

electron model. On the other hand, the all-*cis* polyenes seem to show a different behavior (Table III). The  $\lambda_{\max}$  vs.  $n$  curve would probably cross  $\lambda_{\text{crit}}$  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,<sup>6</sup> where we shall demonstrate that second-order effects may play a dominant role already for small  $\pi$ -electron molecules.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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

Gerhard Binsch<sup>1</sup> and Ilana Tamir

*Contribution from the Department of Chemistry and the Radiation Laboratory,<sup>2</sup> 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  $\pi$ -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.<sup>3</sup> The two important approaches proposed by Hückel<sup>4</sup> and by Craig<sup>5</sup> 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  $\pi$ -electron SCF calculations<sup>6</sup> 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  $4n$   $\pi$  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.<sup>7</sup> 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<sup>8-10</sup> 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<sup>10</sup> 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  $\pi$ -electron systems. The results will be discussed in terms of a theoretical aromaticity criterion that may be formulated as follows: *A conjugated  $\pi$ -electron system is called aromatic if it shows neither strong first-order nor second-order double-bond fixation.*

(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).

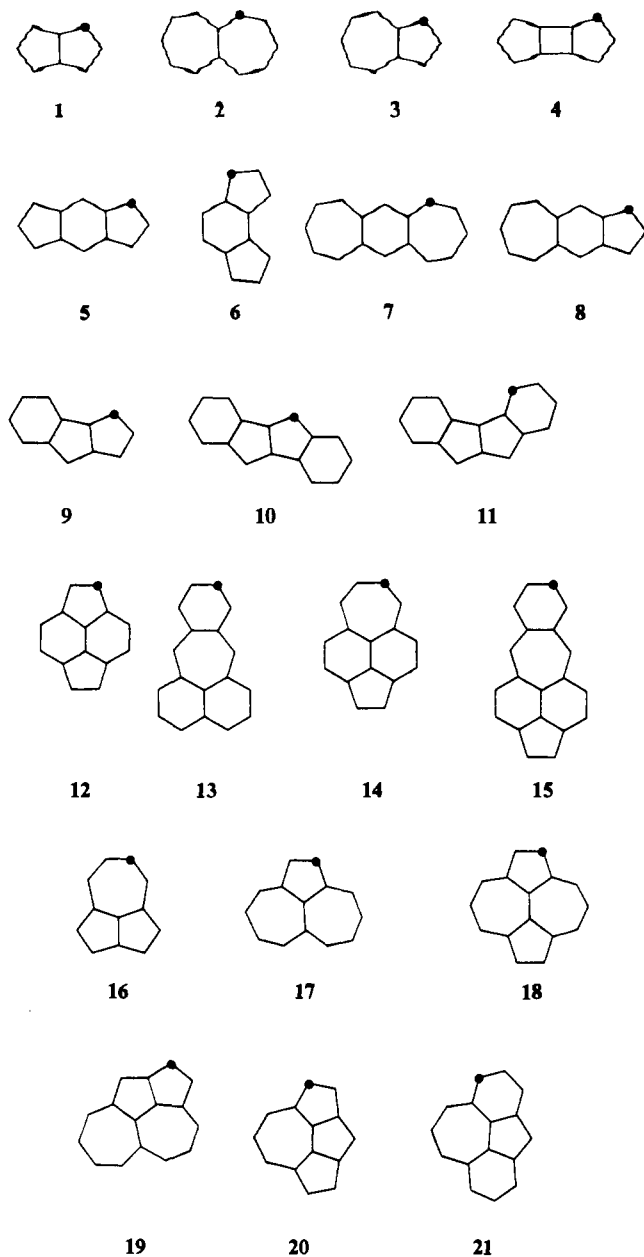


Figure 1. Topologies of nonalternant hydrocarbons.

## Results and Discussion

**Nonalternant Hydrocarbons.** The approximate SCF theory developed in paper IV of this series<sup>11</sup> was used for the calculation of the first-order and second-order bond distortions in the nonalternant systems of Figure 1. All effects were evaluated at idealized planar zero-order geometries, characterized by uniform carbon-carbon bond lengths of 1.40 Å and regular bond angles wherever applicable.

