoms of conjugated molecules can be calculated with quite unexpected accuracy (±0.1%), using the localized bond model for the σ bonds and calculating the π binding energy by the Pople method. However, although this approach represents a very considerable advance over anything previously reported, it is still of limited chemical value; it cannot be applied to reactions even of conjugated molecules since transition states do not normally have the symmetry necessary for the π approximation to be applicable, nor can it be applied to many problems concerning the behavior of unconjugated molecules, *e.g.*, conformational equilibria and steric hindrance.

However, in view of the unexpected success of the π calculations, it seems reasonable to hope that an analogous treatment of σ bonds might prove equally successful; if so, we would have a complete solution of the basic problems of chemistry. Preliminary calculations of this kind for diatomic molecules have indeed proved very promising,[5] and Pople, Santry, and Segal[4] have reported preliminary calculations for larger molecules. Here we describe our own initial efforts in this direction, which already seem to have achieved a degree of accuracy almost in the "chemical" zone.

Theoretical Approach

The Pople SCF MO method is now familiar, and the problems involved in its extension to σ-bonded systems have been discussed in a formal manner by Pople, Santry, and Segal. The following pictorial representation has the advantage of clarifying these problems and will also help to illustrate our own approach.

In the original Pople treatment of conjugated systems, the π MOs ψ_μ are written as linear combinations of p AO's ϕ_i of the participating atoms (eq 1). The choice of

$$\psi_\mu = \sum_i a_{\mu i}\phi_i \qquad (1)$$

basis set functions ϕ_i is unambiguous, since the orientation of each ϕ_i is determined by the geometry of the π system. In calculations for a three-dimensional, σ-bonded system, the situation is more complicated.

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[2] Robert A. Welch Postdoctoral Fellow.

[3] A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692, 3255 (1965); *J. Chem. Phys.*, **44**, 759 (1966); *Tetrahedron*, **21**, 1817, 3423 (1965); *Tetrahedron Letters*, **50**, 4503 (1965); M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414, (1965); M. J. S. Dewar, G. J. Gleicher, and C. C. Thompson, Jr., *ibid.*, **88**, 1349 (1966).

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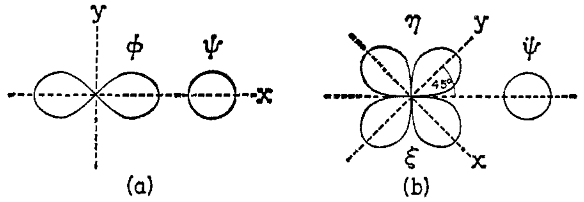


Figure 1. Illustrating the interactions between an electron in an s AO (ψ) of atom N, and an electron in a p AO (ϕ) of atom M.

Each atom other than hydrogen will contribute at least three p AO's; the orientation of these orbitals is arbitrary, since there will normally be no reference frame to fix the choice of coordinate axes. Since the choice of axes is arbitrary, the results of the calculation must be independent of it. While this condition is automatically met in a complete Roothaan SCF MO treatment, the same is not necessarily the case in the simplified version of Pople. The following example illustrates the difficulty.

Consider the interactions between two electrons, one occupying an s AO (ϕ) of atom M, and the other, a p AO (ψ) of atom N, ψ having its axis along the line joining the two nuclei (Figure 1a). In a coordinate system where this line is one of the coordinate axes, ψ will be represented as a single p AO. The terms in the total energy that represent the interactions between the two electrons are of two kinds; first there will be a one-electron resonance integral β, given by

$$\beta = \int \phi \mathrm{H}^{\mathrm{C}} \psi \mathrm{d}\tau \qquad (2)$$

where H^{C} is the core operator; secondly there will be an electron repulsion term γ, given by

$$\gamma = \int\int \phi^2(1) \frac{e^2}{r_{12}} \psi^2(2)\ \mathrm{d}\tau_1 \mathrm{d}\tau_2 \equiv (\phi\phi,\psi\psi) \qquad (3)$$

in the usual notation for such integrals.

Suppose now that we calculate these interactions in a coordinate system rotated through 45° about the z axis (Figure 1b). The AO ϕ must now be written as a linear combination of the p_x AO (ξ) and the p_y AO (η); *i.e.*

$$\phi = \frac{1}{\sqrt{2}}(\xi + \eta) \qquad (4)$$

The corresponding one- and two-electron interaction terms, β' and γ', are then given by eq 5 and 6. If our

$$\beta' = \int \phi \mathrm{H}^{\mathrm{C}} \psi\ \mathrm{d}\tau = \frac{1}{\sqrt{2}}\left(\int \xi \mathrm{H}^{\mathrm{C}} \psi\ \mathrm{d}\tau + \int \eta \mathrm{H}^{\mathrm{C}} \psi\ \mathrm{d}\tau\right) \qquad (5)$$

$$\begin{aligned} \gamma' &= \int\int \phi^2(1) \frac{e^2}{r_{12}} \psi^2(2)\ \mathrm{d}\tau_1 \mathrm{d}\tau_2 = \\ &\frac{1}{2}\int\int \xi^2(1) \frac{e^2}{r_{12}} \psi^2(2)\ \mathrm{d}\tau_1 \mathrm{d}\tau_2 + \frac{1}{2}\int\int \eta^2(1) \frac{e^2}{r_{12}} \psi^2(2)\ \mathrm{d}\tau_1 \mathrm{d}\tau_2 + \\ &\int \xi(1)\eta(1) \frac{e^2}{r_{12}} \psi^2(2)\ \mathrm{d}\tau_1 \mathrm{d}\tau_2 \equiv \frac{1}{2}[(\xi\xi,\psi\psi) + (\eta\eta,\psi\psi) + \\ &2(\xi\eta,\psi\psi)] \end{aligned} \qquad (6)$$

calculation is to be independent of the choice of coordinate axes, it is necessary that

$$\beta \equiv \beta' \qquad (7)$$

$$\gamma \equiv \gamma' \qquad (8)$$

Equation 7 will be automatically satisfied if we make the usual assumption that one-electron resonance integrals are proportional to overlap integrals. The second condition will be met in a full Roothaan treatment where all electron repulsion integrals are included; however, in the standard Pople treatment, where integrals involving overlap between different AO's are neglected, complications will arise, since the final integral in eq 6 will be set equal to zero. Since the remaining integrals in eq 6 are equal, from symmetry, eq 8 will be satisfied only if

$$(\phi\phi,\psi\psi) = (\xi\xi,\psi\psi) = (\eta\eta,\psi\psi) \qquad (9)$$

Since these integrals represent the mutual repulsions of two clouds of charge, one representing the distribution of an electron occupying a p AO, the other the distribution of an electron occupying an s AO, the condition implied in eq 8 is equivalent to the assumption that such clouds of charge are spherically symmetrical. This is the CNDO approximation of Pople, *et al.*[4] (complete neglect of differential overlap). In it one assumes that electron repulsion integrals of the type $(\chi\chi,\omega\omega)$ depend on the nature of the orbitals χ and ω and on their distance apart, but not on their orientation.

