Physical and Inorganic Chemistry

Ground States of Conjugated Molecules. II. Allowance for Molecular Geometry[1a,b]

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In part I a semiempirical SCF–MO method was developed which enabled the heats of formation of aromatic hydrocarbons to be calculated with useful accuracy. This treatment has now been refined by making it self-consistent for changes in the integrals with bond length; calculations are reported for a number of alternant and nonalternant cyclic polyenes with results in very satisfactory agreement with experiment. The earlier calculations for cyclic polyenes have been repeated using more realistic geometries; the present results not only account for Hückel's rule but seem to predict correctly the ring size at which the (4n + 2)-membered cyclic polyenes cease to be aromatic.

Introduction

The purpose of the work described in this series of papers is to develop a satisfactory theoretical treatment of molecules in their ground states. Most of the published work in this field has made use of the HMO (Hückel MO) method which is known to be unsatisfactory for compounds other than alternant aromatic hydrocarbons,[2] while the more refined MO treatments have been applied mostly to calculations of excitation energies. Our object is to develop a general treatment of conjugated molecules, based on a semiempirical SCF–MO approach, sufficiently accurate and reliable to be of practical value in organic chemistry.

In the first paper of this series,[1b] which we shall refer to as part I, it was shown that a simple treatment of this

kind could give estimates for the heats of formation of aromatic hydrocarbons accurate to about ±0.2 kcal./mole per C–C bond. In that preliminary investigation it was assumed for simplicity that all "aromatic" C–C bonds had a common length (1.40 Å.) and that cyclic polyenes form regular polygons. The purpose of the work described here was to refine the treatment by removing these simplifying assumptions.

Theoretical Approach

1. Basic Method. The basic approach was the same as that described in part I, *i.e.*, a semiempirical SCF–MO treatment with neglect of overlap, following the general scheme for closed-shell molecules proposed first by Pople.[3] This can be regarded as a refined Hückel treatment in which the coulomb integrals α_i ($\equiv F_{ii}$) and resonance integrals β_{ij} ($\equiv F_{ij}$) are calculated instead of being treated as parameters; *i.e.*

$$F_{ii} = W(2p)_i + \frac{1}{2}q_i(ii,ii) + \sum_{j \neq i} (q_j - c_j)(ii,jj) \quad (1)$$

$$F_{ij} (i \neq j) = \beta_{ij} - \frac{1}{2}p_{ij}(ii,jj) \quad (2)$$

where W_i is the valence state ionization potential of atom i, q_i and p_{ij} are, respectively, the π-electron charge density of atom i and the bond order of the bond between atoms i and j, c_j is the core charge of atom j in units of the electronic charge, β_{ij} is the one-electron resonance integral between atoms i and j, and (ii,jj) is an integral representing the mutual repulsion of two electrons in AO's of atoms i and j. The MO's ψ_m are expressed as linear combinations of the n AO's ϕ_i

$$\psi_m = \sum_{i=1}^{n} a_{mi}\phi_i \quad (3)$$

(1) (a) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM11531-01; (b) for part I of this series, see A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, in press.

(2) See M. J. S. Dewar, *Rev. Mod. Phys.*, 35, 586 (1963).

(3) J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953); A. Brickstock and J. A. Pople, *ibid.*, 50, 901 (1954).

The coefficients a_{mi} are given by the set of simultaneous equations

$$\sum_j a_{mj}(F_{ij} - E_m\delta_{ij}) = 0 \quad (i = 1, 2, \ldots, n) \quad (4)$$

where δ_{ij} is the Kroenecker delta, and E_m is a solution of the secular equation

$$\det |(F_{ij} - E_m\delta_{ij})| = 0 \quad (5)$$

Since the quantities q_i, p_{ij} are functions of the coefficients a_{mi}, eq. 4 and 5 have to be solved by an iterative procedure.

The various integrals appearing in the Pople method are normally treated as parameters; the values used here followed the pattern established in part I.

(1) The two-center repulsions (ii,jj) were estimated by variants of the uniformly charged sphere approximation.[4] Two sets of integrals were calculated; one, the set of "upper–upper" integrals $(\bar{ii},\bar{jj})$, represent the repulsions between pairs of electrons localized in p-lobes or SPO's[5] (split p-orbitals) on the same side of the nodal plane; the other "upper–lower" set $(\bar{ii},jj)$ represent repulsions between electrons in SPO's on opposite sides of the nodal plane. Two sets of integrals were used in calculating the matrix elements F_{ij} (eq. 1 and 2).

(a) In the first set, which resembled the values recommended by Pariser and Parr,[4] all the integrals appearing in eq. 1 and 2 were given upper–lower values; this treatment, which also resembles the original treatment of Pople, is designated below as PPP.

(b) The second set corresponded to a modified SPO treatment[5] in which different values are used for repulsion integrals (ii,jj) arising from expansion of the molecular coulomb (J) integrals, and molecular exchange (K) integrals. As Chung, Dewar, and Sabelli[6] have pointed out, the original SPO scheme of using normal values for the J integrals, and upper–upper values for K integrals, is too extreme, leading to a correlation energy of 5.9 e.v. for a pair of 2p electrons. This energy is now known[7] to be about 2.0 e.v.; we therefore used an approximation intermediate between the PPP and extreme SPO treatments, in which

$$(ii,jj)^J = \frac{1}{6}(\bar{ii},\bar{jj}) + \frac{5}{6}(\bar{ii},jj) \quad (6)$$

$$(ii,jj)^K = \frac{1}{3}(\bar{ii},\bar{jj}) + \frac{2}{3}(\bar{ii},jj) \quad (7)$$

Note that the SPO calculations reported here are not directly comparable with those in part I, where the numerical factors in eq. 6 were $\frac{1}{4}$ and $\frac{3}{4}$, those in eq. 7 were $\frac{1}{2}$ and $\frac{1}{2}$.