Two different parameter sets were employed. The first, referred to as PPP, was identical with the one used in the previous paper<sup>11</sup> ( $\beta_0 = -2.367$  eV,  $\gamma_{11} = 11.00$  eV). For this set we have derived<sup>11</sup> a critical value,  $\lambda_{\text{crit}}$ , of  $1.22\beta_0^{-1}$ . The results denoted by CD<sup>12</sup> were obtained

(11) G. Binsch, I. Tamir, and R. D. Hill, *J. Amer. Chem. Soc.*, **91**, 2446 (1969).

**Table I.** Largest Eigenvalues of the Bond-Bond Polarizability Matrices for the Nonalternant Hydrocarbons of Figure 1

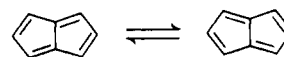
System	$\lambda_{\text{max}}, \beta_0^{-1}$		System	$\lambda_{\text{max}}, \beta_0^{-1}$	
	PPP	CD		PPP	CD
1	3.1539	3.6388	10	0.6569	0.5756
1 <sup>2-</sup>	0.4732		11	1.1328	0.9794
2	2.5916	2.4707	12	0.6921	0.6294
3	1.1079	1.0274	13	0.6528	0.5889
4	1.8317	1.6579	14	0.6770	0.5992
5	1.4314	1.3737	15	0.7405	0.6357
5 <sup>2-</sup>	0.6205		16	1.1080	1.0191
6	0.6513	0.5232	17	1.1074	0.9746
6 <sup>2-</sup>	0.5167		18	0.9096	0.8630
7	1.3763	1.2496	19	0.7780	0.6749
8	1.3200	1.1486	20	1.1172	1.0058
9	0.9063	0.7380	21	1.1900	1.0504

with  $\beta_0 = -1.752$  eV and  $\gamma_{11} = 10.98$  eV, changing  $\lambda_{\text{crit}}$  to  $1.25\beta_0^{-1}$ . We tend to prefer the PPP parameters with the "spectroscopic"  $\beta_0$  for the calculation of the second-order effects, because our second-order perturbation formalism<sup>11</sup> makes use of the coefficients of the virtual orbitals and of the energies of singly excited singlet configurations, but the "thermochemical" CD parameters<sup>12</sup> for the first-order double-bond fixations are determined by the SCF bond orders which only depend on the occupied orbitals. The  $\pi$ -bond orders  $P_{\mu\nu}$  are related to the "first-order bond lengths"<sup>8,9</sup>  $R_{\mu\nu}^{(1)}$  by

$$R_{\mu\nu}^{(1)} = A - kP_{\mu\nu}$$

where the constants  $A$  and  $k$  are found to have values around 1.50 and 0.17, respectively, if  $R_{\mu\nu}^{(1)}$  is expressed in ångström units.<sup>8,9</sup> It should be noted that the bond orders to be reported below refer to the idealized geometries as defined previously and are thus inferior in sophistication to those calculated by Dewar and Gleicher<sup>6</sup> on the basis of a procedure that allowed for self-consistent variations in the first-order bond lengths. However, for the conclusions we wish to draw in the present paper, this latter refinement is of no consequence.

The largest eigenvalues of the bond-bond polarizability matrices pertaining to the nonalternant hydrocarbons of Figure 1 are collected in Table I. Of all the systems examined, pentalene (1) shows by far the strongest tendency for second-order double-bond fixation, the  $\lambda_{\text{max}}$  value being substantially above the critical value,  $\lambda_{\text{crit}}$ . The normalized components of the eigenvector  $\mathbf{D}_{\text{max}}$  belonging to  $\lambda_{\text{max}}$  are given in Figure 2. The distortion pattern is of such a nature as to fix the molecule in one of its Kekulé-type structures. An equivalent distortion pattern is obtained by reversing the sign of  $\mathbf{D}_{\text{max}}$ . This means that the second-order effects result in a dynamic distortion of pentalene and that the structure of this particular molecule should be represented by an equilibrating or oscillating mixture of two isoenergetic forms of lower symmetry rather than by a "resonance arrow."



This conclusion is in agreement with results previously obtained by different methods.<sup>13</sup> Although first-order

(12) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965).