Our experience indicates, however, that this approximation is too severe. In spite of very extensive trials, we have been unable to devise any satisfactory scheme for calculating heats of formation of molecules based on the CNDO approximation. This is not surprising, for the directivity of valence probably depends at least partly on the variation with orbital orientation of repulsion integrals involving p AO's. If so, one would not expect to be able to calculate heats of formation accurately, using an approximation in which these variations are neglected.

If such variations in the repulsion integrals are to be included in our treatment, we must then include three- and four-orbital repulsion integrals, involving overlap of orbitals on a common center. In other words, *all* two-center repulsion integrals must be included. We can still, of course, neglect three- and four-center integrals, involving overlap between AO's of different atoms, for neglect of these does not affect the invariance of our calculations to choice of coordinate axes. Thus in the notation of Figure 1, and with χ representing an AO of a third atom, we can set

$$(\chi\phi,\psi\psi) = (\chi\xi,\psi\psi) = (\chi\eta,\psi\psi) = 0 \qquad (10)$$

without affecting the invariance to rotation, for the contribution of such integrals will be zero no matter what axes we choose.

This is the NDDO approximation of Pople, *et al.*[4] (neglect of diatomic differential overlap); it involves obvious technical difficulties, and no calculations have as yet been reported in which the full NDDO scheme has been adopted. Not only are there a large number of additional integrals to be evaluated, but it is also difficult to estimate them by the kind of semiempirical approach we have used for the two-orbital integrals.[1,5] While the NDDO approximation may prove essential, and while we are at present developing an appropriate program for applying it, we decided first to try the following intermediate approximation in the hope that it might combine simplicity with adequate accuracy.

Consider the integrals (km,ln) between AO's of two atoms M and N. First we transform the AO's of the atoms into the coordinate system of Figure 2. The repulsion integrals between the original AO's can at once be expressed in terms of corresponding integrals between the transformed AO's. In this new system, all three-orbital integrals involving overlap between pairs of p AO's vanish through symmetry, as also do most of the corresponding four-orbital integrals. We now assume that the remaining three- and four-orbital integrals can be neglected. The neglect of integrals involving overlap between an s AO and p AO of a given center can be shown to have no effect on the invariance of the calculations to choice of coordinate axes. The neglect of integrals involving four distinct p AO's can in principle affect this invariance; however, various arguments indicate that such effects are negligible (see below). With these assumptions our problem is greatly simplified, for the remaining two-center integrals are now of the standard two-orbital type, *i.e.*, (kk,ll). This approach might be termed the PNDDO approximation (partial neglect of diatomic differential overlap).

There are ten distinct integrals of this kind to be considered for the orbitals indicated in Figure 2, *viz.*

$$\mathrm{s}\sigma_M\text{–}\mathrm{s}\sigma_N,\ \mathrm{s}\sigma_M\text{–}\mathrm{p}\sigma_N,\ \mathrm{p}\sigma_M\text{–}\mathrm{s}\sigma_N,\ \mathrm{p}\sigma_M\text{–}\mathrm{p}\sigma_N,\ \mathrm{s}\sigma_M\text{–}\mathrm{p}\pi_N,$$
$$\mathrm{p}\pi_M\text{–}\mathrm{s}\sigma_N,\ \mathrm{p}\pi_M\text{–}\mathrm{p}\pi_N,\ \mathrm{p}\sigma_M\text{–}\mathrm{p}\pi_N,\ \mathrm{p}\pi_M\text{–}\mathrm{p}\sigma_N,\ \mathrm{p}\pi_M\text{–}\mathrm{p}\pi_N^* \qquad (11)$$

The last integral, $\mathrm{p}\pi_M\text{–}\mathrm{p}\pi_N^*$, is one between the p_y AO of M and the p_z AO of N, or conversely. For n atoms, there are therefore $5n(n-1)$ different integrals; in our computer program, each set of integrals is stored in one-half of an $n \times n$ matrix, five such matrices being required.

Our treatment also involves repulsion integrals between orbitals of a single center; here the three- and four-orbital integrals vanish through symmetry, only two-orbital integrals of the type (kk,mm) and (km,km) remaining. Integrals of the latter type must be retained since otherwise we could not distinguish between singlet and triplet states of atoms; thus the difference in energy between the singlet and triplet configurations $(1s)^2(2s)^2(2p)^2$ of carbon arises from an integral of this type where ϕ_k and ϕ_m are different 2p AO's.

We neglect inner electrons, *e.g.*, the 1s electrons in carbon; we treat the valence electrons as moving in the field of a set of cores, each composed of a nucleus and a set of occupied inner AO's. Thus the core of carbon is an ion C^{4+}, consisting of the nucleus and a pair of 1s electrons.

The one-center repulsion integrals (kk,mm) and (km,km) are estimated from spectroscopic data for the corresponding atom by a procedure considered in detail below. In this it is assumed that the repulsion between a pair of electrons in the valence shell of a given atom has a value independent of the orbitals occupied by the electrons and depending only on their relative spins, *i.e.*

$$\text{repulsion between electrons of like spin} = A_M^+ \qquad (12)$$

$$\text{repulsion between electrons of opposite spin} = A_M^- \qquad (13)$$

The repulsion integrals can be expressed in terms of these quantities as

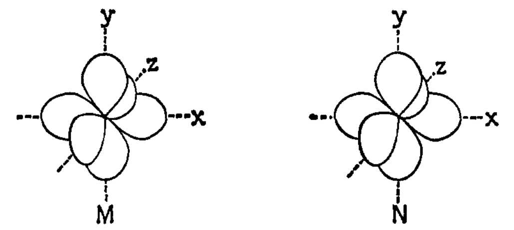


Figure 2. Illustrating calculation of electron repulsion integrals.

$$(kk,mm) = A_M^- \qquad (k = m \text{ or } k \neq m) \qquad (14)$$

$$(km,km) = A_M^- - A_M^+ \qquad (k \neq m) \qquad (15)$$

In order to make the treatment as general as possible, we derived an expression for the total electronic energy (E_{el}) for an open-shell SCF MO treatment. Here q_i^α, q_j^β are respectively the densities of α-spin and β-spin electrons in the AO's ϕ_i and ϕ_j given by

$$q_i^\alpha = \sum_\mu n_\mu^\alpha a_{\mu i}^2 \qquad q_j^\beta = \sum_\nu n_\nu^\beta a_{\nu j}^2 \qquad (16)$$

where n_μ^α and n_μ^β are the numbers of electrons (zero or unity) occupying the corresponding MO's ψ_μ^α and ψ_ν^β. Likewise p_{ij}^α and p_{ij}^β are the corresponding bond orders, defined by eq 17. In the case of a closed-shell

$$p_{ij}^\alpha = \sum_\mu n_\mu^\alpha a_{\mu i} a_{\mu j}$$
$$p_{ij}^\beta = \sum_\nu n_\nu^\beta a_{\nu i} a_{\nu j} \qquad (17)$$

molecule, the net charge densities q_i and bond orders p_{ij} are given by

$$q_i = 2q_i^\alpha = 2q_i^\beta \quad p_{ij} = 2p_{ij}^\alpha = 2p_{ij}^\beta \qquad (18)$$

