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Ground States of Conjugated Molecules. XI.[1] Improved Treatment of Hydrocarbons[2]

Michael J. S. Dewar[3] and Carlos de Llano

Contribution from the Department of Chemistry,
The University of Texas, Austin, Texas 78712. *Received July 25, 1968*

Abstract: Previous papers of this series[1,4] have shown that the heats of formation of conjugated hydrocarbons, and of conjugated organic molecules containing nitrogen and/or oxygen, can be calculated with "chemical" accuracy by a semiempirical SCF–MO treatment based on the Pople[5] method. The key feature of this is the use of a thermocycle[6] to determine the one-electron core resonance integrals, previous workers having estimated these from spectroscopic data. In the previous papers,[4] however, the bond energies of σ bonds were treated as independent parameters, rather than ascribed the values calculated in the thermocycle.[6] This inconsistency has now been removed for calculations involving hydrocarbons, simultaneously reducing the number of parameters in the treatment, extending the calculations more reliably to compounds (*e.g.*, polyenes) in which there is strong bond alternation, and increasing the accuracy of the results. The calculated heats of formation seem to agree with experiment to within the claimed limits of experimental error in almost every case, if allowance is made when necessary for ring strain.

Previous papers[1,4] of this series have described a semiempirical SCF–MO treatment of conjugated systems which allows their heats of formation and geometries to be calculated with quite unexpected accuracy. The results of these calculations agreed with experiment to within the limits of experimental error in almost every case, and the exceptions mostly referred to strained molecules where the observed heats of atomization were smaller than those calculated by amounts that could reasonably be attributed to ring strain. Here we describe a further refinement of the treatment of hydrocarbons which simultaneously reduces the number of parameters, increases the accuracy of the results, and allows the treatment to be extended with greater certainty to molecules in which there is a marked alternation of bond lengths.

The treatment is essentially a version of the Pople method,[5] *i.e.*, an SCF–LCAO–MO approximation in which differential overlap is neglected and in which the σ electrons are regarded as localized. Previous calculations of this kind had given very disappointing results for the ground-state energies of molecules, and it had been supposed that these shortcomings were an inevitable consequence of deficiencies in the whole theoretical approach. However, we were able to show that the fault lay rather in the procedures used to estimate the one-electron core resonance integrals (β), previous workers having used values determined from spectroscopic data. Such values are inappropriate to calculations for ground states. We[4] used instead a procedure devised by Dewar and Schmeising,[6] in which β is found by comparing the calculated and observed heats of formation ($E_{\pi b}$) of the π bond in ethylene, $E_{\pi b}$ being determined as a function of bond length from the following thermocycle.

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[1] Part X: M. J. S. Dewar and J. Klemen, *J. Chem. Phys.*, 49, 499 (1968).

[2] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[3] Author to whom inquiries should be addressed.

[4] (a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, 42, 756 (1965); (b) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965); (c) *ibid.*, **87**, 692 (1965); (d) M. J. S. Dewar and C. C. Thompson, Jr., *ibid.*, **87**, 4414 (1965); (e) M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, **21**, 1817 (1956); (f) *ibid.*, **21**, 3423 (1965); (g) *J. Chem. Phys.*, **44**, 759 (1966); (h) M. J. S. Dewar, G. J. Gleicher, and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **88**, 1349 (1966); (i) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965); (j) *Tetrahedron Letters*, 4503 (1965); (k) M. J. S. Dewar, J. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968).

[5] J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953).

[6] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

$$\begin{tikzcd}
\mathrm{C}\overset{r'}{-}\mathrm{C} \arrow[r, "c'"] \arrow[rrr, bend right, "-E^0_{\mathrm{C=C}} + E^0_{\mathrm{C-C}}"'] & \mathrm{C}\overset{r}{-}\mathrm{C} \arrow[r, "E_{\pi\mathrm{b}}"] & \mathrm{C}\overset{r}{=}\mathrm{C} \arrow[r, "-c''"] & \mathrm{C}\overset{r''}{=}\mathrm{C}
\end{tikzcd} \qquad (1)$$

Here $E^0_{\mathrm{C-C}}$ and r' are respectively the bond energy and bond length of a pure σ bond between sp^2-hybridized carbon atoms, $E^0_{\mathrm{C=C}}$ and r'' are corresponding quantities for the double bond, and c' and c'' are respectively the energies required to compress a single bond or stretch a double bond to the length r at which β is to be estimated. (Note that here, and in the following paragraphs, there are apparently strange inversions of sign, due to the convention that bond energies are positive, while heats of formation, and quantities such as $E_{\pi\mathrm{b}}$, are negative.)