(2) The one-center repulsion integrals (ii,ii) were estimated empirically by the method of Pariser and Parr,[4] as improved by Parr and Snyder.[8]

(3) The one-electron resonance integrals β_{ij} were estimated by the method of Dewar and Schmeising,[9] using the data listed in part I.

(4) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
(5) M. J. S. Dewar and N. L. Sabelli, *J. Phys. Chem.*, **66**, 2310 (1962).
(6) A. L. H. Chung, M. J. S. Dewar, and N. L. Sabelli in "Molecular Orbitals in Chemistry, Physics, and Biology," Academic Press, New York, N. Y., 1964.
(7) E. Clementi, *J. Chem. Phys.*, **38**, 2248 (1963); **39**, 175 (1963); see A. L. H. Chung and M. J. S. Dewar, *ibid.*, **39**, 1741 (1963).
(8) R. G. Parr and L. C. Snyder, *ibid.*, **34**, 1661 (1961).
(9) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

When the coefficients a_m and orbital energies E_m have been calculated, the total π-energy E_π of the molecule can be estimated from the expression[2]

$$E_\pi = 2\sum_m^{occ} E_m - \sum_m \sum_n (2J_{mn} - K_{mn}) \quad (8)$$

where J_{mn} and K_{mn} are, respectively, the coulomb and exchange integrals between the MO's ψ_m and ψ_n, and $\sum^{occ}$ implied summation over occupied MO's. This can be expressed in an equivalent form more convenient for computation

$$E_\pi = \sum_i q_i W_i + \frac{1}{4}q_i q_i^2(ii,ii) + \frac{1}{2}q_i \sum_{j \neq i}(q_j - 2)(ii,jj) +$$
$$2\sum_i \sum_j p_{ij}\left[(\beta_{ij} - \frac{1}{4}p_{ij}(ii,jj)\right] \quad (9)$$

The total π-binding energy, $E_{\pi b}$, is a sum of the π-energy E_π and the mutual repulsion of the charged atoms of the core. For reasons pointed out in part I, this repulsion energy was calculated using a Goeppert–Mayer–Sklar potential with neglect of penetration integrals.

$$E_{\pi b} = E_\pi + \sum_i \sum_j c_i c_j (ii,jj) \quad (10)$$

2. *Allowance for Variations in Bond Length.* In part I, all bonds between carbon atoms were assumed to have a common length (1.397 Å.). The treatment described there could of course be extended at once to systems with varying bond lengths, provided that these are known initially; our problem was to calculate the bond lengths in cases where these are not known.

This should in principle be done by minimizing the energy of the molecule with respect to variations in the coordinates of the individual atoms; however, we have not been able as yet to think of a way of doing this which would not involve an unreasonable amount of computer time. We therefore adopted a simpler procedure based on the well-known empirical observation that there is a one-to-one relation between bond length and bond order in conjugated systems. In our iterative program[1b] for solving eq. 4 and 5, the bond orders p_{ij} are recalculated in each cycle; we arranged for the bond lengths (r_{ij}) of bonds between adjacent atoms to be calculated from these, and for the corresponding integrals β_{ij} and (ii,jj) in turn to be recalculated using the new bond lengths. On repeating the iterative cycle, we then obtained as our final result a set of MO's which were self-consistent for variations in the β_{ij} and (ii,jj) with bond length. This approach is, of course, open to two main objections. First, there is the difficulty common to all self-consistent calculations, that the iterations may either not converge or may converge to a false solution; so far this does not seem to have happened in any of the cases we have studied. A second difficulty is that our procedure allows only for changes in the integrals for pairs of atoms which are directly linked; however, in the Pople treatment the β_{ij} are set equal to zero for nonbonded atoms, while the small changes in the (ii,jj) should be largely compensated by corresponding changes in the core repulsions. It is therefore unlikely that our procedure will lead to solutions differing significantly from those provided by a rigorous treatment. In our calculations

for hydrocarbons, we assumed a linear relation between bond order and bond length, as suggested by Dewar and Schmeising[9]

$$r_{ij} \text{ (in Å.)} = 1.504 - 0.166p_{ij} \qquad (11)$$

3. Calculation of Resonance Energies. As in part I, we estimated resonance energy by a "chemical" procedure, equating it to the difference between the calculated heat of formation of a given molecule and heat of formation calculated for a single classical structure using empirical bond energies. Assuming additivity of bond energies and assuming that C–C σ-bonds in conjugated systems have a common bond energy E_{CC}, the heat of formation (ΔH) of a hydrocarbon may be written[1]

$$\Delta H = N_{CH}E_{CH} + N_{CC}E_{CC} + E_{\pi b} \qquad (12)$$

where N_{CH} and N_{CC} are the number of CH and CC bonds, respectively. The heat of formation (ΔH^C) of a classical structure can likewise be written

$$\Delta H^C = N_{CH}E_{CH} + N'E' + N''E'' \qquad (13)$$

where N' is the number of single C–C bonds of bond energy E', and N'' is the number of double bonds of energy E''. Hence the resonance energy E_R is given by

$$\begin{aligned} E_R &= \Delta H^C - \Delta H \\ &= N'E' + N''E'' - N_{CC}E_{CC} - E_{\pi b} \\ &= N_{CC}\left[-E_{CC} + \frac{1}{2}(E'' + E') - \right. \\ &\qquad \left. \frac{N' - N''}{2N_{CC}}(E'' - E') \right] - E_{\pi b} \quad (14) \end{aligned}$$

Since the bond energy E_{CC} cannot be estimated directly it is convenient to rewrite this expression in the form

$$E_R = N_{CC}\left[A - \frac{N' - N''}{2N_{CC}}(E'' - E') \right] - E_{\pi b} \qquad (15)$$

Here A is treated as a parameter, found from the experimental value for E_R for benzene. The values used for the bond energies E'' and E' were those listed in part I.

