stituents on both the carbon and nitrogen atoms of the nitrilimine promote the formation of 1,4-dihydro-*s*-tetrazines; experimentally, several reaction paths were observed in the formation of the *s*-tetrazines.

1,4-Dihydro-*s*-tetrazines with more weakly electron-attracting or electron-repelling substituents, such as alkyl-substituted derivatives, are better prepared by oxidation of the corresponding hexahydro-*s*-tetrazines. The reaction of formaldehyde with aryl-[14] or alkyl-monosubstituted[5,7] hydrazines gives a variety of products. Since the simple hydrazone is often not capable of stable existence,[19,20] the dimer or a hexahydro-*s*-tetrazine can be a major product of the reaction. Skorianetz and Kovats[21] describe high concentration, low temperature, and basic medium as conditions conducive to the formation and stabilization of aliphatic hexahydro-*s*-tetrazines. Selective oxidation of the hexahydro-*s*-tetrazine with mercuric oxide gives both the 1,2,3,4-tetrahydro-*s*-tetrazine and the 1,4-dihydro-*s*-tetrazine. 1,4-Dimethyl-1,4-dihydro-*s*-tetrazine cation radical was identified from oxidation reactions of 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, 1-formyl-1-methylhydrazine, methylhydrazine, and equimolar mixtures of methylhydrazine–formaldehyde. The several reactions, some with very poor yields, undoubtedly have a commonality in their condensation to the *s*-tetrazine, regardless of the oxidation state of the labile monomer. Formally, formaldehyde and methylhydrazine may be considered as the most likely reactants. Iodate ion in aqueous solution, like mercuric sulfate,[22] oxidizes one methyl group of 1,1-dimethylhydrazine to formaldehyde. 1-Formyl-1-methylhydrazine may hydrolyze to formaldehyde and methylhydrazine in a manner similar to that observed for substituted formamides.[23] 1,2-Dimethylhydrazine is oxidized to azomethane which may isomerize[24] to formaldehyde methylhydrazone.[25]

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(20) The preparation of the monomer of formaldehyde phenylhydrazone has been reported: B. V. Ioffe and V. S. Stopskii, *Dokl. Akad. Nauk SSSR*, **175**, 1064 (1967).

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(22) R. Preussmann, H. Hengy, and A. Von Hodenberg, *Anal. Chim. Acta*, **42**, 95 (1968).

(23) S. Langlois and A. Broche, *Bull. Soc. Chim. Fr.*, 812 (1964).

(24) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961, p 327.

(25) An examination of the products of the reaction between 1,2-dimethylhydrazine and mercuric oxide by ultraviolet spectra confirmed initial formation of azomethane (R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954)); subsequent decrease of azomethane is accompanied by a corresponding increase of formaldehyde methylhydrazone and tetrahydro- or dihydro-*s*-tetrazines.

Double-Bond Fixation in Conjugated π-Electron Systems. IV. Self-Consistent Field Formalism and Applications to Alternant Hydrocarbons

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Contribution from the Department of Chemistry and the Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556. *Received October 14, 1968*

Abstract: The theory of double-bond fixation in conjugated π-electron systems, developed in previous papers of this series, is reformulated in an approximate SCF scheme. It is shown that the basic features of the one-electron formalism can be retained in the many-electron model for closed shells if the change in π-electron energy due to nuclear displacements is considered to arise from a one-electron perturbation. The modified theory is applied to alternant hydrocarbons. Previous conclusions regarding the importance of second-order bond fixation in monocyclic and benzenoid hydrocarbons are essentially confirmed, whereas the prediction that second-order effects become important also in long polyene chains is shown to have been an artifact of the one-electron model.

In previous papers of this series[3-5] a general theory of double-bond fixation was developed in the framework of a one-electron model and applied to linear, cyclic, benzenoid, and nonalternant hydrocarbons. It was shown that second-order bond distortions can be examined by comparing the largest negative eigenvalue, Λ_{max}, of a matrix, whose elements are the second partial derivatives of the π-electron energy with respect to the bond lengths, with the curvature of the σ potential. If the magnitude of Λ_{max} exceeds a critical value Λ_{crit}, the molecule is predicted to suffer second-order distortions, in a static or dynamic sense, and the distortion pattern is determined by the normalized components of the eigen-

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(1) (a) Alfred P. Sloan Research Fellow; (b) AEC Summer Research Participant, 1968.