The heat of atomization (ΔH_{a}) of a conjugated hydrocarbon can be written in the form

$$-\Delta H_{\mathrm{a}} = n_{\mathrm{H}}E_{\mathrm{CH}} + \Sigma E^r_{\mathrm{C-C}} - E_{\pi\mathrm{b}} \qquad (2)$$

where n_{H} is the number of CH bonds of bond energy E_{CH}, $E^r_{\mathrm{C-C}}$ is the bond energy of a C=C σ bond of length r, and $E_{\pi\mathrm{b}}$ is the total π-bond energy, calculated by the SCF-MO treatment. The σ-bond energies are of course automatically estimated in the course of determining β, being given by

$$E^r_{\mathrm{C-C}} = E^0_{\mathrm{C-C}} - c' \qquad (3)$$

In the previous papers[4] of this series, however, the program indicated above was not carried out in its entirety, for the σ-bond energy of a C=C σ bond in an aromatic ring was treated as an independent parameter, being assigned a value slightly different from that given by eq 3. Not only did this assumption increase the number of parameters in the treatment, but it also made it difficult to carry out calculations for molecules (*e.g.*, polyenes) in which there is a marked variation in the lengths of bonds. We have now removed this inconsistency, thus increasing the validity of the treatment and reducing the number of parameters in it. Surprisingly, and very gratifyingly, this has simultaneously led to improved agreement with experiment.

Theoretical Approach

The theoretical basis of our treatment has been discussed in detail[4a,b] and need not be repeated. Here we shall be concerned only with the choice of parameters in treating hydrocarbons. Furthermore, the methods used to estimate the one-center integrals (valence-state ionization potentials W_i and one-center repulsion integrals (ii,ii)) and the two-center repulsion integrals (ii,jj) were clear-cut and not open to simple modification, although we have, for reasons indicated below, used values slightly different from those in the preceding papers; our main concern has therefore been with the estimation of the one-center core resonance integrals ($\beta_{ij}{}^{\mathrm{c}}$), and with the possible need for introducing corrections for vertical correlation by the SPO treatment described in parts I[4a] and II.[4b]

In order to estimate $\beta_{ij}{}^{\mathrm{c}}$ from the thermocycle of eq 1, six quantities need to be known, *i.e.*, $E^0_{\mathrm{C-C}}$, r', a', $E^0_{\mathrm{C=C}}$, r'', and a'', where a' and a'' are the Morse constants for a C—C σ bond and for a C=C double bond. Of these only r'' and a'' are known directly from experiment, a'' being found from the force constant for the C=C bond in ethylene, and r'' being the bond length. The corresponding double-bond energy cannot be determined directly, although it is subject to the condition

$$4E_{\mathrm{CH}} + E^0_{\mathrm{C=C}} = -\Delta H_{\mathrm{a}}(\text{ethylene}) \qquad (4)$$

The quantities $E^0_{\mathrm{C-C}}$, r', and a' cannot be measured directly since they refer to a theoretical abstraction (a pure C—C σ bond) rather than to any bond occurring in any real molecule. The only feasible procedure seems[4a] to be to estimate r' from an assumed relation between bond order (p) and bond length (extrapolated to zero bond order), and then to estimate $E^0_{\mathrm{C-C}}$ and a' from r' by using empirical relations between bond energy and bond length, and between force constant and bond length, for carbon–carbon bonds.

The available evidence suggests[6] that the p/r relation is linear for carbon–carbon bonds, the points for benzene, graphite, and ethylene lying on a straight line within the limits of experimental error. There is, however, a residual uncertainty due to uncertainty in the length of the C=C bond in ethylene, the experimental values (1.333,[7] 1.337,[8] and 1.339 Å[9]) varying over a range of 0.006 Å. The corresponding p/r plots on extrapolation give values for r' varying from 1.509 to 1.524 Å.

Various forms have been suggested for the bond energy–bond length relation for carbon–carbon bonds; we have adopted the tractrix equation of Dewar and Schmeising,[6] *viz.*

$$r = \frac{1}{b}\{a \ln [a + (a^2 - D^2)^{1/2}] - a \ln D - (a^2 - D^2)^{1/2}\} \qquad (5)$$

where D is the bond energy, r is the bond length, and a and b are parameters. For the present purpose, the parameters a and b are most logically determined by fitting the bond length and bond energy for the C–C bond in diamond (where both quantities are known unambiguously) and in ethylene (where the values are required explicitly in the thermocycle).

The last relation required is the one between force constant (k) and bond length; following most previous workers, we have used an inverse power series, *viz.*

$$k = \frac{A}{r^2} + \frac{B}{r^4} + \frac{C}{r^6} \qquad (6)$$

The parameters A, B, and C can be found by fitting data for ethane, ethylene, and acetylene. Here again the results depend on the value assumed for r''.