This procedure for calculating E_R is somewhat different from that given previously.[1] Both methods give identical results for compounds in which the total number of single and double bonds is the same; otherwise, there are small differences as can be seen by comparing the values in Table XI with those in Table X of part I.[1b]

Both procedures are of course open to the criticism that the bond lengths in aromatic hydrocarbons fluctuate, so that the use of a single value for E_{CC} is not strictly correct; however, the mean values of the bond lengths may vary little from one hydrocarbon to another, so the use of a mean value for E_{CC} cannot in fact lead to any serious error. We have checked this point by calculating the total C–C σ-bond energies for several open-chain polyenes, first for equal bond lengths, and secondly for bond lengths corresponding to the calculated bond orders; details will be given in part III.[10] Even here, when bond alternation is far more extreme than in any aromatic hydrocarbon, the errors introduced by using a mean value for E_{CC} were negligible.

(10) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 692 (1965).

To avoid ambiguity, it should be emphasized that the quantities E', E'', E_{CC}, and E_{CH} are bond energies defined in the usual chemical sense, *i.e.*, their values are determined empirically to give the best fit with heats of formation of unconjugated molecules from atoms in their ground states.

4. Computational Methods. The calculations were carried out with the CDC 1604 computer at the University of Texas, using modifications of a program written originally by Dr. N. L. Sabelli for the IBM 7090 computer at the University of Chicago and adapted by her to the CDC 1604 here. The main program required little modification, being written in Fortran 2 which is almost compatible with the CDC 1604; however, we had to replace the eigenvalue subroutine. The present subroutine is one written by Dr. Burton S. Garbow at the Applied Mathematics Division, Argonne National Laboratory, library number ANL F202. Calculations were also carried out by the simple HMO method with neglect of overlap, the values for β being estimated by the method of Dewar and Schmeising.[9] These were carried out using the same program; in this the computer is instructed to carry out a fixed number of iterations, and by setting this number equal to zero, the results of a simple Hückel treatment are printed.

Results and Discussion

A. Alternant Aromatic Hydrocarbons. In order to calculate the heats of formation of aromatic hydrocarbons using eq. 12, it is necessary to know E_{CC}, the bond energy of the σ-component of an "aromatic" C–C bond. It is not easy to estimate this empirically; a value has been listed by Dewar and Schmeising,[9] but this is certainly not definitive. Accordingly, in part I eq. 12 was tested by rewriting it in the form

$$E_{CC} = \frac{1}{N_{CC}}[\Delta H - N_{CH}E_{CH} - E_{\pi b}] \qquad (16)$$

This can be used to calculate E_{CC} in the case of hydrocarbons for which ΔH is known, and if eq. 12 applies, the different values for E_{CC} should agree. The values, in fact, not only agreed with each other with a mean deviation of *ca.* 0.25%, but they also agreed well with the value estimated in a totally different way by Dewar and Schmeising.[9]

In part I, all C–C bonds were assumed to have a common length (1.397 Å.). Allowance for variations in bond length can be made in two different ways. In the case of hydrocarbons where the bond lengths are known from independent measurements, the method of part I can be applied directly to find $E_{\pi b}$ and hence E_{CC}. Results for eight hydrocarbons are listed in Table I. Alternatively, one can use the method outlined above to calculate both bond lengths and heats of formation of hydrocarbons, without reference to experiment; the results for the eleven hydrocarbons treated in part I are listed in Table II, while Table III compares mean deviations in E_{CC} for the three treatments.

It will be seen that the deviations in E_{CC} are considerably greater for the values calculated using experimental bond lengths than for either of the other two sets. This is probably due to errors in the experimentally determined bond lengths, for a very small

Table I. Values of E_{CC} Using Experimental Bond Lengths[a]

Molecule[b]	Formula	$-\Delta H_f$	$E_{\pi b}$, e.v. Hückel	$E_{\pi b}$, e.v. PPP	$E_{\pi b}$, e.v. SPO	E_{CC}, e.v. Hückel	E_{CC}, e.v. PPP	E_{CC}, e.v. SPO
Benzene (I)	C_6H_6	57.414	6.453	7.932	7.268	4.064	3.817	3.928
Naphthalene (II)	$C_{10}H_8$	91.042	11.271	13.895	12.720	4.030	3.792	3.899
Anthracene (III)	$C_{14}H_{10}$	124.592	15.383	19.053	17.369	4.057	3.827	3.933
Phenanthrene (IV)	$C_{14}H_{10}$	124.900	15.756	19.665	17.938	4.053	3.809	3.917
3,4-Benzphenanthrene (VII)	$C_{18}H_{12}$	158.229	20.348	25.445	23.153	4.035	3.792	3.901
Chrysene (IX)	$C_{18}H_{12}$	158.520	20.268	25.398	23.118	4.052	3.808	3.917
Triphenylene (X)	$C_{18}H_{12}$	158.581	20.595	25.831	23.452	4.040	3.790	3.904
Perylene (XI)	$C_{20}H_{12}$	172.874	21.808	27.629	25.033	4.080	3.837	3.945
Mean E_{CC}						4.051	3.809	3.918
Mean deviation						0.30%	0.34%	0.33%

[a] Notations are defined in text; values of E_{CC} and ΔH_f taken at 298°K. [b] The geometry of each benzenoid hydrocarbon is shown in Figure 1 of part I.