The expression for E_{el} is shown in eq 19. Here

$$\begin{aligned} E_{el} = {} & \sum_k^{(M)}\Bigg((q_k^\alpha + q_k^\beta)W_k + \sum_m^{(M)}\Bigg\{\sum_{N\neq M}\Big[k_x m_x V_{kN}^\pi + \\ & (k_y m_y + k_z m_z)V_{kN}^\pi\Big](p_{km}^\alpha + p_{km}^\beta) + \frac{1}{2}\Big[q_k^\alpha q_m^\alpha - (p_{km}^\alpha)^2 + \\ & q_k^\beta q_m^\beta - (p_{km}^\beta)^2\Big]A_M^+ + \frac{1}{2}(q_k^\alpha q_m^\beta + q_k^\beta q_m^\alpha)A_M^-\Bigg\}\Bigg) + \\ & \sum_k^{(M)}\sum_{l>k}^{(N)}\Bigg\{2(p_{kl}^\alpha + p_{kl}^\beta)\Big[k_x l_x \beta_{kl}^\sigma + (k_y l_y + k_z l_z)\beta_{kl}^\pi\Big]\Bigg\} + \\ & \sum_m^{(M)}\sum_n^{(N)}\Bigg\{(p_{km}^\alpha p_{ln}^\alpha + p_{km}^\beta p_{ln}^\beta + p_{km}^\alpha p_{ln}^\beta + p_{km}^\beta p_{ln}^\alpha - \\ & p_{kn}^\alpha p_{lm}^\alpha - p_{kn}^\beta p_{lm}^\beta)\Big[k_x l_x m_x n_x \gamma_{kl}^{\sigma\sigma} + (k_y l_y m_y n_y + \\ & k_z l_z m_z n_z)\gamma_{kl}^{\pi\pi} + k_x m_x(l_y n_y + l_z n_z)\gamma_{kl}^{\sigma\pi} + (k_y m_y + \\ & k_z m_z)l_x n_x \gamma_{kl}^{\pi\sigma} + (k_y m_y l_z n_z + k_z m_z l_y n_y)\gamma_{kl}^{\pi\pi *}\Big]\Bigg\} \qquad (19) \end{aligned}$$

ϕ_k and ϕ_m are AO's of one atom M, while ϕ_l and ϕ_n are AO's of some other atom N; the summations are labeled accordingly to avoid confusion.

The integral W_k represents a sum of the kinetic energy of an electron occupying the AO ϕ_k and its potential energy due to attractions by the core of the corresponding atom (M). The integrals V_{kN}^σ and V_{kN}^π represent respectively the attractions between an electron in a σ-type AO (s or pσ) or a π-type AO, ϕ_k, and the core of atom N. The quantities A^+ and A^- have already been defined (eq 14 and 15). The remaining one-electron integrals $\beta_{kl}{}^{\sigma}$ and $\beta_{kl}{}^{\pi}$ are resonance integrals between AO's of atoms M and N in the local coordinate system of Figure 2. There are five nonvanishing combinations of this type, *i.e.*

$$\mathrm{s}\sigma\text{–}\mathrm{s}\sigma,\ \mathrm{s}\sigma\text{–}\mathrm{p}\sigma,\ \mathrm{p}\sigma\text{–}\mathrm{s}\sigma,\ \mathrm{p}\pi\text{–}\mathrm{p}\pi,\ \mathrm{p}\sigma\text{–}\mathrm{p}\sigma \tag{20}$$

where the first symbol designates the orbital ϕ_k, the second ϕ_l.

The quantities γ_{kl} are two-orbital repulsion integrals for orbitals of atoms M and N, again in the local coordinate system of Figure 2; *i.e.*

$$\gamma_{kl} \equiv (kk,ll) \tag{21}$$

The integrals are labeled with superscripts to indicate the types of orbital involved; the distinction between sσ and pσ types follows automatically from the nature of the AO's. Thus if ϕ_k and ϕ_m are p AO's, the integral $\gamma_{kl}{}^{\sigma\pi}$ is of the pσ–pπ type, while if $k = m$ and ϕ_k is a σ AO, the integral is of the sσ–pπ type. (Note that in our scheme $\gamma_{kl}{}^{\sigma\pi}$ vanishes if ϕ_k is an s AO and $k \neq m$, since three- and four-orbital integrals involving s–p overlap are neglected.)

The quantities $k_x, k_y \ldots n_z$ are involved in the transformation of the original basis set of AO's into the locally oriented sets of Figure 2. They are defined in (22), where $i = k, l, m,$ or n, and other terms are defined in eq 23. X_p, Y_p, and Z_p are the coordinates of atom P in the original coordinate system used to specify the positions of the atoms in the molecule.

$$\begin{array}{lcccc}
 & \multicolumn{4}{c}{\text{Type of orbital } \phi_i} \\
 & \mathrm{s} & \mathrm{p}_x & \mathrm{p}_y & \mathrm{p}_z \\
i_x = & 1 & X & Y & Z \\
i_y = & 0 & -rY/R & rX/R & 0 \\
i_z = & 0 & -rXZ/R & -rYZ/R & R/r
\end{array} \tag{22}$$

$$X = |X_\mathrm{M} - X_\mathrm{N}|/r;\ Y = |Y_\mathrm{M} - Y_\mathrm{N}|/r;\ Z = |Z_\mathrm{M} - Z_\mathrm{N}|/r;\ r = (X^2 + Y^2 + Z^2)^{1/2};\ R = (X^2 + Y^2)^{1/2} \tag{23}$$

The elements of the F matrix for the α-spin electrons are given in eq 24–26. Equation 25 refers to off-diagonal matrix elements between AO's ϕ_k and ϕ_m of the same atom M, while eq 26 refers to corresponding elements between AO's of two different atoms M and N. Here the electron repulsion integrals have been left in their original form, over AO's set up in the original coordinate system; in order to evaluate them, the AO's ϕ_k, ϕ_l, ϕ_m, and ϕ_n for each pair of atoms M and N are transformed into the local coordinate system of Figure 2.

$$F_{kk} = W_k{}^{(\mathrm{M})} + \sum_{\mathrm{N}\neq\mathrm{M}} [k_x{}^2 V_{k\mathrm{N}}{}^{\sigma} + (k_y{}^2 + k_z{}^2) V_{k\mathrm{N}}{}^{\pi}] + q_k{}^{\beta} A_\mathrm{M}{}^- + \sum_{m\neq k}^{(\mathrm{M})} (q_m{}^{\alpha} A_\mathrm{M}{}^+ + q_\mathrm{m}{}^{\beta} A_\mathrm{M}{}^-) + \sum_l^{(\mathrm{N})}\sum_n^{(\mathrm{N})} (p_{ln}{}^{\alpha} + \mathrm{p}_{ln}{}^{\beta})(kk,ln) \tag{24}$$

$$F_{km}{}^{(\mathrm{M})} = \sum_{\mathrm{N}\neq\mathrm{M}} [k_x m_x V_{k\mathrm{N}}{}^{\sigma} + (k_y m_y + k_z m_z) V_{k\mathrm{N}}{}^{\pi}] - p_{km}{}^{\alpha} A_\mathrm{M}{}^+ + \sum_l^{(\mathrm{N})}\sum_n^{(\mathrm{N})} (p_{ln}{}^{\alpha} + p_{ln}{}^{\beta})(lm,ln) \tag{25}$$

$$F_{kl}{}^{(\mathrm{M,N})} = k_x l_x \beta_{kl}{}^{\sigma} + (k_y l_y + k_z l_z)\beta_{kl}{}^{\pi} - \sum_m^{(\mathrm{M})}\sum_n^{(\mathrm{N})} p_{mn}(km,ln) \tag{26}$$