(2) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-634.

(3) G. Binsch, E. Heilbronner, and J. N. Murrell, *Mol. Phys.*, **11**, 305 (1966).

(4) G. Binsch and E. Heilbronner in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, p 815.

(5) G. Binsch and E. Heilbronner, *Tetrahedron*, **24**, 1215 (1968).

vector belonging to $\Lambda_{\max}$. The most characteristic feature of these second-order effects is their general tendency to result in a reduction of molecular symmetry, whereas first-order distortions always reflect the full symmetry with which the calculation was started. The phenomena are related to the well-known Jahn–Teller or pseudo-Jahn–Teller effects, which may in fact be regarded as special manifestations of our theory.

In the present paper we redevelop the theory in the framework of an approximate SCF model for closed-shell ground states. The motivation for going to a more sophisticated many-electron formalism was fourfold.

(1) In our first paper[3] we presented qualitative arguments which led us to conclude that electron-repulsion effects will in all likelihood only exert a minor influence on our results for alternant hydrocarbons. It is desirable to put this surmise on a more quantitative basis. (2) We have been unable to find a computationally feasible way for taking proper account of the nonuniform charge distribution in nonalternant hydrocarbons within our one-electron formalism. (3) For a similar reason it has so far not been possible to extend the treatment to conjugated systems containing heteroatoms. (4) Although we have attempted to apply the formalism also to excited states, our method for doing this is clearly deficient. In particular, a distinction between singlet and triplet states can obviously not be made in any one-electron theory.

Applications of the SCF formalism to alternant hydrocarbons will be discussed in the present paper. Nonalternant and hetero systems will be dealt with in the succeeding paper.[6] The last point will be deferred to a future publication.

Theory

For the study of second-order double-bond fixations in a conjugated molecule we need to know the elements of the matrix[3,4]

$$\left[\left(\frac{\partial^2 E_\pi}{\partial R_{\mu\nu}\partial R_{\kappa\lambda}}\right)_{R_0}\right] \qquad (1)$$

at some conveniently chosen fixed planar geometry R_0.

In setting up the formalism in an LCAO SCF scheme, we make use of the simplified Roothaan[7] equations for an orthonormal basis set of atomic 2p orbitals with the

$$\sum_{\nu}(F_{\mu\nu} - \delta_{\mu\nu}\varepsilon_i)c_{i\nu} = 0 \qquad (2)$$

approximations introduced by Pople[8] where the symbols have their standard meanings. The total π-electron

$$\begin{aligned} F_{\mu\mu} &= H_{\mu\mu} + {}^1/_2 P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\lambda(\neq\mu)} P_{\lambda\lambda}\gamma_{\mu\lambda} \\ &= \alpha_{\mu\mu} + {}^1/_2 P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\lambda(\neq\mu)} (P_{\lambda\lambda} - Z_\lambda)\gamma_{\mu\lambda} \qquad (3) \end{aligned}$$

$$F_{\mu\nu} = H_{\mu\nu} - {}^1/_2 P_{\mu\nu}\gamma_{\mu\nu} = \beta_{\mu\nu} - {}^1/_2 P_{\mu\nu}\gamma_{\mu\nu} \qquad (4)$$

energy is given by eq 5 and is thus seen to be a function of

$$E_\pi = {}^1/_2 \sum_{\mu\nu} P_{\mu\nu}(F_{\mu\nu} + H_{\mu\nu}) \qquad (5)$$

the variables $\alpha_{\mu\mu}$, $\beta_{\mu\nu}$, $\gamma_{\mu\mu}$, and $\gamma_{\mu\nu}$. To obtain the elements of the matrix (1), one could in principle differentiate eq 5 twice with respect to the bond distances. This is in essence the approach we suggested in our first paper,[3] and a similar procedure has since also been proposed by Amos.[9] Unfortunately, the formulas are so highly complicated, especially for nonalternants, as to become intractable for molecules of chemically interesting size.