Table II Values of E_{CC} Based upon Average Bond Lengths with Self-Consistent Bond Integrals[a]

Molecule[b]	Formula	$-\Delta H_f$	$E_{\pi b}$, e.v PPP	$E_{\pi b}$, e.v SPO	E_{CC}, e.v. PPP	E_{CC}, e.v. SPO
Benzene (I)	C_6H_6	57.414	8.039	7.368	3.800	3.911
Naphthalene (II)	$C_{10}H_8$	91.042	13.667	12.547	3.813	3.914
Anthracene (III)	$C_{14}H_{10}$	124.592	19.106	17.531	3.824	3.922
Phenanthrene (IV)	$C_{14}H_{10}$	124.900	19.439	17.763	3.823	3.928
Pyrene (V)	$C_{16}H_{10}$	139.545	22.377	20.396	3.835	3.940
Naphthacene (VI)	$C_{18}H_{12}$	158.312	24.455	22.418	3.843	3.940
3,4-Benzphenanthrene (VII)	$C_{18}H_{12}$	158.229	25.160	22.988	3.805	3.909
1,2-Benzanthracene (VIII)	$C_{18}H_{12}$	158.346	24.961	22.813	3.820	3.923
Chrysene (IX)	$C_{18}H_{12}$	158.520	25.158	22.985	3.819	3.923
Triphenylene (X)	$C_{18}H_{12}$	158.581	25.286	22.979	3.816	3.926
Perylene (XI)	$C_{20}H_{12}$	172.874	28.052	25.575	3.819	3.923
Mean E_{CC}					3.820	3.924
Mean deviation					0.21%	0.17%

[a] Notations are defined in text; values of E_{CC} and ΔH_f taken at 298°K. [b] The geometry of each benzenoid hydrocarbon is shown in Figure 1 of part I.

Table III. Mean Deviations in E_{CC} Calculated by Various Methods

Treatment	Mean deviation in E_{CC}, %: Equal bond lengths	Exptl. bond lengths	Calcd. bond lengths
Hückel	0.15	0.30	..
PPP	0.22	0.34	0.21
SPO	0.19	0.33	0.17

error in the mean bond length would lead to a large error in E_{CC}. This is illustrated by the results in Table IV, showing how the values for E_{CC} calculated

Table IV. E_{CC} for Naphthalene with Constant Bond Lengths[a]

Av. bond length, Å.	$E_{\pi b}$, e.v.	E_{CC}, e.v.
1.39	13.976	3.784
1.40	13.462	3.831
1.41	12.967	3.876

[a] Values from PPP taken at 298°K.

from the heat of formation of naphthalene by the method of part I (i.e., with equal bond lengths) vary with the assumed bond length. Evidently the discrepancy in E_{CC} from the mean (see Table I) would be explained by an error of only 0.004 Å. in the value for the mean bond length which is probably within experimental error.

The agreement between the first and third columns of Table III must be regarded as a fortuitous consequence of the fact that the mean bond lengths in aromatic hydrocarbons vary very little from one compound to another; evidently the bond length used in part I was well chosen. The small residual variations in E_{CC} may be due partly to experimental errors in the determination of heats of formation; however, discrepancies could also arise from the fact that the measured heats of formation refer to measurements made at 25° and so include contributions from both zero-point energies and vibrational energies, whereas the calculated values should in principle refer to molecules in their equilibrium configurations. It is true that some allowance for the vibrational energy is tacitly made by using an empirical value for E_{CC}, but this would be satisfactory only if the vibrational energy were an accurately additive function of the bonds in the molecule—which is most unlikely to be the case. Table V lists values for the bond lengths calculated by the method of this paper, together with experimental values where these are available. The agreement is at least as satisfactory as for any other method that has been tried, and the discrepancies are mostly within the limits of experimental error. Here again many of the remaining discrepancies may be due to differences between the observed bond lengths (which are r_0 values). The only serious discrepancy occurs in the 2,3- and 12,15-bonds of naphthacene; here the experimental values are much longer than those calculated—and certainly the experimental values do seem improbably long on chemical grounds.

Table V. Bond Lengths (Å.) of Aromatic Molecules

Molecule[a]	Bond[b]	Lit. value	PPP	SPO
Benzene (I)[c]	1–2	1.397	1.393	1.393
Naphthalene (II)[d]	1–2	1.363	1.373	1.369
	2–3	1.415	1.416	1.422
	1–9	1.421	1.421	1.426
	9–10	1.418	1.403	1.396
Anthracene (III)[d]	1–2	1.366	1.369	1.362
	2–3	1.419	1.422	1.432
	1–13	1.434	1.428	1.437
	13–14	1.428	1.412	1.409
	9–13	1.399	1.395	1.402
Phenanthrene (IV)[e]	1–2	1.373	1.381	1.378
	2–3	1.406	1.407	1.410
	3–4	1.373	1.381	1.378
	1–13	1.409	1.410	1.413
	4–14	1.411	1.411	1.413
	9–10	1.352	1.361	1.356
	9–14	1.444	1.438	1.445
	13–14	1.394	1.400	1.394
	12–13	1.445	1.441	1.447
Pyrene (V)[f]	2–3	1.39	1.393	1.393
	4–5	1.39	1.359	1.354
	4–12	1.45	1.441	1.449
	3–12	1.42	1.400	1.398
	12–15	1.39	1.409	1.406
	15–16	1.45	1.431	1.438
Naphthacene (VI)[g]	1–2	1.385	1.364	1.358
	2–3	1.479	1.429	1.440
	1–13	1.431	1.436	1.445
	13–14	1.439	1.421	1.422
	12–13	1.398	1.390	1.385
	12–18	1.409	1.412	1.415
	15–18	1.475	1.419	1.413
3,4-Benzphenanthrene (VII)[h]	1–2	1.378	1.378	1.375
	2–3	1.409	1.410	1.415
	3–4	1.374	1.378	1.374
	4–16	1.391	1.414	1.418
	5–6	1.352	1.365	1.361
	6–17	1.430	1.430	1.436
	5–16	1.443	1.432	1.438
	14–15	1.446	1.434	1.439
	1–15	1.433	1.414	1.417
	14–17	1.412	1.390	1.382
	15–16	1.431	1.401	1.394