Using this framework, our treatment then depends on the choice of just two quantities, $E^0_{\mathrm{C=C}}$ and r'', the values chosen being such as to conform to the experimental data for ethylene. In practice, this corresponds to a choice of $E^0_{\mathrm{C=C}}$ that makes E_{CH} close to 102 kcal/mole (see eq 4), and a value of r'' in the range 1.334–1.339 Å.

Choice of Parameters. The quantities which have to be determined[4a] in order to apply eq 2 to hydrocarbons are the one-center integrals W_{c} and $(ii,ii)_{\mathrm{c}}$, the

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(7) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959).

(8) H. C. Allen and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958).

(9) See C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

two-center repulsion integrals (ii,jj), and the quantities appearing in the thermocycle for determining β_{ij}^c (eq 1). In calculating heats of atomization, W_c can be ignored, since terms involving W_c cancel when one subtracts from the total energy of a molecule the total energy of the atoms of which it is composed.

As in previous papers,[4] W_c and (ii,ii) were found by the Pariser–Parr procedure;[10] here, however, we have used the valence-state ionization potential and electron affinity for carbon recommended by Hinze and Jaffé[11] for the sake of uniformity, since we have used their values for nitrogen and oxygen in calculations for heteroconjugated molecules (see the following paper of this series, and ref 4g). The corresponding values for W_c and $(ii,ii)_c$ are

$$W_c = 11.16 \text{ eV}; \quad (ii,ii)_c = 11.13 \text{ eV} \tag{7}$$

The two-center repulsion integrals (ii,jj) were found by the uniformly charged sphere approximation used previously.[4] In the general case, a distinction is drawn (SPO approximation) between integrals $(ii,jj)^J$ arising from expansions of molecular Coulomb integrals $J_{\mu\nu}$, and integrals $(ii,jj)^K$ arising from expansions of molecular exchange integrals $K_{\mu\nu}$. In the case of carbon atoms

$$(ii,jj)^K = ae^2(r_{ij}^2 + R^2)^{-1/2} + (1 - a)e^2/r_{ij} \tag{8}$$

$$(ii,jj)^J = \frac{1}{2}[(ii,jj)^K + e^2(r_{ij}^2 + R^2)^{-1/2}] \tag{9}$$

where

$$R = e^2/(ii,ii) \tag{10}$$

The value of the mixing parameter (a) determines the allowance made for vertical correlation; setting $a = 1$ leads to the conventional Pople approximation in which the J- and K-type integrals have a common value

$$(ii,jj)^J = (ii,jj)^K = e^2(r_{ij}^2 + R^2)^{-1/2} \tag{11}$$

Ohno[12a] and Klopman[12b] have also used this approximation for repulsion integrals in Pople calculations.

The quantities in eq 1 were determined by assuming values for $E^0_{\text{C=C}}$ and r'' and using the empirical relationships indicated in the previous section. Calculations were carried out with various sets of values for $E^0_{\text{C=C}}$ and r'', covering the whole acceptable range, and also with varying values of a in eq 8 and 9. Each set of parameters was tested by comparing the calculated heats of atomization of ten aromatic hydrocarbons (I–X), for which reliable thermochemical data are available, with experimental values.

The best results were given by a Pople-type treatment (*i.e.*, $a = 1$ in eq 8 and 9) with $E^0_{\text{C=C}} = 128.2$ kcal/mole and $r'' = 1.338$ Å. This value for $E^0_{\text{C=C}}$ leads to a bond energy of just the expected magnitude (102.2 kcal/mole), while the value for r'' is the mean of the two most reliable (spectroscopic) determinations[8,9] of the bond length in ethylene.

It is therefore unnecessary to introduce the additional parameter a in eq 8 and 9, corresponding to the SPO approximation. Since the SPO idea was introduced[13] solely with the object of improving semiempirical calculations at a time when the results given by them seemed far from satisfactory, and since our investigations have now shown that the Pople method, when properly applied, can give results in essentially complete agreement with the available experimental data, there seems at present no need to introduce specific corrections for vertical correlation by the SPO procedure, at any rate in calculations for conjugated hydrocarbons of the kind reported here.

Table I lists final values for the various quantities assumed for carbon–carbon and carbon–hydrogen bonds. Data for triplet bonds are included since these were needed to determine the constants in eq 6.

Table I. Quantities Assumed for C–C and C–H Bonds

Bond	Type	r, Å	D, eV[a]	$10^{-5}k$, dynes/cm[b]	a, nm^{-1} [c]
C—C	sp^3–sp^3	1.5444	3.6957	4.57	. . .
C═C	sp^2–sp^2	1.3380	5.5600	10.90	23.177
C≡C	sp–sp	1.2050	. . .	17.20	. . .
C—H	sp^2	. . .	4.4375	. . .	. . .
C—C	sp^2–sp^2	1.5120	3.9409	. . .	20.022

[a] Bond energy. [b] Force constant; see T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, New York, N. Y., 1959. [c] Morse constant.