There is, however, an alternative way of approaching the problem. Suppose we have solved Schrödinger's equation for the motion of the electrons in the field of the nuclei; then the Hellmann–Feynman theorem states that the change in total energy on variation of one of the nuclear coordinates X_k is given by

$$\frac{\mathrm{d}E}{\mathrm{d}X_k} = \left\langle \Psi \left| \frac{\partial H}{\partial X_k} \right| \Psi \right\rangle \qquad (6)$$

This means that the derivative $\mathrm{d}E/\mathrm{d}X_k$ may be expressed as the result of a one-electron perturbation operating on the wave function.

Now it is well known that the Hellmann–Feynman theorem will in general not be satisfied for an approximate wave function, although it can be shown[10] to hold for a Hartree–Fock wave function. One should not conclude, however, that this invalidates our argument. The situation has been expressed very clearly by Hurley:[11] "If an approximate wavefunction does not satisfy eq 6 there is no compelling *a priori* reason for preferring either side of the equation as an approximation to the exact value of $\mathrm{d}E/\mathrm{d}X$. When eq 6 holds, it establishes an equivalence between two methods of approximating the exact $\mathrm{d}E/\mathrm{d}X$, rather than establishing the validity of either approximation." Since the right-hand side of eq 6 leads to a much simpler formalism, we will henceforth adopt the view that the changes in π-electron energy on variation of a particular bond length may be considered to arise from a one-electron perturbation which can be absorbed in the core parameter β of eq 4, and that this $\beta_{\mu\nu}^{\mathrm{core}}$ may be taken to be a unique function of the individual bond $\mu\nu$.[12]

If the π-electron wave function is determined in an LCAO SCF scheme, the first-order change in π-electron energy is obtained by a straightforward application of perturbation theory. To calculate second-order changes in energy, however, is a more difficult problem, since second-order effects depend on changes in the wave function. These changes should be made in such a way as to keep the wave function self-consistent to first order in the perturbation. This problem has been treated by several authors,[13] and some numerical results have been obtained

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(6) G. Binsch and I. Tamir, *J. Amer. Chem. Soc.*, **91**, 2450 (1969).

(7) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(8) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(9) A. T. Amos, *Theoret. Chim. Acta* (Berlin), **8**, 91 (1967).

(10) A. C. Hurley in "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 161.

(11) On pp 168 and 169 of ref 10.

(12) It may perhaps be worthwhile to express the essential difference between the two approaches in a more perceptual way. Using the left-hand side of eq 6 amounts to moving the atomic 2p basis functions *together with* the nuclei, and this will obviously alter the electron repulsion integrals. In basing the perturbation calculation on the right-hand side of eq 6 one only moves the nuclei and allows the MO's to adjust themselves to the new potential, but the AO's remain at their original positions. The AO's will therefore be slightly off-center in the perturbed wave function and, strictly speaking, this will also change the core Coulomb parameter α. Since we incorporate the one-electron perturbation exclusively in the core β, we have to be careful in specifying an explicit functional form for $\beta(R)$.

(13) See, for instance, H. H. Greenwood and T. H. J. Hayward, *Mol. Phys.*, **3**, 495 (1960); R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 550 (1963); G. Diercksen and R. McWeeny, *ibid.*, **44**, 3554 (1966); A. T. Amos and G. G. Hall, *Theoret. Chim. Acta* (Berlin), **5**, 148 (1966).

by an iterative procedure. Since the principal purpose of our work is to arrive at conclusions of a qualitative nature rather than numerical results that are very accurate on an absolute basis, we have decided not to go to these somewhat lengthy computations and have instead adopted a simpler though less rigorous approach which has been suggested by Pople.[14] The relationship between Pople's method and the rigorous treatment has been discussed by Lefebvre and Moser[15] and more recently by Amos and Musher.[16]