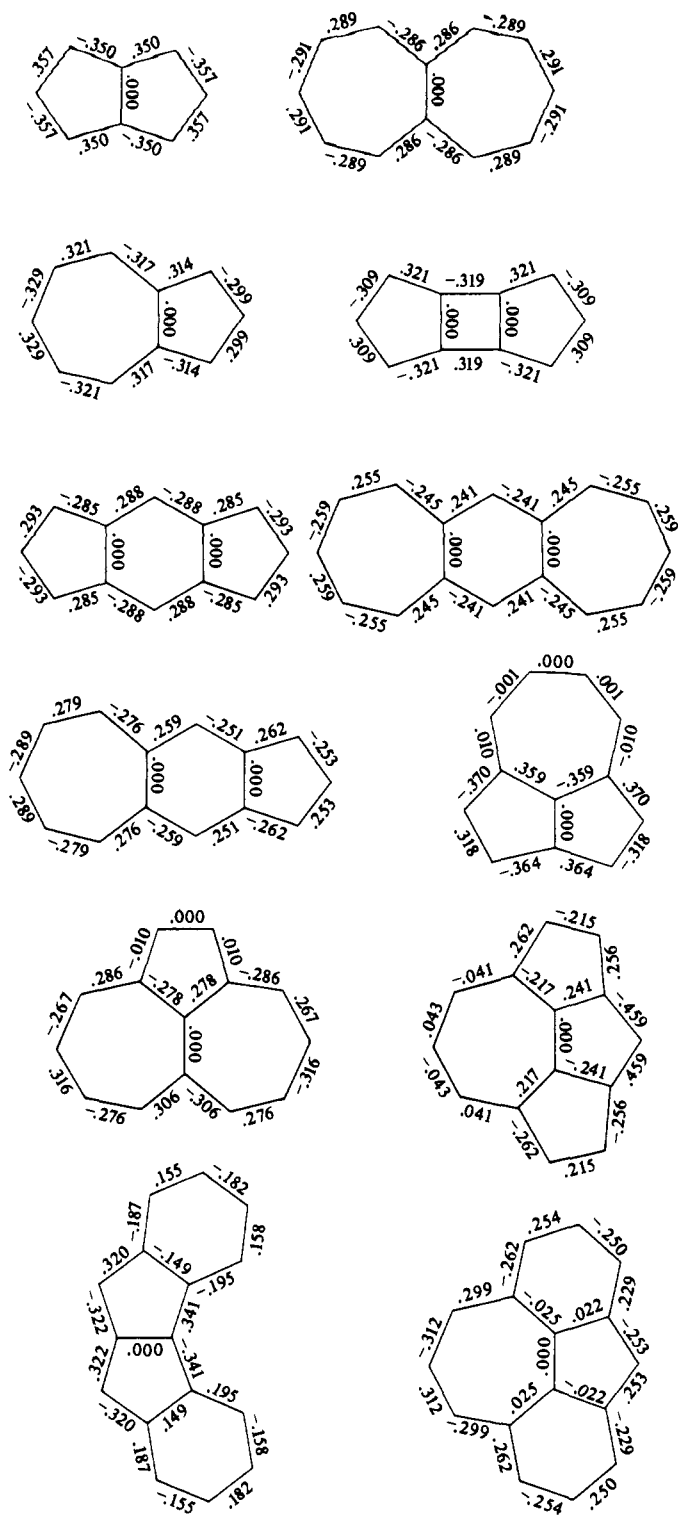


Figure 2. Normalized components of the eigenvectors  $D_{\max}$  for systems showing intermediate and strong second-order double-bond fixation.

double-bond fixations turn out to be insignificant in pentalene,<sup>14</sup> the molecule would nevertheless have to be

(13) P. C. den Boer-Veenendaal and D. H. W. den Boer, *Mol. Phys.*, **4**, 33 (1961); L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962); T. Nakajima, Y. Yaguchi, R. Kaeriyama, and Y. Nemoto, *Bull. Chem. Soc. Japan*, **37**, 272 (1964).

(14) With the exception of azulene as a typical example, first-order double-bond fixations are only reported (Table II) for those systems in which they are found to be strong or moderately strong. For all the

called nonaromatic according to our criterion. The second-order effects extend over the entire molecular framework and in view of their magnitude it is not surprising that all attempts at synthesis of **1** have so far met with failure, except for the hexaphenyl derivative.<sup>15</sup> By adding two more electrons to neutral pentalene, second-order bond distortions are seen to disappear completely (Table I). The pentalene dianion has indeed been prepared<sup>16</sup> and is found to be a perfectly stable species.