Molecule[a]	Bond[b]	Lit. value	PPP	SPO
1,2-Benzanthracene (VIII)	1–2		1.384	1.382
	2–3		1.403	1.406
	3–4		1.384	1.381
	4–15		1.407	1.408
	5–6		1.357	1.353
	6–16		1.445	1.453
	7–17		1.409	1.411
	8–9		1.370	1.364
	9–10		1.421	1.429
	10–11		1.370	1.364
	11–18		1.427	1.433
	12–13		1.389	1.385
	13–14		1.447	1.454
	5–15		1.443	1.451
	7–16		1.389	1.385
	8–17		1.427	1.433
	12–18		1.410	1.411
	14–15		1.399	1.394
	13–16		1.417	1.417
	17–18		1.409	1.402
	1–14		1.407	1.411
Chrysene (IX)[i]	1–2	1.360	1.378	1.374
	2–3	1.392	1.410	1.415
	3–4	1.379	1.378	1.375
	4–14	1.405	1.414	1.418
	14–15	1.465	1.435	1.439
	11–12	1.365	1.366	1.361
	12–13	1.418	1.432	1.437
	1–13	1.427	1.415	1.418
	13–14	1.406	1.401	1.394
	11–18	1.423	1.429	1.436
	15–18	1.397	1.390	1.383
Triphenylene (X)[e]	1–2	1.384	1.387	1.584
	2–3	1.394	1.401	1.402
	1–14	1.402	1.404	1.405
	13–14	1.435	1.450	1.455
	14–15	1.408	1.400	1.396
Perylene (XI)[j]	1–2	1.418	1.413	1.419
	2–3	1.370	1.375	1.371
	3–15	1.411	1.421	1.425
	1–14	1.397	1.381	1.375
	14–20	1.425	1.422	1.426
	15–20	1.424	1.404	1.397
	13–14	1.471	1.456	1.462

[a] The geometries of these molecules are given in Figure 1 of part I. [b] Bond numbering follows the conventions of the "Ring Index." [c] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 170. [d] D. W. J. Cruikshank and R. A. Sparks, *Proc. Roy. Soc.* (London), A258, 270 (1960). [e] C. A. Coulson and C. W. Haigh, *Tetrahedron.* 19, 527 (1963). [f] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955. [g] J. M. Robertson, V. C. Sinclair, and J. Trotter, *Acta Cryst.*, 14, 697 (1961). [h] F. L. Hirshfeld, S. Sandler, and G. M. J. Schmidt, *J. Chem. Soc.*, 2108 (1963). [i] D. M. Burns and J. Iball, *Proc. Roy. Soc.* (London), A257, 491 (1960). [j] A. Camerman and J. Trotter, *ibid.*, A279, 129 (1964).

Table VI. π-Binding Energies of the Configurations of [18]Annulene

Configuration[a]	$E_{\pi b}$, e.v.
I	20.378
II	20.251
III	20.330
IV	20.036
V	20.242
VI	20.098
VII	20.038
VIII	19.951

[a] Configurations are shown in Figure 1.

Table VII. π-Binding Energies of the Configurations of [20]Annulene

Configuration[a]	$E_{\pi b}$, e.v.
I	22.422
II	22.248
III	21.732
IV	22.117
V	21.855
VI	21.849
VII	21.623

[a] Configurations are shown in Figure 2.

B. Cyclic Polyenes. The calculations for annulenes (cyclic polyenes) in part I were based on the unrealistic assumption that such molecules form regular polygons. As was pointed out above, this must lead to errors in the calculated heats of formation and resonance energies since these, in an SCF treatment, depend on the distances between nonbonded atoms. This point is well illustrated by some calculations for [18]annulene and [20]annulene. Figures 1 and 2 show possible geometries for these compounds and Tables VI and VII the corresponding π-binding energies ($E_{\pi b}$) calculated by
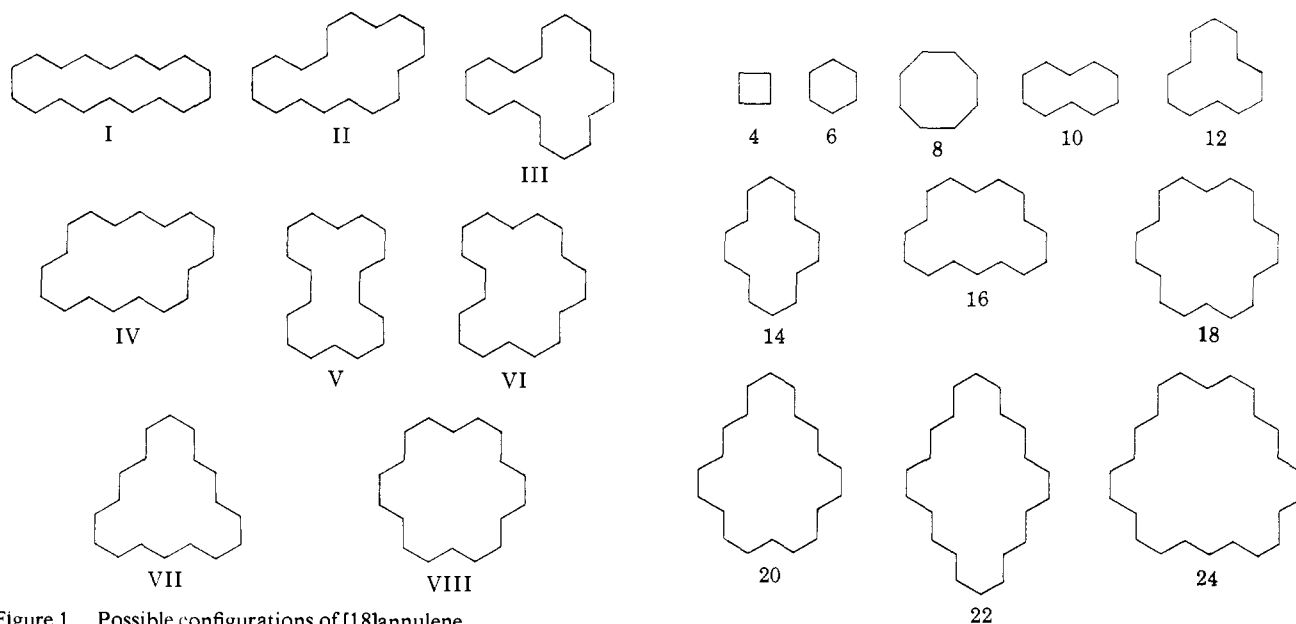
Figure 1. Possible configurations of [18]annulene.
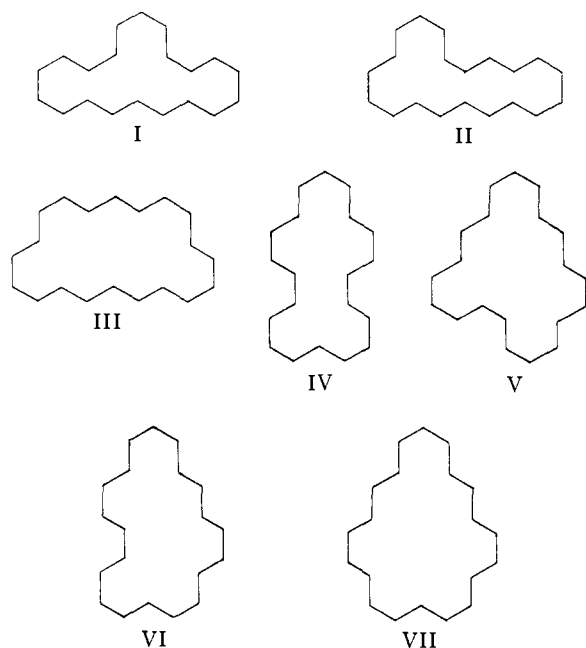