With the approach adopted in this paper and with Pople's[14,17] formulas one obtains the following expressions for the first and second derivatives of the π-electron energy with respect to the bond distances, where the bond

$$\frac{\partial E_\pi}{\partial R_{\mu\nu}} = 2P_{\mu\nu}\frac{d\beta_{\mu\nu}}{dR_{\mu\nu}} = 2P_{\mu\nu}\beta'_{\mu\nu} \tag{7}$$

$$\frac{\partial^2 E_\pi}{\partial R_{\mu\nu}\partial R_{\kappa\lambda}} = 2\pi_{\mu\nu,\kappa\lambda}\beta'_{\mu\nu}\beta'_{\kappa\lambda} + 2\delta_{\mu\nu,\kappa\lambda}P_{\mu\nu}\beta''_{\mu\nu} \tag{8}$$

orders $P_{\mu\nu}$ and the bond–bond polarizabilities $\pi_{\mu\nu,\kappa\lambda}$ are defined by

$$P_{\mu\nu} = 2\sum_{j}^{\text{occ}} c_{j\mu}c_{j\nu} \tag{9}$$

$$\pi_{\mu\nu,\kappa\lambda} =$$

$$-2\sum_{i}^{\text{occ}}\sum_{k}^{\text{unocc}} \frac{(c_{i\mu}c_{k\nu} + c_{i\nu}c_{k\mu})(c_{i\kappa}c_{k\lambda} + c_{i\lambda}c_{k\kappa})}{\varepsilon_k - \varepsilon_i - \sum_{\rho\sigma}(c_{i\rho}{}^2c_{k\sigma}{}^2 - 2c_{i\rho}c_{k\sigma}c_{i\sigma}c_{k\rho})\gamma_{\rho\sigma}} \tag{10}$$

Equations 7 and 8 are formally analogous to those derived in the one-electron model.[3] However, the bond orders and bond–bond polarizabilities have now to be calculated by eq 9 and 10, respectively, using the coefficients and orbital energies obtained as solutions of eq 2, and the derivatives refer to the core parameter β. Furthermore, within the adopted approximations, eq 7 and 8 also apply to nonalternant hydrocarbons and to conjugated systems containing heteroatoms.

Results and Discussion

The second-order effects for the molecules to be discussed in this paper were evaluated at planar zero-order geometries, characterized by uniform carbon–carbon bond lengths of 1.40 Å and regular bond angles (*i.e.*, 120° for the all-*trans* open-chain polyenes and the frameworks of Figure 1, regular polygon angles for all others). The standard Pariser–Parr[18] parameters were employed, and all energy quantities are expressed in units of the core integral β_0 at 1.40 Å ($\beta_0 = -2.367$ eV).

For the calculation of the matrix elements of eq 8 we need to know the first and second derivatives of the core resonance integral with respect to bond distance. The first derivative β' was computed on the usual assumption of an exponential behavior of β on distance (*vide infra*). We have previously shown[3,4] that uncertainties in the functional form of β do not influence our results critically *via* the term involving β' in eq 8, but that errors in β'' may cause an appreciable shift in the eigenvalues Λ. An explicit computation of β'' can be avoided if one solves the simplified eigenvalue problem

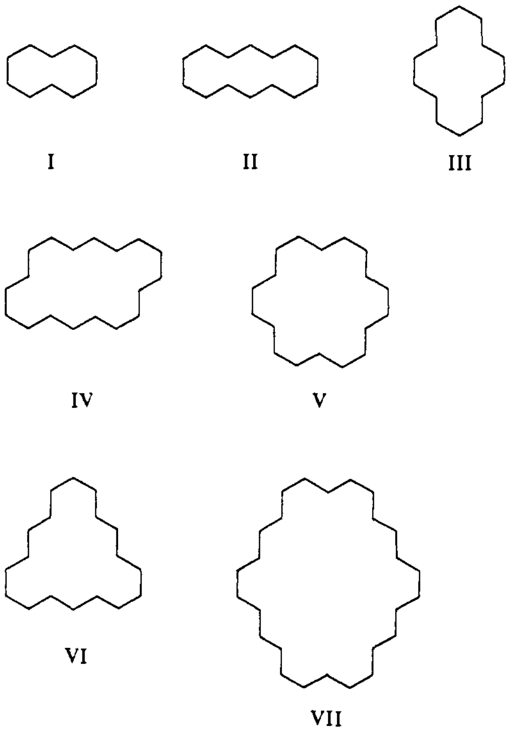

Figure 1. Geometries of the annulenes.