The corresponding bond-order/bond-length relation for carbon–carbon bonds is

$$r\,(\text{Å}) = 1.512 - 0.174p \tag{12}$$

The parameters in the tractrix equation (5) for carbon–carbon bonds have the following values, with r in Å and D in eV.

$$a = 106.249 \text{ eV} \qquad b = 209.965 \text{ eV/Å} \tag{13}$$

The bond length (Å)/force constant (dyne/cm) relation for carbon–carbon bonds is

$$k = \frac{31.5138519}{r^2} + \frac{130.0713143}{r^4} + \frac{70.2685024}{r^6} \tag{14}$$

(The constants in the equations were determined by the computer and are given with unnecessary precision, solely in order to ensure that our calculations can be duplicated exactly by others.)

The calculations reported in the next section were carried out by the "variable β" method of part II,[4b] in which the bond lengths are recalculated at each step of the SCF iterative cycle, using eq 12. The initial geometries were set up assuming all bond angles in polyene chains to be 120°, all rings to be regular polygons, and with three fixed values for carbon–carbon bond lengths, *viz.*

essential single C—C bond: $r = 1.48$ Å

essential double C═C bond: $r = 1.35$ Å

other CC bonds: $r = 1.397$ Å

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(10) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(11) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, 84, 540 (1962).

(12) (a) K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964); (b) G. Klopman, *J. Am. Chem. Soc.*, **87**, 3300 (1965).

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


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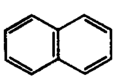
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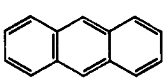
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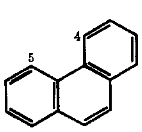

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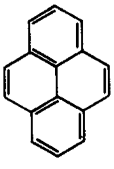
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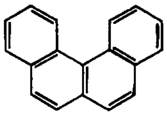
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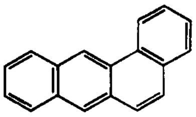
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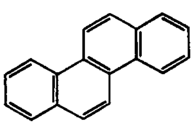
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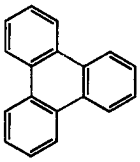
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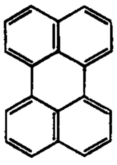
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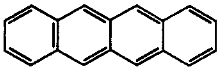
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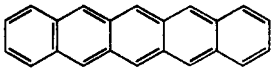
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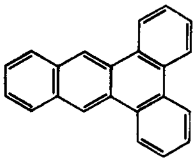
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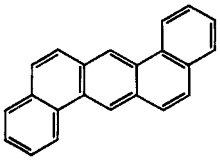
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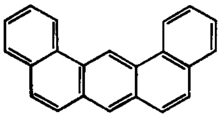
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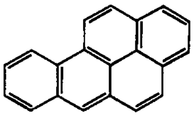
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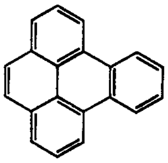
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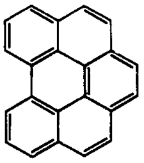
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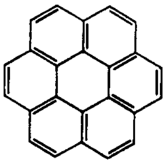
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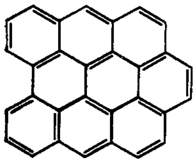
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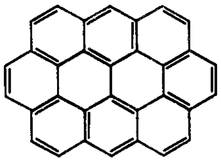
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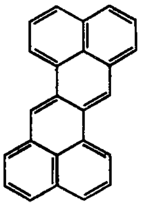
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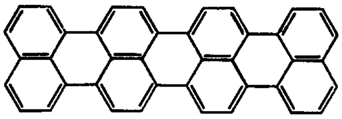
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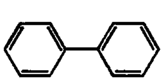
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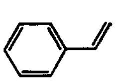
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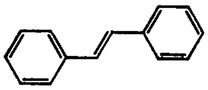
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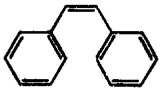
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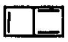
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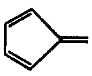
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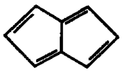
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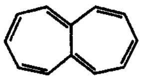
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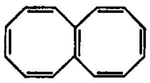
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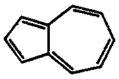
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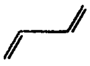
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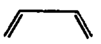
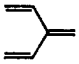

XXXVII


XXXVIII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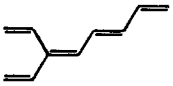
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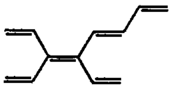
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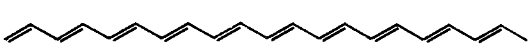
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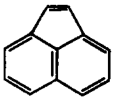
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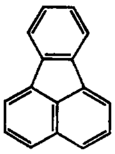
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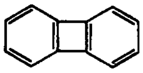
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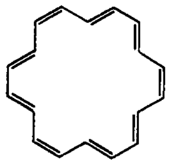
XLVI