The calculations were carried out at the Computation Center of The University of Texas, using first a CDC 1604 digital computer, and later a CDC 6600. The program, while somewhat complex, followed a fairly conventional path. The integrals β_{km} and γ_{km}, and the quantities k_x etc. of eq 22, are first computed and stored. An initial F matrix is then set up, using assumed values for the q's and p's; in the case of hydrocarbons, we set the charge density (q) equal to unity for each valence orbital, and each bond order (p) equal to zero. The F matrix is then diagonalized, new q's and p's are computed, and the process is continued until the sum of the energies of the occupied orbitals converges to within a predetermined limit. The total electronic energy is then computed (eq 19) and the total bonding energy found from it by adding the core repulsion and subtracting the total energy of the isolated atoms. The following section indicates the procedure we have followed in estimating the various integrals and other quantities appearing in the treatment.

Calculations of Integrals Etc.

The quantities appearing in this treatment are of five types: (a) valence-shell ionization potentials, W_k; (b) one-center repulsion integrals, (kk,mm) and (km,km); (c) one-electron resonance integrals, β_{kl}; (d) two-center repulsion integrals, γ_{kl}; (e) the core repulsion and core-electron attraction. For reasons indicated above, we are prepared if necessary to treat any or all of these quantities as parameters, our sole purpose being to develop a reliable and general method for calculating heats of formation of molecules of all kinds (including transition states) with "chemical" accuracy. However, one must obviously try to minimize the number of arbitrary parameters in a treatment such as this; we have accordingly adopted the course of introducing parametric functions for the calculation of the various quantities, these functions containing the minimum number of parameters and being chosen on the basis of physical intuition. In this connection, empirical data for atoms can be regarded as free information, for we are concerned only with the heats of formation of molecules, not with their total binding energies. The true parameters in our treatment are those whose values must be fixed by reference to properties of specific molecules; the number of such "molecular" parameters must be kept as small as possible if the method is to be useful and convincing. The procedure we followed in the calculations reported here was as follows.

(a and b) Valence-Shell Ionization Potentials and One-Center Repulsion Integrals. These were estimated for carbon from spectroscopic data by the following[5] procedure. We represent the core of the carbon atom as the ion C^{4+}, consisting of the nucleus and two 1s electrons. The quantities W_s or W_p should then represent the energy of a 2s or 2p electron, respectively, moving in the field of this core, and one might therefore try to equate them to the appropriate fourth ionization potentials of carbon, *i.e.*

$$C^{3+}(1s)^2(2s) \rightarrow C^{4+}(1s)^2 \quad \Delta H = W_s$$

$$C^{3+}(1s)^2(2p) \rightarrow C^{4+}(1s)^2 \quad \Delta H = W_p \qquad (27)$$

However, the orbitals in C^{3+} are smaller than those in neutral carbon and their binding energies correspondingly greater; the quantities W_s and W_p were therefore chosen to give a best fit to the energies of various states of neutral and singly ionized carbon.

We assume that the repulsion between two valence-shell electrons has the same value, regardless of the orbitals occupied by the electrons; for electrons of parallel spin, the repulsion is A^+, and for electrons of opposite spin, A^-. Thus the energy (E^1 or E^3) of a carbon atom in the singlet or triplet states $(1s)^2(2s)^2(2p)^2$, represented by single determinants with $S_z = 0$ or $\pm\hbar$, respectively, are given in eq 28 and 29. The

Singlet $(1s)(\overline{1s})(2s)(\overline{2s})(2p)(\overline{2p})$

$$E^1 = 2W_s + 2W_p + 2A^+ + 4A^- \qquad (28)$$

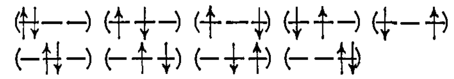
Triplet $(1s)(\overline{1s})(2s)(\overline{2s})(2p_x)(2p_y)$

$$E^3 = 2W_s + 2W_p + 3A^+ + 3A^- \qquad (29)$$

quantities A^+ and A^- are related to the one-center repulsion integrals by eq 14 and 15.

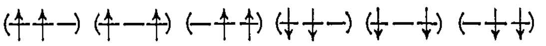
In order to estimate A^+ and A^- it is necessary to determine E^1 and E^3 from spectroscopic data. The single determinants in eq 28 and 29 do not of course correspond to true states of carbon. There are 15 possible configurations, corresponding to the possible partitions of two electrons between the three 2p AO's; these are indicated in (30) and (31). In our approximation, all

States with $S_z = 0$



(30)

States with $S_z = \pm\hbar$



(31)

the "singlet" configurations of (30) have the same energy E^1, while all those of (31) have energy E^3. In practice these 15 configurations correspond to the following 15 real states of carbon.

^1S, one state

^1D, five substates ($M = 2, 1, 0, -1, -2$)

^3P, nine substates ($M = 1, 0, -1;\ S = 1, 0, -1$) (32)

In order to obtain correct representations of these states, we should construct appropriate linear combinations of the configurations indicated in (30) and (31). Since configurations of different multiplicity do not mix, the six triplet states of (31) lead only to six substates of ^3P (those with $S_z = \hbar$ or $-\hbar$). Since these substates have the same energy (that of the state ^3P), we can equate this energy to A^+. The remaining states are the ^1S and ^1D states, and the three substates of ^3P with $S_z = 0$. These are represented by a set of nine orthogonal linear combinations of the configurations of (30) and (31). Now it is easily shown that the *total* energy of such a set of linear combinations is the same as the sum of the individual energies of the original configurations; the total energy of the nine configurations is of course $9E^1$, while that of the nine real states and substates is $[(^1S) + 5(^1D) + 3(^3P)]$, where (^1S), (^1D), and (^3P) are the energies of the corresponding states. Hence

$$E^1 = \frac{1}{9}[(^1S) + 5(^1D) + 3(^3P)] \qquad (33)$$

The configuration thus appears as a weighted mean or *barycenter*[5] of the appropriate states. The energies of barycenters can thus be calculated from spectroscopic data, and the results can then be used to determine the various one-center integrals A^+, A^-, W_s, and W_p.

This treatment of atoms may seem rather primitive, but it is fully justified by its practical success.[5] The number of appropriate barycenters for a given atom is usually greater than the number of parameters; the energies of all the barycenters are given well by this approach for a wide variety of different atoms.

In calculating the binding energy of a molecule, we naturally compare its calculated total energy with a sum of the energies of ground-state barycenters of the component atoms, for, since we use a single Slater determinant to describe the molecule, it would be inconsistent not to use a similar description for its component atoms.