Figure 3. Geometries of the annulenes.

Figure 2. Possible configurations of [20]annulene.

the PPP method; here, as throughout, the calculations for the 4n-membered annulenes were carried out by the open-shell SCF–MO method of part I for the lowest triplet states, assuming the two highest occupied MO's (which are degenerate) to be each singly occupied.

These calculations indicate that the π-energies, and hence the heats of formation, of annulenes should depend critically on their molecular geometries. Of course the calculations are still unrealistic in that they neglect the effect of nonbonded interactions; thus configuration I could exist in a planar form only if the bond angles were greatly distorted from their equilibrium value of 120°. It would clearly be a difficult matter to predict the most stable configuration, allowing for such factors; indeed X-ray analysis indicates that [18]annulene exists in the "open" configuration VIII, which is predicted to be the least stable on the
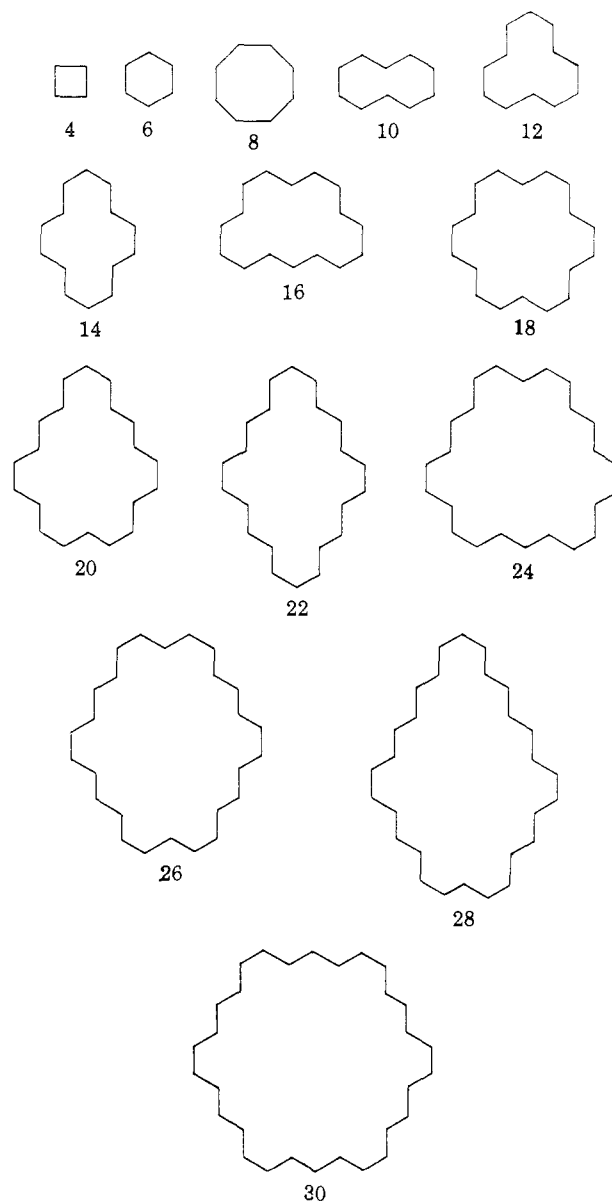
basis of its π-energy. However, it is clear that any realistic calculations must be based on reasonable geometries. Guided by the results for [18]annulene, we have therefore calculated π-binding energies ($E_{\pi b}$) and resonance energies (E_R), from eq. 15 for the annulenes up to [30]annulene, using the "open" geometries indicated in Figure 3. The results are listed in Table VIII and plotted as a function of ring size in Figure 4.