Results

Heats of Atomization. Table II shows heats of atomization calculated for a number of conjugated hydrocarbons of various types, together with experimental values where these are available. The agreement between the calculated and observed heats of atomization is excellent, there being only five compounds for which the difference is significantly greater than the claimed limits of experimental error; moreover in three of these (XLIII, XLIV, XLV) discrepancies in the observed sense would be expected in view of ring strain, a factor which is neglected in the present treatment. Indeed, the differences for XLIII and XLIV are almost identical, as would be expected on this basis, and their values (~0.54 eV or 12 kcal/mole) are close to that calculated, assuming a reasonable value for the bending force constant of a C–C (sp^2–sp^2) bond. The difference for biphenylene (2.87 eV or 66 kcal/mole) seems rather large for the strain in a four-membered ring, but it is difficult to be sure of this in the absence of any good analogies.

In the two remaining compounds for which there are discrepancies (XI and XLVI), there are good reasons for doubting the reliability of the thermochemical data. Thus the heat of atomization reported for [18]-annulene (XLVI) seems improbably large, since it would imply that the conversion of XLVI to three molecules of benzene should be thermoneutral and the chemical properties of XLVI are inconsistent with so great a measure of resonance stabilization. In view of this, and in view of the fact that XLVI is the *only*

Table II. Heats of Atomization and Resonance Energies of Conjugated Hydrocarbons

Compound	−(Heat of atomization), eV Calcd	Obsd	Dif	Resonance energy (calcd), eV
I	57.157	57.16[a]	0.00	0.869
II	90.612	90.61[b]	0.00	1.323
III	123.889	123.93[c]	−0.04	1.600
IV	124.222	124.20[c]	+0.02	1.933
V	138.624	138.88[d]	−0.26	1.822
VI	157.767	157.48[e]	+0.29	2.478
VII	157.580	157.49[e]	−0.09	2.291
VIII	157.772	157.73[e]	+0.04	2.483
IX	157.943	157.76[e]	+0.18	2.654
X	172.146	172.04[d]	+0.11	2.619
XI	157.112	157.56[c]	−0.45	1.822
XII	190.294	...	...	2.004
XIII	191.348	...	...	3.058
XIV	191.238	...	...	2.948
XV	191.238	...	...	2.948
XVI	172.380	...	...	2.853
XVII	172.111	...	...	2.584
XVIII	186.892	...	...	3.128
XIX	201.527	...	...	3.524
XX	187.107	...	...	3.862
XXI	201.893	...	...	4.539
XXII	143.096	...	...	2.694
XXIII	246.564	...	...	5.309
XIV	109.751	109.76[f]	−0.01	1.699
XXV	75.909	75.83[a]	+0.08	0.858
XXVI	128.526	128.48[e]	+0.05	1.712
XXVII	128.536	...	...	1.722
XXVIII	51.471	...	...	−0.292
XXIX	51.489	...	...	−0.274
XXX	56.335	...	...	0.047
XXXI	70.532	...	...	0.006
XXXII	108.145	...	...	0.094
XXXIII	126.580	...	...	−0.235
XXXIV	126.714	...	...	−0.010
XXXV	89.458	89.19[h]	+0.27	0.169
XXXVI	42.054	42.05[a]	0.00	0.003
XXXVII	42.085	41.95[i]	+0.14	0.034
XXXVIII	60.814	...	...	0.000
XXXIX	60.788	...	...	−0.025
XL	98.329	...	...	−0.010
XLI	117.093	...	...	−0.009
XLII	192.154	...	...	0.001
XLIII	104.861	104.32[j]	+0.54	1.335
XLIV	138.668	138.11[j]	+0.56	2.141
XLV	104.873	102.00[g]	+2.87	1.346
XLVI	168.990	172.36[k]	+3.37	0.126

[a] American Petroleum Institute Project 44, Carnegie Press, Pittsburgh, Pa., 1955. [b] D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **6a**, 1723 (1960). [c] A. Magnus, H. Hartmann, and F. Becker, *Z. Physik. Chem.* (Leipzig), **197**, 75 (1951). [d] F. Klages, *Ber.*, **82**, 358 (1949). [e] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955. [f] G. S. Parks and L. M. Vaughan, *J. Am. Chem. Soc.*, **73**, 2380 (1951). [g] A. F. Bedford, J. G. Carey, D. T. Millar, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3895 (1962). [h] E. Kovats, H. H. Gunthard, and P. A. Plattner, *Helv. Chim. Acta*, **38**, 1912 (1955). [i] J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946). [j] R. H. Boyd, R. L. Christensen, and R. Pua, *J. Am. Chem. Soc.*, **87**, 3554 (1965). [k] A. E. Breezer, C. T. Mortimer, H. D. Springall, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc.*, 216 (1965).