(c) The one-electron resonance integral β_{kl} can be interpreted physically as the energy of an electron occupying the overlap cloud between the AO's ϕ_k and ϕ_l, and moving in the field of the core and remaining electrons. We would therefore expect β_{kl} to be proportional (a) to the magnitude of the overlap cloud, *i.e.*, to the overlap integral S_{kl}; (b) to some mean of the binding energies of the AO's ϕ_k and ϕ_l; (c) and to the distance between the overlap cloud and the nuclei of the atoms of which ϕ_k and ϕ_l are AO's. The last two conditions follow since the potential field in the overlap region arises mainly from the two atoms. We therefore adopted the following expression for β_{kl}.

$$\beta_{kl} = (\beta_{kl})_0 S_{kl}(I_k + I_l)[r_{kl}^2 + (\rho_k + \rho_l)]^{-1/2} \qquad (34)$$

Here I_k and I_l are the valence-state ionization potentials of the AO's ϕ_k and ϕ_l, calculated for the appropriate barycenters by the method of ref 5; r_{kl} is the internuclear distance between the atoms of which ϕ_k, ϕ_l are AO's; ρ_k and ρ_l are quantities appearing in the expressions for two-center repulsion integrals (see below); $(\beta_{kl})_0$ is a parameter to be determined empirically, being the same for all valence orbitals of a given atom. The overlap integrals S_{kl} were calculated in the usual way using Slater–Zener orbitals ($Z = 3.25$ for carbon). In order to reduce the number of parameters in the treatment, we assumed that β_0 has a common value β_{xy} for orbitals of two atoms x and y, regardless of the type of orbitals (s or p) and mode of overlap (σ or π), and that

$$\beta_{xy} = \sqrt{\beta_{xx}\beta_{yy}} \qquad (35)$$

Equation 34 is more complicated than the corresponding expressions used by other authors; we have tried a number of such simpler expressions, but with less success. Thus omission of the terms I_k and I_l leads to results for unsaturated molecules such as ethylene in which the orbitals appear in the wrong order of energy; it is essential to use different values of β for s and p AO's. Again, omission of the term in r gave heats of formation for acetylene that were much too low; it is apparently necessary to use for β an expression that increases more rapidly with decreasing bond length than does the corresponding overlap integral.

(d) The two-center integrals $(\phi\phi,\psi\psi)$ were estimated in two different ways, one for the CNDO calculations and one for the PNDDO approximation. The integral $(\phi\phi,\psi\psi)$ must in each case obey two boundary conditions. As the internuclear distance r tends to zero, the integral should approximate to a one-center repulsion integral, while, when $r \rightarrow \infty$, the integral should approximate to e^2/r.

In the CNDO calculations, we adopted expression 36, one which has been used successfully in previous work.[3,5] Here ρ_k and ρ_l are constants characteristic

$$\gamma_{kl} = e^2[r_{kl}^2 + (\rho_k + \rho_l)^2]^{-1/2} \qquad (36)$$

of the two atoms, chosen to make γ_{kl} approach the corresponding one-center integral as $r_{kl} \rightarrow 0$; *i.e.*

$$2\rho_k = e^2/A_k^- \qquad 2\rho_l = e^2/A_l^- \qquad (37)$$

In the second approach, different values were assumed for the integral γ_{kl}, depending on the nature of the orbitals involved and their mode of overlap. Two arguments guided us in choosing a suitable expression for the integrals. First, an analysis of the role of electron correlation, using a model[5] similar to that invoked in the SPO approach,[6] suggested that the integrals should fall into three distinct groups, *i.e.*, (38)–(40).

I. correlation large: sσ:sσ; pπ:pπ; sσ:pπ (38)

II. correlation medium: sσ:pσ; pσ:pπ (39)

III. correlation small: pσ:pσ (40)

Secondly, this subdivision of the integrals also appears in the values estimated theoretically, using Slater–Zener orbitals;[7] these are shown in Table I.

Table I. Values for Carbon–Carbon Two-Center Repulsion Integrals

		Value of integral, ev	
Class	Type	Calcd using Slater–Zener AO's	Calcd from (41)–(43)
1	sσ:sσ	9.28	
	sσ:pπ	9.12	7.13
	pπ:pπ	8.98	
	p$\pi(x)$:p$\pi(y)$	8.98	
2	sσ:pσ	9.61	7.81
	pπ:pσ	9.41	
3	pσ:pσ	9.99	8.45

Our object was to duplicate this pattern, subject to the condition that the integral (ii,kk) between orbitals of two identical atoms should converge to the corresponding one-center integral (ii,ii) at zero internuclear separation. The expressions we adopted are given in eq 41–43, where in class II, the orbital ϕ_k is the one of

Class I

$$(ii,kk) = e^2[r_{ik}^2 + (\rho_i + \rho_k)^2]^{-1/2} \qquad (41)$$

Class II

$$(ii,kk) = e^2[r_{ik}^2 + (\rho_i + \rho_k T_{ik})^2]^{-1/2} \qquad (42)$$

Class III

$$(ii,kk) = e^2[r_{ik}^2 + (\rho_i T_{ik} + \rho_k T_{ik})^2]^{-1/2} \qquad (43)$$

the $\rho\sigma$ type, and where

$$T_{ik} = e^{-r_{ik}/2(\rho_i+\rho_k)} \qquad (44)$$

The values calculated in this way for carbon atoms at an internuclear distance of 1.55 A are listed in the last column of Table I.

(e) Core Repulsion. Having calculated the total electronic energy (E_{el}), we can then find the total energy of a molecule by adding to this the core repulsion. Our last problem is to decide how to calculate this.

In the π calculations, the repulsion between two cores M and N was set equal to the corresponding two-center repulsion integral; however, if we try to do this in the present case, we find that the molecule collapses to a point. The repulsion between point charges (*i.e*,, the nuclear repulsion) is much greater at short distances than is the corresponding repulsion between clouds of charge representing occupied orbitals; this enhanced repulsion is one of the factors that keeps the atoms in a molecule at bond's length. In the π calculations, this difficulty did not arise since we assumed Morse functions for the σ components of bonds; here our calculations include all the valence electrons, so there is no escape.

Nor is it satisfactory to set the core repulsion equal to a point charge potential, *i.e.*, to $Z_M Z_N e^2/R$, where Z_M and Z_N are the nuclear charges, for in this case the calculated binding energy is too small. The reason for this is implied in the literature. Consider for example H_2. The potential field in which the electrons move is greater than that in an isolated hydrogen atom; consequently, the orbitals of H_2 are more compact than one would expect for a combination of ordinary 1s hydrogen AO's. Indeed, if we carry out an orbital treatment, regarding the nuclear charges (Z) as variation parameters, we find the best agreement with experiment given by a value of Z considerably greater than unity. In our treatment, where the "atomic" parameters are fixed from spectroscopic data for isolated atoms, we assume in effect that the effective nuclear charge is the same for each atom in isolation as it is when the atom forms part of a molecule. In order to get realistic binding energies, either we must abandon this assumption or we must make some allowance for it by compensating changes in the other parameters. In this case the changes are best made in the nuclear repulsion, because this does not affect calculations of the electron distribution or orbital energies.