These results are in striking agreement with experiment, particularly the ones given by the SPO method. All the [4n]annulenes are correctly predicted to be nonaromatic, the more so since the rings of intermediate size ($n = 8$–16) would be seriously destabilized by ring strain. The [4n + 2]annulenes are predicted to be aromatic up to and including [22]annulene; this also seems to be in agreement with the experimental work of Jackman, Sondheimer, and their collaborators,[11] who have found that [22]annulene is aromatic, whereas

(11) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, and A. A. Bothner-By, *J. Am. Chem. Soc.*, 84, 4307 (1962).
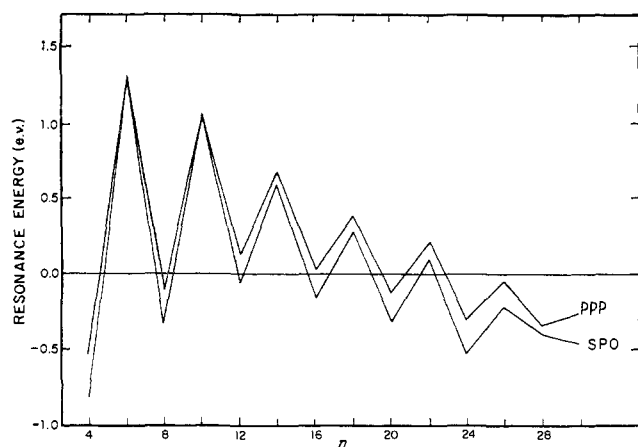
Figure 4. Resonance energies of annulenes as a function of ring size, calculated by the PPP and SPO methods for the geometries indicated in Figure 3.

Figure 5. Geometries of the nonbenzenoid hydrocarbons.

[30]annulene is not. It will be amusing to see if [26]-annulene proves to be nonaromatic as we predict! Of course the energy differences involved are so small that we cannot attach too much significance to this

and so be nonaromatic, but it had not proved possible to predict with any assurance the ring size at which this would occur.

Table VIII. π-Binding Energies and Resonance Energies of the Annulenes

	PPP		SPO	
n	$E_{\pi b}$, e.v.	E_R e.v.	$E_{\pi b}$, e.v.	E_R, e.v.
4	3.815	−0.534	3.091	−0.815
6	7.841	1.318	7.177	1.318
8	8.589	−0.108	7.485	−0.327
10	11.933	1.061	10.844	1.079
12	13.177	0.131	11.667	−0.051
14	15.909	0.689	14.294	0.623
16	17.438	0.043	15.489	−0.135
18	19.951	0.382	17.854	0.277
20	21.623	−0.120	19.215	−0.315
22	24.147	0.229	21.573	0.090
24	25.785	−0.305	22.901	−0.535
26	2 .211	−0.054	25.160	−0.229
28	30.106	−0.339	26.977	−0.365
30	32.350	−0.263	28.824	−0.471

Table IX. Resonance Energies of Nonbenzenoid Hydrocarbons

			E_R,[b] e.v.	
Molecule[a]	Formula	Hückel	PPP	SPO
Butalene (I)	C_6H_4	0.984	0.191	0.391
Fulvene (II)	C_6H_6	0.896	0.136	0.321
Pentalene (III)	C_8H_6	1.530	0.589	0.710
Heptafulvene (IV)	C_8H_6	1.227	0.156	0.372
Azulene (V)	$C_{10}H_8$	2.166	1.225	1.226
Fulvalene (VI)	$C_{10}H_8$	2.117	0.550	0.833
Heptalene (VII)	$C_{12}H_{10}$	2.232	0.689	0.787
Sesquifulvene (VIII)	$C_{12}H_{10}$	2.521	0.867	1.036
Octalene (IX)	$C_{14}H_{1.}$	2.573	0.279	0.268
Heptafulvalene (X)	$C_{14}H_{12}$	2.783	0.711	1.008

[a] Geometries of these molecules will be found in Figure 5.
[b] The values of $E_{\pi b}$ used to compute E_R were derived from molecular structures where all bonds were 1.40 Å.

agreement, but it is certainly far from discouraging. Previous investigations[12] had indicated that the higher [4n + 2]annulenes should suffer from bond alternation

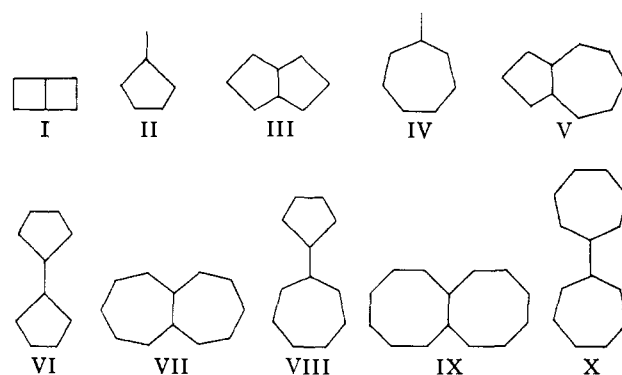(12) Cf. H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), **A251**, 172 (1959).