Another molecule exhibiting nearly equalized bond orders, but very strong second-order double-bond fixation, is heptalene (**2**). Following a number of unsuccessful attempts, heptalene has eventually been synthesized,<sup>17</sup> but its properties leave little doubt that it should be regarded as a polyolefin rather than an aromatic system. Our prediction is in agreement with a theoretical investigation of the heptalene problem by den Boer, *et al.*<sup>18</sup> Using a different approach, these authors also concluded that heptalene should show bond alternation. The well-known and extensively studied<sup>19</sup> azulene molecule (**3**), on the other hand, is not subject to this bond-alternation phenomenon. It will be noted, however, that the largest eigenvalue of the bond-bond polarizability matrix of **3** is still fairly close to the critical value.

Another system worth commenting on is **4**, colloquially known as "bowtienes." There are ten  $\pi$  electrons in the neutral molecule, and a naive application of Hückel's rule would therefore predict it to be aromatic. Our calculations indicate that it is not.

Comparison of **1**, **9**, **10**, and **11** reveals an interesting trend. Second-order effects decrease from very strong in **1** to very weak in **9** to unimportant in **10** (Table I), but first-order double-bond fixations change in the opposite direction (Table II). Our criterion allows none of these systems to be called aromatic. However, whereas this statement applies to the entire molecule in the case of pentalene, first-order double-bond fixations are localized essentially in the pentalene segment of **9** and **10**. In particular, there are two very short bonds (1-16 and 8-9) flanked by very long bonds in **10**. There is an obvious way for **10** to get rid of this localized nonaromaticity by adding reagents across the 1-16 and 8-9 bonds so as to yield products consisting of two aromatic benzene rings held together by a saturated carbon framework. Experimentally, **10** is in fact found to undergo such addition reactions with great ease.<sup>20</sup> In the isomer **11**, first-order bond fixations are moderate and localized in the six-membered rings, and second-order effects are also of an intermediate magnitude (Table I), but more pronounced in the pentalene segment of the molecule (*cf.* Figure 2). Obviously **11** is a case for which a clear-cut distinction between aromatic and nonaromatic cannot be made, but this need not be a drawback if one accepts the contention that aromaticity can reasonably be expected to be a continuous rather than discontinuous property of molecules.

remaining systems, including pentalene, first-order effects are of the same order of magnitude as in azulene, *i.e.*, insignificant.

(15) E. LeGoff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).

(16) T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

(17) H. J. Dauben and D. J. Bertelli, *ibid.*, **83**, 4659 (1961).

(18) P. C. den Boer-Veenendaal, J. A. Vliegthart, and D. H. W. den Boer, *Tetrahedron*, **18**, 1325 (1962).

(19) For a review see: E. Heilbronner in ref 3a, p 171.

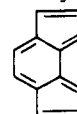
(20) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2255, 2263 (1952); C. C. Chuen and S. W. Fenton, *J. Org. Chem.*, **23**, 1538 (1958).