We therefore calculated the core repulsion from an appropriate parametric function. The function chosen must satisfy two boundary conditions. For large r_{ik}, it must approach the corresponding interelectronic repulsion between neutral atoms in order that the net potential due to a neutral atom should vanish at large distances, while for small r_{ik} it must have a value between this and that calculated for point charges. We

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[6] See M. J. S. Dewar and N. L. Sabelli, *J. Phys. Chem.*, **66**, 2310 (1962).

[7] We are grateful to Dr. F. A. Matsen for these values.

have tried a large number of possible one-parameter functions of this type; the most successful was that of

$$C_{\mathrm{MN}} = E_{\mathrm{MN}} + [Z_{\mathrm{M}}Z_{\mathrm{N}}e^2/r_{\mathrm{MN}} - E_{\mathrm{MN}}]e^{-\alpha_{\mathrm{MN}}r_{\mathrm{MN}}} \quad (45)$$

eq 45. Here C_{MN} is the core repulsion between atoms M and N; E_{MN} is the corresponding electronic repulsion between neutral atoms M and N (*i.e.*, (*kk*,*mm*) summed over the valence orbitals); Z_{M} and Z_{N} are the formal core charges in units of *e* (*i.e.*, the number of valence electrons) of the two atoms; α_{MN} is a parameter. In order to reduce the number of parameters in the treatment, we assumed (*cf.* eq 35) that the value of α_{MN} for two dissimilar atoms M and N is given in terms of the parameters α_{MM} and α_{NN} for pairs of similar atoms by

$$\alpha_{\mathrm{MN}} = \sqrt{\alpha_{\mathrm{MM}}\alpha_{\mathrm{NN}}} \quad (46)$$

Our treatment contains very few "molecular" parameters, *i.e.*, parameters whose value has to be determined from data for molecules rather than atoms. There are just two molecular parameters for each kind of atom X, *i.e.*, the parameter β_{XX} that appears in the expression for one-electron resonance integrals involving orbitals of X, and the parameter α_{XX} that appears in the expressions for corresponding core repulsion.

The attraction between an electron in an AO *i* of one atom M and the core of atom N, was set equal to *minus* the sum of repulsions between the electron and the valence electron of N (*cf.* the corresponding approximation in the π treatment[3]).

Application to Hydrocarbons

The method outlined above has been applied to a variety of hydrocarbons. The general procedure was as follows: (a) the parameters β_{HH} and α_{HH} were chosen to give the correct internuclear distance and bond energy in H_2; (b) assuming various values for β_{CC}, α_{CC} was chosen to give the correct heat of formation for CH_4; (c) heats of formation were then calculated for acetylene, ethane, and propane, using the values of β_{HH} and α_{HH} from step a, and with the various pairs of values for β_{CC} and α_{CC} from step b; (d) having thus established optimum values for the parameters, calculations were carried out for a number of other saturated and unsaturated hydrocarbons.

In order to apply this treatment, it is necessary to know the Cartesian coordinates of the atoms in a molecule; these must be calculated from the known (or assumed) bond lengths and bond angles. In our case the positions of the atoms are specified by the bond lengths, bond angles, and dihedral angles of the bonds in the molecule; we have written a program whereby the coordinates of the atoms are calculated from these data. In the calculations reported below, we assumed tetrahedral geometry for sp^3 carbon and trigonal geometry for sp^2 carbon (bond angles, 120°). The assumed bond lengths are shown in Table II. The values for the parameters in the treatment are listed in Table III, while Table IV compares calculated and observed heats of formation for the various compounds. Except when otherwise stated, saturated C_2 units were assumed to have the conformation observed for propene (*i.e.*, one sp^3 CH bond eclipsing the C=C bond). Other calculated quantities will be found below (see Discussion).

Table II. Bond Lengths for CC and CH Bonds

Bond	Hybridization	Length, nm
C—C	sp^3–sp^3	0.1534
	sp^2–sp^2	0.1520
	sp^3–sp	0.1459
	sp^2–sp^2	0.1483
C$\overset{...}{-}$C	(Aromatic)	0.1397
C=C	. . .	0.1337
C≡C	. . .	0.1205
C—H	sp^3	0.1093
	sp^2	0.1083
	(Benzene)	0.1084
	sp	0.1059

Table III. Parameters for Carbon and Hydrogen

Atom	β_{XX}, pm	α_{XX}, nm^{-1}
C	45.84	47.08
H	27.87	14.8

Table IV. Comparison of Calculated and Observed Heats of Formation (ΔH_f) of Hydrocarbons from Atoms in the Gas Phase at 25°

	ΔH_f, kcal/mole		
Compound	Obsd[a]	Calcd	$\delta\Delta H_f$[b]
Ethane	674.6	677.3	2.7
Ethane (eclipsed)	671.7[c]	676.5	4.8
Propane	954.3	957.3	3.0
n-Butane	1234.7	1237.5	2.8
n-Pentane	1514.7	1517.6	2.9
Isobutane	1236.7	1236.8	0.1
Isopentane	1516.6	1516.3	−0.3
Cyclopropane[d]	812.6	809.1	−3.5
Cyclohexane (chair)	1680.0	1680.2	0.2
Cyclohexane (boat)	1678.0[e]	1674.9	3.1
Ethylene	537.7	540.1	2.4
Propene	820.4	822.6	2.2
cis-2-Butene	1102.0	1101.4	−0.6
trans-2-Butene	1103.0	1103.4	0.4
trans-1,3-Butadiene	969.8	971.6	1.8
cis-1,3-Butadiene	967.5[f]	971.3	3.8
Benzene	1318.1	1314.0	−4.1
Allene	675.2	697.2	22.0
Acetylene	391.8	414.0	22.2
Methylacetylene	676.8	704.4	27.6

[a] The thermochemical data are taken from Rossini except where otherwise stated. [b] Difference between calculated and observed heats of formation in kcal/mole. [c] Calculated from the value for staggered ethane, using the experimentally determined height (2.9 kcal/mole) of the rotational barrier; see D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958). [d] Heat of formation calculated for structure with D_{3h} symmetry; see H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **20**, 264 (1966). [e] Calculated from the value for chair conformation, using the experimental value (5.2 kcal/mole) for the heat of conversion to the boat conformation; see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. [f] Calculated from the observed difference in energy between the *cis* and *trans* isomers; see Table V.

Invariance to Rotation

As has been pointed out, the treatment used here is not strictly invariant to choice of coordinate axes, due to the neglect of repulsion integrals involving four p AO's of two different atoms. Four lines of argument suggested, however, that variations of this kind should be small. Firstly, integrals of this type represent quadrupole–quadrupole repulsions and are consequently much smaller than the charge–charge repulsions corresponding to "normal" repulsion integrals; even in the case of adjacent carbon atoms, the integrals have values[7] of only about 0.1 ev. Secondly, the effect of changing the coordinate axes appears only as secondary changes in the values of these integrals, and the net effect in the sum of the integrals between a given pair of atoms should consequently be small. Thirdly, the integrals between a given pair of atoms do not all have the same sign; the resulting cancellations will further reduce their net contribution to the total energy and so likewise to its variation with choice of axes. And finally, the integrals in question, representing as they do higher multipole repulsions, decrease very rapidly with distance; integrals between nonadjacent atoms are essentially negligible.