Table X. Bond Lengths of Nonbenzenoid Hydrocarbons

Molecule[a]	Bond	Lit. value, Å.	Calcd. values, Å. PPP	SPO
Butalene (I)	1–2		1.388	1.390
	2–3		1.407	1.403
	1–4		1.533	1.541
Fulvene (II)	1–2		1.459	1.466
	2–3		1.354	1.350
	3–4		1.446	1.454
	1–6		1.351	1.347
Pentalene (III)	1–2		1.395	1.396
	1–7		1.417	1.416
	7–8		1.418	1.423
Heptafulvene (IV)	1–2		1.458	1.466
	2–3		1.353	1.349
	3–4		1.449	1.459
	4–5		1.355	1.350
	1–8		1.351	1.347
Azulene (V)[b]	1–2	1.391	1.394	1.394
	1–9	1.413	1.402	1.402
	4–5	1.401	1.395	1.395
	5–6	1.385	1.397	1.397
	8–9	1.383	1.403	1.403
	9–10	1.483	1.461	1.461
Fulvalene (VI)	1–2		1.457	1.464
	2–3		1.354	1.350
	3–4		1.449	1.456
	1–1′		1.364	1.357
Heptalene (VII)	1–2		1.393	1.394
	2–3		1.401	1.401
	1–11		1.415	1.413
	11–12		1.425	1.431
Sesquifulvalene (VIII)	1–2		1.449	1.459
	2–3		1.359	1.353
	3–4		1.439	1.449
	1–1′		1.372	1.362
	1′–2′		1.449	1.459
	2′–3′		1.359	1.352
	3′–4′		1.442	1.453
	4′–5′		1.360	1.353
Octalene (IX)	1–2		1.395	1.394
	2–3		1.407	1.408
	3–4		1.389	1.387
	1–13		1.395	1.394
	13–14		1.407	1.408
Heptafulvalene (X)	1–2		1.453	1.462
	2–3		1.354	1.350
	3–4		1.449	1.459
	4–5		1.355	1.350
	1–1′		1.368	1.359

[a] Geometries are given in Figure 5. [b] Fused rings are numbered in accordance with the "Ring Index."

C. *Nonalternant Hydrocarbons.* We have also carried out calculations by the method developed here for the nonalternant conjugated hydrocarbons listed in Figure 5. The resonance energies calculated by the Hückel, PPP, and SPO methods are listed in Table IX and the calculated bond lengths in Table X. Experimental values are also listed where these are available; the resonance energies were calculated from the observed stabilization energies by the method of Dewar and Schmeising.[9] For comparison, calculated resonance energies for a selection of normal alternant aromatic hydrocarbons are shown in Table XI.

Table XI. Resonance Energies of Benzenoid Hydrocarbons

| Molecule[a] | Formula | E_R,[b] e.v. | | |
		Hückel	PPP	SPO
Benzene (I)	C_6H_6	1.318	1.318	1.318
Naphthalene (II)	$C_{10}H_8$	2.413	2.282	2.280
Anthracene (III)	$C_{14}H_{10}$	3.784	3.086	3.078
Phenanthrene (IV)	$C_{14}H_{10}$	3.891	3.455	3.434
Pyrene (V)	$C_{16}H_{10}$	4.254	4.008	3.973
Naphthacene (VI)	$C_{18}H_{12}$	4.485	3.834	3.813
3,4-Benzphenanthrene (VII)	$C_{18}H_{12}$	4.689	4.550	4.520
1,2-Benzanthracene (VIII)	$C_{18}H_{12}$	4.639	4.329	4.307
Chrysene (IX)	$C_{18}H_{12}$	4.711	4.553	4.512
Triphenylene (X)	$C_{18}H_{12}$	4.777	4.792	4.730
Perylene (XI)	$C_{20}H_{12}$	5.395	5.120	5.063

[a] Geometries of these molecules will be found in Figure 1 of part I. [b] The values of $E_{\pi b}$ used to compute E_R were derived from molecular structures with equal bond lengths of 1.40 Å.

The resonance energies for the nonalternant hydrocarbons agree well in general with those of part I.

Once again the resonance energies are uniformly much less than for analogous alternant compounds, and once again the resonance energy for azulene is predicted to be much greater than for the other nonalternants. This is consistent with the experimental evidence, which suggests that azulene alone among these is aromatic.

The remaining nonalternants are, it is true, predicted to have positive resonance energies, but these are relatively small; since the compounds are all quite highly strained, and since this strain would be relieved by reactions in which one or more double bonds were destroyed, one might have expected such compounds to be highly reactive. The values listed in Table X moreover indicate that the bonds in most cases show strong alternation; such compounds would not then be classed as aromatic, being highly reactive and containing "localized" single and double bonds. This point is discussed further in the following paper.[10]

These arguments do not apply to pentalene and heptalene, where the circumferential bonds are predicted to be essentially equal in length. These compounds, though possibly highly reactive, should then show the characteristics typical of aromatic compounds (delocalization of π-electrons, ring current, etc.). While this conclusion could be avoided in the case of heptalene, where ring strain could favor a nonplanar geometry with consequent disruption of the π-systems, the prediction seems quite definite in the case of pentalene. It will be extremely interesting to see if pentalene does indeed turn out to be aromatic, though highly reactive; the available evidence certainly suggests that it is highly reactive, all attempts to prepare it having failed.

Ground States of Conjugated Molecules.
III. Classical Polyenes[1]

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The SCF-LCAO-MO method described in previous[2,3] papers of this series has been applied to a number of classical polyenes (i.e., polyenes for which only single unexcited resonance structures can be written). The results suggest that bond energies are additive in compounds of this type, it being possible to absorb the π-contributions to the "single" bonds into the empirical C–C bond energy. Compounds of this type are therefore "nonresonating" in the chemical sense of the term.

Introduction

For many years it was an accepted principle of chemical theory that the π-electrons in conjugated molecules

are delocalized, and that compounds of this type must, in valence bond terminology, be represented as resonance hybrids rather than by single classical structures. Recently this view has been questioned[4] for the special case of classical conjugated molecules, such a molecule being one for which only a single classical (unexcited) resonance structure can be written. The purpose of this paper is to examine certain aspects of ideas which have been presented[5,6] in this connection.

Much of the controversy over bond fixation and resonance has been based on misunderstandings of the fundamental issues involved. There is, in fact, no such thing as a localized bond; even in saturated molecules, such as paraffins, the valence electrons must, according

(1) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM-11531-01.
(2) M. J. S. Dewar and A. L. H. Chung, *J. Chem. Phys.,* in press.
(3) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.,* 87, 685 (1965).

(4) See M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962.
(5) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron,* 5, 166 (1959); 11, 96 (1960).
(6) M. J. S. Dewar, *ibid.,* 19, 89 (1963).