compound for which there is a large and inexplicable discrepancy between experiment and our calculations, we feel that further discussion would be unprofitable until the heat of combustion has been independently redetermined. Similar remarks apply in the case of XI, although here the discrepancy (0.45 eV) is not much greater than the possible error in the heat of combustion. The chemical behavior of XI suggests that it is the least stable of the isomeric tetracyclic hydrocarbons VI, VII, VIII, IX, and XI; the reported heat of atomization therefore seems too large. Moreover, an error in this direction might have been expected since XI is notoriously difficult to purify and easily undergoes oxidation to a cyclic peroxide; the heat of combustion was measured 30 years ago when modern techniques such as gas chromatography and zone refining were not available, and there is the further possibility that XI may have undergone oxidation while being equilibrated with oxygen under pressure in the bomb before combustion. Any prior oxidation of XI would have led to a low value for the heat of combustion and a correspondingly high value for the heat of atomization.

Since our method neglects steric effects, one might expect similar though smaller discrepancies in the case of compounds such as phenanthrene (IV) where the hydrogen atoms in the 4 and 5 positions obstruct one another. Table III shows that the calculated heats of atomization of such compounds tend to be greater than observed, although the differences are not significantly greater than the claimed limits of experimental error. However, the values in the last column, calculated on the assumption that each hydrogen opposition introduces a strain energy of 0.044 eV (1.0 kcal/mole), do agree much better with experiment, suggesting both that the strain energy has this very reasonable value and that the estimated limits of error may have been conservative. Steric effects may also account for the discrepancy (0.28 eV or 6.5 kcal/mole) in the case of VI, this being somewhat greater than the estimated error in the heat of combustion.

Table III. Heats of Atomization of Phenanthrene Derivatives

Compound	−(Heat of atomization), eV Uncorrected	Observed	Corrected
IV	124.222	124.20	124.18
VII	157.580	157.49	157.54
VIII	157.772	157.78	157.68
IX	157.943	157.76	157.81
X	172.146	172.04	172.06

Classical Polyenes. Bond Localization and Resonance Energies. In part III,[4c] it was shown that the calculated heats of formation of a large number of classical polyenes could be quantitatively interpreted in terms of the localized bond model, using a single value (E') for the bond energy of each "single" bond, and a single value (E'') for the bond energy of each "double" bond. This was indicated in particular by plotting the total calculated carbon–carbon bond energy for linear polyenes, and for radialenes, against the number of single bonds; if the bonds are localized,[14] the plots should be parallel straight lines of slope ($E' + E''$), that for the radialenes passing through the origin and that for linear polyenes having an intercept E''. Figure 1 shows that this relation is obeyed very accurately by the heats of formation calculated here. The values of E' and E'' found from these plots are

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[14] For a discussion of the meaning of the term "bond localization," see (a) M. J. S. Dewar, *Tetrahedron, Suppl.*, No. 8, 75 (1966); (b) *Chem. Eng. News*, 43, 86 (Jan 11, 1965).

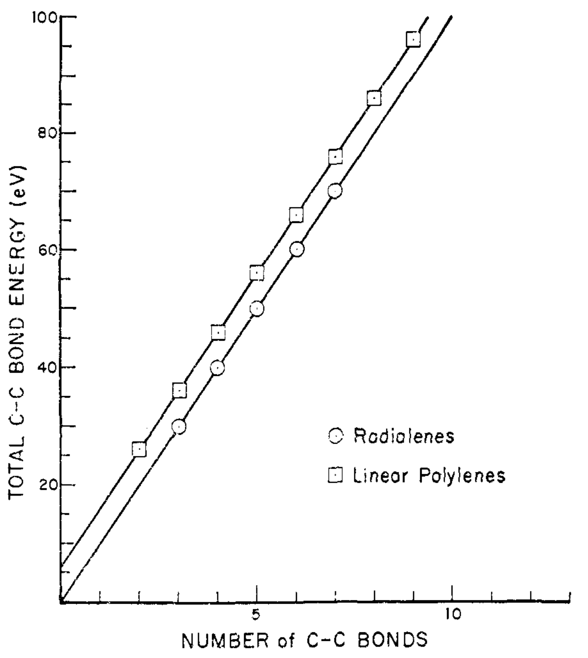

Figure 1. Plot of total carbon–carbon bond energy *vs.* number of single bonds for linear polyenes and radialenes.