Obviously, however, these arguments needed to be checked experimentally. We therefore repeated the calculations for a number of molecules in various orientations relative to the coordinate axes; in each case the eigenvalues, total energies, charge densities, and bond orders were identical with the accuracy with which they are printed (seven significant figures in the total energy, four in the other quantities). As a further check, we carried out calculations for carbon monoxide and hydrogen cyanide in various orientations; here again the results were quite unaffected by choice of coordinate axes, although these molecules contain heteroatoms and the neglected quadrupole–quadrupole integrals should be greatest for triple bonds since these are so short. It seems clear from these results that our procedure is for all practical purposes invariant to rotation of the coordinate axes, any variations being entirely negligible.

Discussion

The agreement between the calculated and observed heats of formation in Table IV is rather remarkable, the differences in most cases being less than 4 kcal/mole (0.15 ev). The only serious discrepancies (~1 ev) occur in the case of allene and the acetylenes; these are probably due to our use of a nuclear potential which does not increase sufficiently rapidly at short distances. Thus our method correctly predicts the heat of formation (and so by implication the strain energy) of cyclopropane, in which the bonds are single; on the other hand, attempts to calculate bond lengths, by minimizing the total energy of a molecule with respect to them, have given values which are much too small.

Several other qualitative checks also seem satisfactory. Thus ethane is correctly predicted to be most stable in the staggered conformation, cyclohexane in the chair conformation, and 2-butene and 1,3-butadiene in *trans* configurations; previous SCF MO calculations for 1,3-butadiene had incorrectly predicted the *cis* form to be more stable.[8]

Admittedly the differences in energy are not predicted exactly; this is clear from the data listed in Table V. In one case our procedure even leads to a qualitatively incorrect prediction, *i.e.*, that normal paraffins should be more stable than their branched isomers, while the predicted barrier to rotation in ethane is too small. Nevertheless, the over-all picture is very encouraging, given that the work described here represents only a preliminary approach to the problem and given that the errors in the calculated heats of formation are less by two orders of magnitude than those derived from other recent SCF MO calculations.[4,9]

Table V. Comparisons of Energies of Isomeric Hydrocarbons

Reaction	Energy change, kcal/mole Calcd	Obsd
Ethane (staggered → eclipsed)	0.8	2.9
1,3-Butadiene (*trans* → *cis*)	0.3	2.2[a]
2-Butene (*trans* → *cis*)	2.0	1.0
Cyclohexane (chair → boat)	2.0	5.3
n-Butane → isobutane	−2.0	0.7
n-Pentane → isopentane	−1.9	1.3

[a] J. G. Aston, *Discussions Faraday Soc.*, **10**, 73 (1951).

The objective of these calculations was admittedly different from ours. Both Pople and Segal[4] and Lipscomb, *et al.*,[9] were trying to devise some simple semiempirical MO procedure that would reproduce the results to be expected from an *a priori* Roothaan-type approach. The parameters were therefore chosen in such a way as to make the results of the two calculations agree for small molecules where *a priori* calculations have, or could, be made. This procedure of course ensured that the semiempirical treatments would give poor estimates of heats of formation, seeing that heats of formation calculated by the Hartree–Fock method are known to be very inaccurate.

Another check on our work is provided by the photoionization potentials measured for various hydrocarbons by Al-Joboury and Turner.[10] The ionization potentials of a molecule should, according to Koopman's theorem, be approximately equal to the calculated orbital energies; Table VI shows that this parallel exists in a remarkable way for a variety of hydrocarbons and for all measured ionization potentials up to about 19 ev. The photoionization spectra show numerous peaks in this region, due to the possibility of producing ions in vibrationally excited states; our calculations suggest that in several cases Turner, *et al.*,[10] may have mistaken multiple peaks as being due to different vibrational states of a single ion, rather than to two or more different ions of similar energy. Similar difficulties arise in attempts to correlate observed electronic spectra of molecules with calculated excitation energies.

The last column of Table VI shows orbital energies calculated by Palke and Lipscomb[9b] by an *a priori* SCF LCAO MO method, using the POLYATOM program. It will be seen that their orbital energies run parallel to ours but are in general greater; the correlation with measured photoionization potentials is clearly poor. Another comparison of this kind is provided by the population analyses shown in Table VII; here again our values run parallel to those given by the *a priori* procedure and also to those reported by Pople and Segal.

Our method predicts small dipole moments for several of the compounds studied; values are listed in Table VIII. The available experimental evidence (last column

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(8) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

(9) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353, 2361, 2367 (1966); (b) W. E. Palke and W. N. Lipscomb, *ibid.*, **88**, 2384 (1966).

(10) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 5141 (1963); 4434 (1964); 616 (1965).

Table VI. Comparisons of Ionization Potentials with Orbital Energies

Compound	Ionization potential, ev	Orbital energy, ev This paper	Ref 9b
Methane	12.99	13.88	14.74
Ethane	11.49	12.51	13.08
		13.04	13.38
	14.74	14.98	16.15
	19.18	20.80	22.51
Ethylene	10.48	10.86	10.09
		12.76	13.77
	12.50	12.94	15.28
	14.39	15.25	17.51
	15.63		
	19.13	19.18	21.28
Acetylene	11.36	11.06	11.03
	16.27	13.63	17.85
	18.33	18.08	20.44
Propane	11.07	12.01	
		12.49	
		12.85	
	13.17	13.73	
		13.90	
	15.17	14.68	
	15.70	15.46	
	18.57	19.67	
n-Butane	10.50	11.63	
		12.39	
	12.36	12.78	
		13.07	
		13.21	
		14.13	
	14.13	14.36	
		14.47	
	15.69	15.79	
Isobutane	10.78	11.88	
		12.54	
	12.54	13.48	
		13.79	
	14.51	14.59	
		15.40	
	18.63	18.68	
Cyclohexane	9.79	11.51	
	11.33	12.23	
		12.59	
	12.22	12.69	
		13.48	
	14.37	15.10	
		15.51	
Benzene	9.25	10.15	
	11.49	11.54	
	12.19	12.72	
		12.86	
	13.67	13.45	
	14.44	15.67	
	16.73	16.07	
	18.75	18.98	
1,3-Butadiene (*trans*)	9.08	10.16	
	11.25	11.70	
		11.83	
	12.14	12.58	
		13.09	
	13.23	14.39	
		14.71	
	18.78	17.99	
		19.24	

Table VII. Population Analyses for Hydrocarbons

		Population		
Compound	Orbital	This paper	Ref 9b	Ref 3
Methane	H	1.077	0.876	0.965
	C2s	1.136	1.274	1.081
	C2p	0.852	1.088	1.020
Ethane	H	1.064	0.876	0.967
	C2s	1.199	1.248	1.042
	C2pσ	0.872	0.981	1.007
	C2pπ	0.865	1.074	1.044
Ethylene	H	1.033	0.860	0.954
	C2s	1.243	1.197	...
	C2pσ	0.844	1.013	
	C2pπ	0.845	1.072	...
	C2pπ*(a)	1.000	1.000	...
Acetylene	H	0.941	0.812	0.893
	C2s	1.263	1.105	
	C2pσ	0.797	1.086	...
	C2pπ	1.000	1.000	...