$$||\boldsymbol{\pi} - \lambda\mathbf{I}|| = 0 \tag{11}$$

where the elements of $\boldsymbol{\pi}$ are defined by eq 10 and $\mathbf{I}$ is the unit matrix. The terms in β'' can now be absorbed[3,4] in the critical value λ_{crit}, and errors in the functional form of β can partly be compensated for by adjusting λ_{crit} to experimental data.

An estimate for λ_{crit} may be obtained as follows. Diagonalization of the $\boldsymbol{\pi}$ matrix of benzene yields a $\lambda_{\max}$ value of 0.791 (in units of $\beta_0{}^{-1}$) and the corresponding eigenvector $\mathbf{D}_{\max}$ transforms as the B_{2u} representation of the D_{6h} symmetry group; that is, the energetically most favorable second-order distortion corresponds to bond alternation. This eigenvalue should be related to the experimental force constant[19,20] $k_{B_{2u}} = 3.94$ mdyn Å^{-1} for the B_{2u} carbon–carbon stretching mode of benzene by the equation,

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(14) J. A. Pople, *Proc. Roy. Soc.* (London), **A233**, 233 (1955).

(15) R. Lefebvre and C. Moser, "Calcul des fonctions d'onde moleculaire," Centre Nationale de la Recherche Scientifique, Paris, 1958, p 109.

(16) A. T. Amos and J. I. Musher, *Mol. Phys.*, **13**, 509 (1967).

(17) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955); J. A. Pople and P. Schofield, *Proc. Roy. Soc.* (London), **A233**, 241 (1955).

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

(19) R. D. Mair and D. F. Hornig, *ibid.*, **17**, 1236 (1949).

(20) There has been a long-standing controversy concerning the correct assignment of the vibrational frequencies to the B_{2u} normal mode in benzene, but more recent evidence[21] clearly favors the Mair–Hornig assignment.

(21) F. A. Miller, *J. Chem. Phys.*, **24**, 996 (1956); J. R. Scherer and J. Overend, *Spectrochim. Acta*, **17**, 719 (1961); S. Brodersen, J. Christoffersen, B. Bak, and J. T. Nielsen, *ibid.*, **21**, 2077 (1965).

Table I. Largest Eigenvalues of the Bond–Bond Polarizability Matrices of the [*n*]Annulenes

n	λ_{max}, β_0^{-1}	*n*	λ_{max}, β_0^{-1}
6[a]	0.7910	18[a]	0.9585
10[a]	0.9057	18 (IV)	0.9972
10 (I)	0.9102	18 (V)	0.9784
14[a]	0.9407	18 (VI)	1.0022
14 (II)	0.9488	26 (VII)	1.0026
14 (III)	0.9989		

[a] Regular polygon.

$$k_{B_{2u}} = k_\sigma + 2\lambda_{max}\beta_0\beta'^2 \text{ (at 1.40 Å)} \qquad (12)$$

where k_σ is the stretching force constant of the pure σ potential at 1.40 Å. The critical value, λ_{crit}, has to satisfy the condition

$$k_\sigma + 2\lambda_{crit}\beta_0\beta'^2 = 0 \text{ (at 1.40 Å)} \qquad (13)$$

Furthermore one has the relationship[3,4,22]

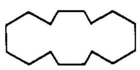
$$2\beta'/k_\sigma = 0.16 \text{ (at 1.50 Å)} \qquad (14)$$