**Table II.** Selected SCF Bond Orders for Nonalternant Hydrocarbons (Parameter Set CD)<sup>a</sup>

System	Bond	Bond order	System	Bond	Bond order		
<b>3</b>	1-2	0.664	<b>9</b>	1-2	0.450		
	1-10	0.609		2-3	0.841		
	4-5	0.603		3-4	0.323		
	5-6	0.656		4-5	0.790		
	6-7	0.647		5-6	0.372		
<b>6</b>	1-2	0.864	6-7	0.614			
	1-12	0.307	7-8	0.683			
	2-3	0.410	8-9	0.646			
	3-4	0.790	9-10	0.675			
	4-5	0.332	10-11	0.634			
	9-10	0.803	11-12	0.294			
	10-11	0.442	1-12	0.773			
	<b>6<sup>2-</sup></b>	1-2	0.652	<b>10</b>	1-2	0.357	
1-12		0.554	2-3		0.622		
2-3		0.640	3-4		0.679		
3-4		0.591	4-5		0.651		
4-5		0.425	5-6		0.673		
9-10		0.479	6-7		0.637		
10-11		0.775	7-8		0.288		
<b>11</b>		1-2	0.749		1-16	0.826	
		2-3	0.561		<b>15</b>	1-2	0.806
		3-4	0.759			2-3	0.450
	4-5	0.507	3-4	0.683			
	5-6	0.578	4-5	0.509			
	6-7	0.537	5-6	0.595			
	15-16	0.485	6-7	0.687			
	1-16	0.536	7-8	0.611			
<b>12</b>	1-2	0.320	8-9	0.463			
	2-3	0.704	9-10	0.805			
	3-4	0.592	1-18	0.500			
	1-12	0.895	<b>16</b>	1-2	0.672		
<b>13</b>	1-2	0.833		2-3	0.600		
	2-3	0.408		3-4	0.492		
	3-4	0.765		4-5	0.770		
	4-5	0.399		5-6	0.477		
	5-6	0.680		1-11	0.642		
	6-7	0.597	<b>17</b>	1-2	0.604		
	7-8	0.739		2-3	0.488		
	8-9	0.526		3-4	0.756		
1-17	0.460	4-5		0.525			
<b>14</b>	1-2	0.828		5-6	0.761		
	2-3	0.411		6-7	0.481		
	3-4	0.649	1-13	0.697			
	4-5	0.647	<b>18</b>	1-2	0.501		
	5-6	0.651		2-3	0.600		
	6-7	0.415		3-4	0.653		
	7-8	0.840		1-14	0.782		
	1-14	0.446	<b>19</b>	1-2	0.821		
<b>19</b>	1-2	0.807		2-3	0.406		
	2-3	0.445		3-4	0.598		
	3-4	0.675		8-9	0.614		
	4-5	0.596		9-10	0.660		
	5-6	0.716		1-12	0.429		
	6-7	0.544					
	7-8	0.445					
	8-9	0.793					
9-10	0.490						
10-11	0.788						
11-12	0.452						
12-13	0.682						
13-14	0.563						
1-14	0.440						

<sup>a</sup> The atomic positions are numbered consecutively, starting with the carbon atom marked by a heavy dot in Figure 1 and proceeding in a clockwise fashion along the periphery (including the atoms involved in the cross-links).

Our calculations indicate that the isomeric indacenes **5** and **6** should both be nonaromatic, but for different reasons. The *s*-indacene **5**, recently prepared by Hafner's group<sup>21</sup> and found to be moderately stable at room temperature but easily undergoing addition reactions, shows fairly strong second-order double-bond fixation. The SCF calculation demonstrates the absence of appreciable second-order effects in the *as*-indacene **6**. This is in striking contrast to previous results in the one-electron model,<sup>10</sup> adding support to an often-voiced suspicion that one-electron calculations may become rather poor for nonalternant systems. The bond orders of Table II reveal very strong first-order double-bond fixation in **6**, extending over the entire molecule and essentially fixing it in a single nonresonating Kekulé-type structure, A. Both molecules become aromatic on addition of two electrons to the  $\pi$  system, **5** because the second-



A

order double-bond fixation disappears (Table I) and **6** because there is an averaging of the bond orders in the dianion (Table II). Experimental evidence<sup>22,23</sup> is in concordance with these conclusions.

In the systems **12** to **15**, all of which are known,<sup>24</sup> second-order double-bond fixations are absent (Table I), but these molecules exhibit localized first-order effects to various degrees (Table II).

Derivatives of the nonalternant molecules **16** and **17** have been prepared by Hafner and his group.<sup>22,25</sup> The  $\lambda_{\max}$  values calculated for **16** and **17** are almost exactly equal to the azulene value (Table I), but second-order effects are strictly confined to the pentalene segment of **16** and the heptalene segment of **17** (Figure 2). Localized first-order bond fixations are moderate but not negligible in both molecules. Our results are in good qualitative agreement with the behavior of **16** and **17** in addition reactions<sup>22,25</sup> and with a recent X-ray analysis<sup>26</sup> of a tetramethyl derivative of **17**.

The last system of Figure 1 we wish to comment on is **21**, whose synthesis is presently being attempted.<sup>27</sup> Of all the *peri*-condensed hydrocarbons examined here, **21** shows the highest tendency for second-order double-bond fixation, the effect being uniformly spread over the entire periphery (Figure 2), whereas first-order effects are conspicuously small. Heilbronner and coworkers<sup>28</sup> have recently obtained theoretical evidence for a very low-lying triplet state in this molecule; there is in fact a dis-

(21) K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, *Angew. Chem.*, **75**, 35 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 123 (1963).