Table VIII. Calculated and Observed Dipole Moments of Hydrocarbons

	Dipole moment, D.	
Compound	Calcd	Obsd
Propane	0.03	0.08[a]
Isobutane	0.05	0.13[b]
cis-2-Butene	0.08	...
Propyne	0.24	0.75[c]
cis-1,3-Butadiene	0.04	...

[a] D. R. Lide, *J Chem. Phys.*, **33**, 1879 (1960). [b] A. A. Maryott and G. Birnbaum, *ibid.*, **24**, 1022 (1956); D. R. Lide and D. E. Mann, *ibid.*, **29**, 914 (1958). [c] F. J. Krieger and H. H. Wenzek, *J. Am. Chem. Soc.*, **60**, 2115 (1938).

of Table VIII) suggests that the calculated moments are of the right order of magnitude.

Summary

While the results reported here are preliminary in nature,[11] they are sufficient to suggest that this kind of approach has exciting possibilities. It seems very likely that it may be improved to a point where heats of formation, etc., of molecules of all kinds may be predicted with an accuracy comparable with that already achieved for conjugated hydrocarbons, using the Hückel approximation. If so, the impact on chemistry would be considerable, for not only would one be able to calculate heats of formation and reaction with "chemical" accuracy, but it would also be possible to predict reaction mechanisms and rates of reaction.

Our results represent a considerable improvement over those of previously reported investigations. The main factors responsible for this seem to be the following: (a) our treatment of the internuclear repulsion as a parameter to allow for the effects of orbital contraction (if the repulsion is treated as one between point charges, the calculated heats of formation must inevitably be too small); (b) our use of different integrals for s and p AO's of a given center, together with a sufficient inclusion of integrals involving one-center differential overlap to make the calculations effectively invariant to choice of coordinate axes; (c) our use of thermochemical data to fix the parameters in our treatment, rather than the results of *a priori* calculations.

There are several obvious ways in which this general approach could be modified and extended, in particular the use of Hartree–Fock AO's in the calculation of over-

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(11) For this reason we have not reported the results (*e.g.*, eigenvalues, eigenvectors, bond orders, etc.) in detail; we will be happy to communicate them to anyone interested.

lap integrals and the use of separate parameters for different types of bonds in place of the approximations of eq 35 and 46. We are studying these and other analogous possibilities, and we are also extending our treatment to include all integrals involving one-center differential overlap (NDDO approximation[5]) in case this should prove necessary in treating molecules containing heteroatoms.

Reversible Photoisomerization of 1,2-Bis(9-anthryl)ethane[1]

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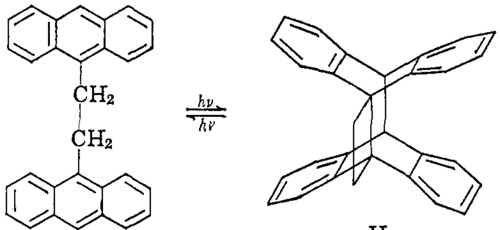
Contribution from the Division of Physical Chemistry, University of Minnesota, Minneapolis, Minnesota. *Received January 21, 1967*

Abstract: The hydrocarbon 1,2-bis(9-anthryl)ethane (I) is photoisomerized efficiently and reversibly. The isomeric product (II) does not absorb appreciably at wavelengths longer than 260 mμ. The quantum yields of the forward and back reactions (0.19 and 0.42, respectively) are independent of the concentration of the reactant. Compound I is strongly fluorescent with maxima at 408, 436, and 460 mμ, and a fluorescent quantum yield of about 0.37. Flash illumination of its deoxygenated solutions produces an absorption transient, similar to but not identical with the lowest triplet of anthracene. No attempt was made to observe the fluorescence or triplet formation of the isomer (II).

The hydrocarbon 1,2-bis(9-anthryl)ethane (I) is efficiently and reversibly photoisomerized.[3] The detailed structure of the photoproduct (II) has not been established definitely. However, as was clearly stated by Roitt and Waters,[3a] its ultraviolet absorption spectrum is in general similar to that of dianthracene,[4] demonstrating that in II the conjugation of the anthracene rings is interrupted. It was postulated[3a] that II is a dimer of I, but molecular weight determinations (with a Mechrolab osmometer[3b]) prove that it is an isomer rather than a dimer of I. Our present finding, that the quantum yields of the photochemical reactions are independent of the concentrations of the reactants, confirms this conclusion unambiguously. Physical evidence (nmr, infrared, and mass spectrographic measurements[5]) is consistent with formula II.



I   II

Compound II is stable at room temperature (in the absence of ultraviolet radiation) but isomerizes at its melting point, re-forming I.

Since the product II does not absorb appreciably at wavelengths longer than 260 mμ, the quantum yield of the forward reaction was measured directly, using light of 365 mμ. The quantum yield of the reverse reaction was estimated from the extinction coefficients, the quantum yield of the forward reaction, and the composition of a steady-state mixture, prepared by prolonged exposure to 254 mμ.

Experimental Section

Methods and Materials. Materials. The 1,2-bis(9-anthryl)-ethane was furnished by Dr. S. Fenton (University of Minnesota). It was recrystallized from *n*-hexane before use. The cyclohexane was Fisher Spectro Grade and was used without further purification.

Determination of Quantum Yields. The intensity of the absorbed light was determined by the use of a ferrioxalate actinometer, following the procedure outlined by Parker.[6] The absorption of the incident light was practically complete, except for those experiments made with the most dilute solutions; for these, the per cent absorption was calculated from the extinction coefficients. Light of the required wavelengths was isolated from the radiation of a Hanovia S-100 mercury arc, using combinations of glass, solution, and Cl_2 gas filters.[7]

Optical Measurements. The absorption spectra were measured with a Cary 15 spectrophotometer. The fluorescence spectrum was measured by T. Bednar of this department, using a deaerated, 5×10^{-6} *M* solution of I in cyclohexane and exciting light of 370 mμ. The fluorescence was observed at right angles to the exciting beam. The spectral resolution of the fluorimeter was estimated to be 10 A. The spectrum was corrected for variation of the sensitivity of the apparatus with wavelength but not for reabsorption, which probably seriously distorted the curve at wavelengths shorter than 400 mμ. Qualitatively similar results were obtained by K. S. W., using a manually operated spectrofluorimeter.[7]

Results

The absorption and fluorescence spectra of I are shown on Figure 1; the absorption spectrum of its isomer (II) is shown on Figure 2. The quantum yield of fluorescence of I was estimated to be 0.37, by comparing its total emission to that from anthracene, for which the fluorescence yield (measured under similar conditions) is 0.31.[8]

Carefully deoxygenated, 10^{-5} *M* solutions of I exhibited large transient changes in absorption, when

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