Taking a value of about 6 mdyn Å^{-1} for the pure σ force constant at 1.50 Å as estimated by Dewar and Schmeising[23] and relating β' at 1.50 Å to β' at 1.40 Å by assuming an exponential behavior of the core resonance integral on bond length, one obtains

$$\lambda_{crit} = 1.22(\beta_0^{-1}) \qquad (15)$$

Cyclic Polyenes. The results for the monocyclic polyenes are given in Table I. It can be seen that λ_{max} shows a general tendency to increase with the number of ring atoms, but there is also a significant dependence on geometry (Figure 1), a feature that could previously[3,4] not be reproduced in the one-electron model. It is interesting to note that the configuration V, which X-ray analysis[24] showed to be the true geometry of [18]annulene, exhibits a smaller tendency for second-order bond fixation than the configurations IV and VI. The eigenvector belonging to λ_{max} has in all cases alternating signs around the ring and only slightly different values for the different types of bonds. The normalized components of $\mathbf{D}_{max}$ for the cisoid bonds in V, for example, are ± 0.2326 and for the transoid bonds ± 0.2372. Our previous conclusion[3,4] that second-order effects become important only for the higher members of the annulene series and that the λ_{max} *vs.* *n* curve is very flat in the region of the critical value λ_{max} is confirmed by the SCF results. However, our tentative estimate of a crossover point between 20 and 30 carbon atoms seems to have been too low.

The results of Table I refer to cyclic polyenes satisfying Hückel's (4*n* + 2) rule. For the monocyclic rings with 4*n* π electrons one usually has a situation where two π electrons have to occupy a pair of degenerate orbitals. Our perturbation treatment does not apply to these cases (formally one would obtain a λ_{max} value of infinity), but such molecules are known to suffer pseudo-Jahn–Teller distortions. In an SCF model the degeneracy can however be lifted by artificially choosing a less symmetric nuclear configuration, such as VIII for [16]annulene. The λ_{max} value of 6.1841 (β_0^{-1}) found for VIII clearly demonstrates the extremely high tendency for second-order bond fixation and the absence of aromatic properties.



VIII

Benzenoid Hydrocarbons. Our one-electron calculations[3,4] revealed no tendency for second-order double-bond fixation in benzenoid hydrocarbons, regardless of their size. The SCF data of Table II lead to the same conclusion. The λ_{max} values actually decrease with increasing size of the π-electron system.

Table II. Largest Eigenvalues of the Bond–Bond Polarizability Matrices of Benzenoid Hydrocarbons

Molecule	λ_{max}, β_0^{-1}	Molecule	λ_{max}, β_0^{-1}
Naphthalene	0.7442	Phenanthrene	0.6893
Anthracene	0.7280	Tetracene	0.7161

Table III. Largest Eigenvalues of the Bond–Bond Polarizability Matrices of the Open-Chain Polyenes

No. of carbon atoms	λ_{max}, β_0^{-1}	No. of carbon atoms	λ_{max}, β_0^{-1}
	All-*trans*		
4	0.3863	16	0.4763
6	0.4262	20	0.4757
8	0.4495	24	0.4700
10	0.4636	28	0.4645
12	0.4710		
	All-*cis*		
4	0.3841	8	0.5443
6	0.5192	10	0.7280

Open-Chain Polyenes. An interesting trend is observed for eigenvalues of all-*trans* open-chain polyenes (Table III). They slowly increase in going from short intermediate length chains, but then reach a maximum and start to decrease again. The maximum is far below the critical value which means that second-order effects will never become important for all-*trans* open-chain polyenes. The SCF bond orders, on the other hand, demonstrate that strong first-order bond fixation persists even in very long all-*trans* polyene chains, in agreement with experiment[25] and with theoretical results obtained by Dewar and Gleicher.[26] Our previous prediction[3,4] that second-order bond fixation should be observed in long polyene chains is thus seen to have been an artifact of a one-

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(22) Although this relationship was derived from a one-electron model, it also holds in the SCF formalism, since the bond orders for ethylene, benzene, and graphite are completely determined by symmetry.

(23) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(24) J. Bregman, F. L. Hirschfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Cryst.*, **19**, 227 (1965); F. L. Hirschfeld and D. Rabinovich, *ibid.*, **19**, 235 (1965).