(22) K. Hafner, *Angew. Chem.*, **75**, 1041 (1963); *Angew. Chem. Intern. Ed. Engl.*, **3**, 165 (1964).

(23) T. J. Katz and J. Schulman, *J. Amer. Chem. Soc.*, **86**, 3169 (1964); T. J. Katz, V. Balogh, and J. Schulman, *ibid.*, **90**, 734 (1968).

(24) B. M. Trost and G. M. Bright, *ibid.*, **89**, 4244 (1967); V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956); M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3051, 3073 (1965).

(25) K. Hafner and J. Schneider, *Ann. Chem.*, **626**, 37 (1959); K. Hafner and G. Schneider, *ibid.*, **672**, 194 (1964); K. Hafner and K. F. Bangert, *ibid.*, **650**, 98 (1961).

(26) E. Carstensen-Oeser and G. Habermehl, *Angew. Chem.*, **80**, 564 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 543 (1968).

(27) E. Heilbronner and A. J. Krubsack, personal communication.

(28) P. Baumgartner, E. Weltin, G. Wagnière, and E. Heilbronner, *Helv. Chim. Acta*, **48**, 751 (1965).

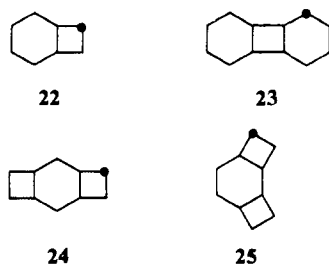


Figure 3. Topologies of alternant hydrocarbons derived from cyclobutadiene.

Table III. Largest Eigenvalues of the Bond-Bond Polarizability Matrices for the Cyclobutadiene Derivatives of Figure 3

System	$\lambda_{\max} \beta_0^{-1}$		System	$\lambda_{\max} \beta_0^{-1}$	
	PPP	CD		PPP	CD
22	0.7928	0.7237	24	0.8411	0.7566
23	0.7419	0.6711	25	1.0051	0.8510

tinct possibility for **21** to have a triplet ground state. Although we have not investigated this point in detail, such a possibility cannot be discounted for all the systems exhibiting strong second-order effects in their lowest singlet states.

**Benzo Analogs of Cyclobutadiene.** Cyclobutadiene itself is subject to pseudo-Jahn-Teller distortions in its lowest singlet state. As already explained,<sup>11</sup> the pseudo-Jahn-Teller effect emerges as a special case in our general theory of second-order double-bond fixation. The eigenvalues collected in Table III demonstrate that the dynamic distortions typical for cyclobutadiene disappear in benzo analogs **22–25** (Figure 3); the only system for which second-order effects may not be entirely negligible is **25**.

Localized first-order double-bond fixations are, however, exceedingly strong in **22**, **24**, and **25** (Table IV), whereas biphenylene (**23**), in spite of having two very long bonds, 5–6 and 11–12, shows no localized double bonds. According to our criterion, biphenylene (**23**) is therefore the only aromatic hydrocarbon in this series, in agreement with experimental evidence.<sup>29</sup> It may perhaps be worthwhile to mention parenthetically that biphenylene does not satisfy Hückel's rule.

**Nitrogen Heterocycles.** We have limited our calculations in the heterocyclic series to a few systems that contain one or two nitrogen atoms, each nitrogen atom contributing one  $\pi$  electron. A great variety of parameters have been suggested in the literature for Pariser-Parr-Pople-type calculations on heterocycles. We have chosen a set that may be regarded as typical, denoted by PPP in Table V. The DG parameters of Table V are taken from a paper by Dewar and Gleicher.<sup>30</sup> Here again we prefer the PPP set for the calculation of the second-order effects and the DG set for the first-order double bond fixations. All results pertain to idealized geometries, identical with those

(29) For a recent review see: M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967; the theoretical aspects of the cyclobutadiene problem have been reviewed by H. E. Simmons and A. G. Anastassiou on p 368 of this volume.

(30) M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966).