$$E' = 4.3499 \text{ eV};\ E'' = 5.5378 \text{ eV} \quad (15)$$

Note that the value of E' is considerably greater (by 0.41 eV or 9.5 kcal/mole) than the value (3.9409 eV; Table I) for a "pure" C—C σ bond, while E'' is only very slightly less (by 0.02 eV or 0.5 kcal/mole) than the value (5.5600 eV; Table I) for a "pure" C=C double bond. The "single" bonds in polyenes have significant double-bond character according to our calculations, their bond orders being approximately 0.2 and their calculated lengths (1.46 Å; see below) being much less than that (1.512 Å) for a "pure" σ bond. The "double" bonds in polyenes, on the other hand, have bond orders close to unity and predicted lengths (1.35 Å) close to that (1.338 Å) for a "pure" double bond. The fact that classical conjugated polyenes have heats of atomization greater than the sum of the bond energies for corresponding number of "pure single" and "pure double" bonds is therefore due to the greater strength of "single" bonds in conjugated systems. If, however, our calculations are valid, the additional strength of such a bond, due to π bonding, is the same, regardless of its environment; the bonds in classical conjugated polyenes can therefore be regarded as localized,[14] the corresponding "polyene" bond energies being given by eq 15.

This result provides a simple and unambiguous definition of resonance energy (*cf.* part III[4c]) as the difference between the heat of formation of a given conjugated compound and that calculated for a corresponding classical structure with "localized" bonds. In the case of hydrocarbons, the corresponding localized bond energies are those listed in eq 15. Thus the calculated heat of atomization (ΔH_a) for a classical structure of benzene (*i.e.*, cyclohexatriene) is

$$\Delta H_a = 3E' + 3E'' + 6E_{\mathrm{CH}} = 56.29 \text{ eV} \quad (16)$$

The experimental value (Table I) is 57.16 eV, so the resonance energy of benzene is 0.87 eV, or 20 kcal/mole. This value is of course much less than the ones commonly quoted in text books, since the latter represent (dubious) estimates of the difference in heat of formation between benzene and an idealized structure with "pure single" and "pure double" bonds. Even if such differences could be estimated unambiguously, they would be of little practical value, for the quantity of interest to chemists is the extra stability of compounds such as benzene in comparison with classical open-chain analogs, rather than in comparison with idealized theoretical concepts. The resonance energies given by the present procedure of course meet this criterion.

The last column of Table II shows resonance energies calculated in this way. Note that the values are uniformly small for all but the benzenoid hydrocarbons, and that in the case of classical polyenes, *i.e.*, ones for which only single classical structures can be written, the resonance energies are virtually zero (<1 kcal/mole), both for open-chain compounds and for cyclic ones (*e.g.*, fulvene). This result suggests that the bonds in all classical polyenes should be regarded as localized (*cf.* part III[4c]), a condition further supported by the constancy of the bond lengths in such compounds (see next section).

Further light concerning bond localization is provided by compounds containing aromatic segments, separated by essential single and double bonds. The results in Table IV show that the resonance energy of such a compound is equal to a sum of the resonance energies of the various aromatic segments in it. Thus the essential single and double bonds can be regarded as localized in our sense, effectively isolating the aromatic segments from one another as efficiently as would an intervening saturated carbon atom; the bond lengths of such bonds are also consistent with this interpretation.

Table IV. Resonance Energies of Composite Hydrocarbons

Compound	Resonance energy, eV	Aromatic segments	Sum of resonance energies of segments, eV
XXIV	1.699	I + I	1.738
XXV	0.858	I	0.869
XXVI	1.712	I + I	1.738
X	2.619	II + II	2.646
XLIII	1.335	II	1.323
XLIV	2.141	I + II	2.192

The results for nonclassical[4c] hydrocarbons are also of interest in connection with the problem of aromaticity: they are generally consistent with the earlier calculations of part II[4b] and provide similar support for Hückel's rule, and for the picture presented by the simple perturbational MO (PMO) method.[15] Thus azulene (XXXV), which can be regarded[15] as a slightly perturbed form of [10]annulene, has a small positive resonance energy, much less than that of the isomeric naphthalene, while butalene (XXVIII or XXIX), pentalene (XXXI), and heptalene (XXXII) have negative resonance energies, in agreement with the PMO prediction that they should be antiaromatic. The negative resonance energies predicted for XXXI

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(15) See ref 14a and references cited there.

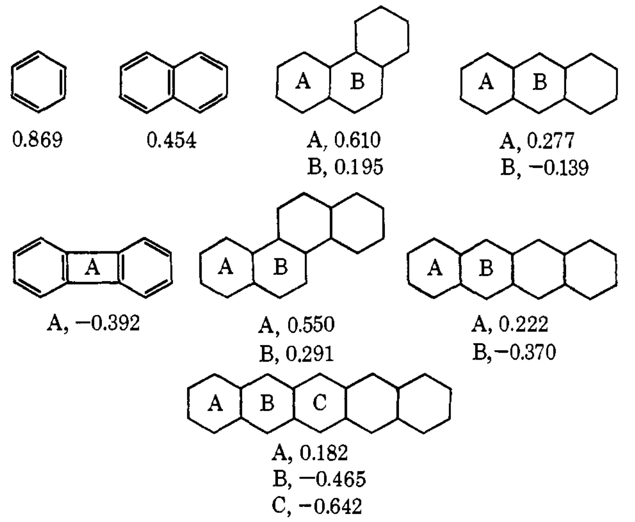

Figure 2. "Aromatic energies" (eV) of rings in polycyclic hydrocarbons.

and XXXII are, however, much smaller than those quoted in part II, for reasons discussed in the next section.