(25) W. Sly, *ibid.*, **17**, 511 (1964).

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

electron model. On the other hand, the all-*cis* polyenes seem to show a different behavior (Table III). The λ_{max} *vs. n* curve would probably cross λ_{crit} if n gets sufficiently large, but since the geometrical constraints imposed on the model eventually become very unrealistic, we have not performed calculations for $n > 10$.

The results of the present paper can be summarized by stating that second-order bond fixation in closed-shell alternant hydrocarbons will become important only for the very large annulenes. This conclusion is to be contrasted with the findings for the nonalternant systems to be discussed in the following paper,[6] where we shall demonstrate that second-order effects may play a dominant role already for small π-electron molecules.

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Double-Bond Fixation in Conjugated π-Electron Systems. V. Self-Consistent Field Calculations for Nonalternant Hydrocarbons and Nitrogen Heterocycles

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Contribution from the Department of Chemistry and the Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556. *Received October 14, 1968*

Abstract: The SCF theory of first-order and second-order double-bond fixation of the preceding paper is applied to a variety of nonalternant hydrocarbons, benzo derivatives of cyclobutadiene, and aza analogs of alternant and nonalternant π-electron systems. It is found that second-order bond distortions play a dominant role in certain systems that have previously been classified as pseudoaromatic. A new aromaticity criterion is proposed which is entirely based on double-bond fixation. The theoretical conclusions are found to be in gratifying agreement with chemical experience in those cases where experimental information is available.

There have been numerous attempts to rationalize and predict aromaticity, or the lack of it, by quantum theory.[3] The two important approaches proposed by Hückel[4] and by Craig[5] may be cast in the form of simple rules. Hückel's rule is, however, limited to monocyclic hydrocarbons and Craig's treatment cannot be applied to systems that lack essential symmetry. The most general approach has been the criterion of resonance energy. There still remain some difficulties, as illustrated by the following examples taken from the recent literature.

By one of the most advanced π-electron SCF calculations[6] on monocyclic conjugated polyenes it was found that the hydrocarbons satisfying Hückel's $(4n + 2)$ rule exhibit positive resonance energies up to ring size of 22 carbon atoms, whereas those with $4n$ π electrons and the larger cycles show negative values. On this basis it was concluded that the former should be aromatic and the latter not. Lack of aromaticity in the lowest singlet states of the latter is accompanied by bond alternation. There is now direct experimental evidence for such a phenomenon in planar cyclooctatetraene.[7] On the other hand, the same computational procedure yielded positive resonance energies for all nonalternant hydrocarbons examined. From these calculations it was not apparent that asymmetric distortions may play an important role in such systems also.

In the context of a recent reexamination of the theory of double-bond fixation[8-10] we were led to the conclusion that asymmetric distortions should be a rather common phenomenon in conjugated hydrocarbons. Such second-order double-bond fixations, of a dynamic nature, were found to be particularly pronounced for molecules such as pentalene and heptalene. We therefore suggested[10] that these systems should be called nonaromatic by the same reasoning applied to the monocyclic hydrocarbons not satisfying Hückel's rule.

In the present paper we report SCF calculations for a variety of π-electron systems. The results will be discussed in terms of a theoretical aromaticity criterion that may be formulated as follows: *A conjugated π-electron system is called aromatic if it shows neither strong first-order nor second-order double-bond fixation.*

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(1) Alfred P. Sloan Research Fellow.

(2) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-635.

(3) For reviews see: (a) D. Ginsburg, Ed., "Non-Benzenoid Aromatic Compounds," Interscience Publishers, New York, N. Y., 1959; (b) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier Publishing Co., New York, N. Y., 1966.

(4) E. Hückel, *Z. Physik*, **70**, 204 (1931); **72**, 310 (1931).

(5) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

(6) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

(7) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).

(8) G. Binsch, E. Heilbronner, and J. N. Murrell, *Mol. Phys.*, **11**, 305 (1966).

(9) G. Binsch and E. Heilbronner in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, p 815.

(10) G. Binsch and E. Heilbronner, *Tetrahedron*, **24**, 1215 (1968).