Table IV. SCF Bond Orders for the Systems of Figure 3 (Parameter Set CD)<sup>a</sup>

System	Bond	Bond order	System	Bond	Bond order
22	1–2	0.960	24	1–2	0.969
	2–3	0.132		2–3	0.104
	3–4	0.739		3–4	0.661
	4–5	0.579		3–10	0.643
	5–6	0.734	25	1–2	0.926
	3–8	0.567		2–3	0.201
23	1–2	0.621	3–4	0.811	
	2–3	0.701	3–10	0.424	
	4–5	0.699	6–7	0.207	
	5–6	0.177	7–8	0.804	
	5–12	0.593	8–9	0.482	

<sup>a</sup> For numbering system see footnote *a* to Table II.

Table V. Parameter Sets for Nitrogen Heterocycles

	PPP, eV	DG, eV
$\beta_0^{\text{CC}}$	–2.367	–1.752
$\beta_0^{\text{CN}}$	–2.367	–1.850
$\gamma_{11}^{\text{C}}$	11.00	10.98
$\gamma_{11}^{\text{N}}$	13.46	12.34
$\alpha_{\text{N}} - \alpha_{\text{C}}$	–3.26	–2.96
Nitrogen Slater charge	3.90	3.57

used for the parent hydrocarbons. The first derivative of the resonance integral for a carbon–nitrogen bond at 1.40 Å was taken to be equal to the corresponding value for the carbon–carbon bond,<sup>11</sup> and an analogous assumption was made for the curvature of the  $\sigma$  potential,<sup>31</sup> leaving  $\lambda_{\text{crit}}$  unchanged from the hydrocarbon value.<sup>11</sup>

The results of Table VI show that second-order effects are rather insensitive to nitrogen substitution in heterocyclic analogs of typical aromatic alternant hydrocarbons and are insignificant in all cases examined. All of them are in fact slightly smaller than the corresponding values for the parent molecules.<sup>11</sup> The first-order bond fixations differ so little from the hydrocarbon values that it does not seem worthwhile to reproduce them here.

First-order double-bond fixations are also unimportant in all the aza- and diazaazulenes of Table VI. However, the introduction of heteroatoms is seen to change  $\lambda_{\max}$  in both directions, and since the azulene  $\lambda_{\max}$  value itself is already fairly close to  $\lambda_{\text{crit}}$ , relatively small shifts can make a qualitatively significant difference. Our calculations predict 5,9-diazaazulene to be nonaromatic and possibly also the 2,5-, 2,7-, and 5,7-diazaazulenes. On the other hand, nitrogen atoms in certain positions may also reduce the importance of second-order effects. It is probably not an accident that the known molecules 1-azaazulene,<sup>32</sup> 1,3-diazaazulene,<sup>32</sup> 6-azaazulene,<sup>21,33</sup> and 6,8-diazaazulene<sup>34</sup> all fall into this latter category.

With one exception, the aza analogs of pentalene

(31) This assumption is clearly not a critical one. In our formalism<sup>11</sup> we only need an average value for the  $\sigma$  potential. Any difference in the curvatures of the  $\sigma$  potential between a carbon–carbon and a carbon–nitrogen bond thus becomes reduced by the ratio of the number of carbon–nitrogen to carbon–carbon bonds.

(32) For references see: W. Keller-Schierlein and E. Heilbronner in ref 3a, p. 277.

(33) K. Hafner and M. Kreuder, *Angew. Chem.*, **73**, 657 (1961).

(34) U. Müller-Westerhoff and K. Hafner, *Tetrahedron Letters*, 4341 (1967).

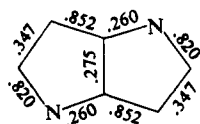
**Table VI.** Largest Eigenvalues of the Bond-Bond Polarizability Matrices for Nitrogen Heterocycles