The resonance energies for the polycyclic benzenoid hydrocarbons are also consistent with the available chemical evidence. Thus the increase in resonance energy with each added ring decreases in the polyacene series, while in the "bent" series (benzene, naphthalene, phenanthrene, chrysene, etc.) the increase in resonance energy per ring is more or less constant. One can get an estimate of the "aromaticity" of a given ring in a polycyclic system by comparing its resonance energy with that of an analogous structure in which the ring in question is missing. Some examples are shown in Figure 2. Note the *negative* values for the central rings in III, XI, and XII. Reactions removing these rings from conjugation take place with exceptional ease.

Bond Lengths. The procedure[4b] used here automatically leads to estimates of bond lengths; the values so found agreed to within a few thousandths of an ångström with those given by the earlier treatment and corresponded equally well with experiment.[16]

Validity of the Bond Order–Bond Length Relation. Our procedure relies on the use of an assumed relation between bond order and bond length (eq 12), bond lengths being calculated from this rather than by minimizing the total molecular energy. While the results obtained seemed to support this procedure in a practical sense, we felt it should be tested in at least one or two cases. We therefore calculated the energy of 1,3-butadiene (XXXVI), and of benzene (I), for a range of bond lengths around the equilibrium value, and so determined by interpolation the geometries (assuming bond angles of 120°) that minimize the total energy. The results are shown in Figure 3, the bond lengths from eq 12 being given in parentheses.

It will be seen that the two sets of values agree almost exactly; this seems to provide good support for our general procedure, based on the use of eq 12, since the bonds in Figure 3 cover the whole range from "localized single" to "localized double."

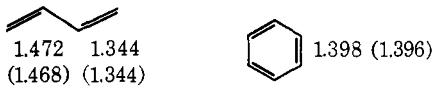

Figure 3. Comparison of bond lengths calculated from the bond-order–bond-length relation with those found by minimizing the total energy.

As a further check, we used the results for benzene, which gave its energy as a function of the carbon–carbon bond length, to calculate the force constant for the symmetrical "breathing" vibration. The value so found (7.4 × 10^5 dynes/cm) was in remarkable agreement with the latest estimate[18] (7.6 × 10^5 dynes/cm) from the vibrational spectrum.

Conclusions

The semiempirical SCF–MO treatment described in this paper seems to represent a notable advance over the earlier version,[4] which in turn was far superior to any other approach that has as yet been proposed. Not only has the treatment of part II[4b] been made entirely self-consistent and the number of parameters in it reduced in the process, but the results are also in better agreement with experiment, and the treatment can now be applied without ambiguity, and apparently with equal success, to the ground-state properties of conjugated hydrocarbons of all kinds, linear or cyclic, aromatic or nonaromatic. The calculated heats of formation in nearly all cases agree with experiment to within the claimed limits of experimental error.

In view of this success, there seems little point in trying to refine the treatment further at the present time, particularly since calculations of this kind, based on the Hückel σ–π approximation, will probably soon be replaced by more elaborate schemes in which all the valence-shell electrons are included.[19] Equally, however, there no longer seems any point at all in carrying out calculations by less refined procedures, in particular the HMO method or variants of it. The treatment described in this paper is almost as easy to use, and it is far more reliable and accurate. While the present version is admittedly applicable only to hydrocarbons, the next paper describes an almost equally successful extension to compounds containing nitrogen or oxygen, and a similar approach has already been applied successfully to the prediction of ^{19}F chemical shifts in aromatic and unsaturated fluorides.[1] We hope soon to extend the treatment to compounds of other elements, and to conjugation involving pπ–dπ bonds.

Meanwhile, in order to facilitate calculations by the procedures described in this paper, we are depositing an appropriate computer program with the Quantum Chemistry Exchange at Indiana University. This program is a simplified version written in basic FORTRAN by Mr. J. Hashmall; it should be easily adapted to almost any computer. It should be added that fuller details of these calculations, and additional results, will be found in a dissertation by one of us.[17]

(16) A limited number of tables of bond lengths are available from M. J. S. D.; full details are also given in a thesis by one of us.[17]

(17) C. de Llano, Ph.D. Dissertation, The University of Texas, 1968.

(18) B. L. Crawford, Jr., and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

(19) See M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967); N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967); and papers in the course of publication.