Positions of N atoms <sup>a</sup>	$\lambda_{\max}, \beta_0^{-1}$		Positions of N atoms <sup>a</sup>	$\lambda_{\max}, \beta_0^{-1}$	
	PPP	DG		PPP	DG
Azabenzenes					
1	0.7839		1, 4	0.7860	
1, 3	0.7571				
Azanaphthalenes					
1, 9	0.7349		1, 6	0.7232	
1, 8	0.7268		2, 8	0.7277	
1, 7	0.7276		2, 7	0.7228	
Azaazulenes					
1	0.9565	0.8217	5, 7	1.2908	1.2421
2	1.1755	1.1181	1, 9	0.9830	0.8404
5	1.1791	1.0762	1, 8	0.8892	0.7501
6	0.9992	0.8591	1, 7	1.0086	0.8671
7	1.1814	1.0984	1, 6	0.8738	0.7507
1, 3	0.9096	0.7804	1, 5	1.0068	0.8365
5, 9	1.3806	1.4411	2, 5	1.2971	1.2310
6, 8	0.9613	0.8393	2, 6	1.0482	0.9232
5, 8	1.0297	0.8778	2, 7	1.2810	1.2204
Azapentalenes					
1	4.1443	2.5078	1, 6	2.1829	1.5476
2	2.0235	1.7386	1, 5	1.1045	0.7882
1, 3	<i>b</i>	<i>b</i>	2, 6	1.6648	1.3927
1, 7	<i>b</i>	<i>b</i>			
Azaheptalenes					
1	1.6279	1.2371	1, 10	1.9572	1.3802
2	3.9074	3.6889	1, 9	1.2934	0.9522
3	1.7685	1.4340	1, 8	1.7961	1.2536
1, 5	1.3601	1.0320	1, 7	1.3908	1.0932
1, 4	1.7240	1.1329	2, 10	(18.6549) <sup>b</sup>	<i>b</i>
2, 4	(10.5346) <sup>b</sup>	(12.8307) <sup>b</sup>	2, 9	1.9806	1.4442
1, 3	1.2846	0.9787	2, 8	(41.8524) <sup>b</sup>	<i>b</i>
1, 11	1.2630	0.9967	3, 9	1.4801	1.1894

<sup>a</sup> The indicated positions of the N atoms refer to the numbering system used for the parent hydrocarbons; see footnote *a* to Table II.

<sup>b</sup> Extreme value due to near-degeneracy.

exhibit strong second-order double-bond fixation. The  $\lambda_{\max}$  values of 1,3-diazapentalene and 1,6-diazapentalene are extremely high due to near-degeneracy and therefore cease to be of numerical significance. First-order double-bond fixations are appreciable in 1-azapentalene and very strong in 1,4-diazapentalene, as shown by the SCF bond orders in the following diagram (DG parameter set).



Thus our criterion prohibits aromaticity in all the aza analogs of pentalene. The same conclusion is reached

for all the azaheptalenes of Table VI on the basis of second-order effects alone.

Molecules having the topology of the pentalene system and containing nitrogen atoms in the bridgehead positions are also called azapentalenes in the literature, but they are really analogs of the pentalene dianion, an aromatic system as we have seen. Their properties are indeed found to be in line with their expected aromatic character.<sup>35</sup>

## Conclusion

Having discussed the results of our calculations in terms of a single concept, it now becomes necessary to be specific about the nature of our aromaticity criterion and its limitations.

(1) Most important of all it should be realized that our criterion assumes the form of a postulate. It does not follow from our theory, nor from our numerical results, nor from chemical experience.

(2) Our criterion does not have the simplicity of a magic rule, but it is closely related to a physical phenomenon, namely the tendency of the  $\pi$  electrons to cluster in certain bonds. It differs from the aromaticity criterion based on resonance energies, which are also relevant to this phenomenon, in two respects. First, resonance energy is a global property of conjugated molecules and is therefore not capable of pinpointing the lack of  $\pi$ -electron delocalization in a particular structural segment. Second, resonance energies computed for the fully symmetrical molecules do not seem to succeed in detecting the dynamic distortions in certain  $\pi$ -electron systems which can also hamper electron delocalization.

(3) Finally we wish to emphasize that our aromaticity criterion is strictly a structural criterion. It has in principle absolutely no bearing on reactivity. In the present paper we have frequently inferred reactive behavior from our results, to be sure, but it is important to realize that these conclusions rest entirely on the chemist's experience and intuition about relationships between structure and reactivity. Thus our criterion covers only a certain facet of the complex problem of aromaticity. Whether it is an important one or not will have to be decided by the experimentalist.

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(35) See, for example: T. W. G. Solomons and C. F. Voigt, *J. Amer. Chem. Soc.*, **88**, 1992 (1966); S. Trofimenko, *ibid.*, **88**, 5588 (1966); R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *ibid.*, **89**, 2618 (1967), and accompanying papers; V. Boekelheide and N. A. Fedoruk, *ibid.*, **90**, 3830 (1968).