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Resonance Theory. VI. Bond Orders

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Abstract: Graph-theoretical and MO formulations of Pauling bond orders are outlined. Negative bond orders and bond orders greater than unity are defined and discussed. The use of Pauling bond orders to correlate various types of chemical and physical properties is justified as being tantamount to using the results of SCF-LCAO-MO calculations. Bond lengths and nmr ortho coupling constants in benzenoid systems can be accurately predicted using functions linear in Pauling bond orders. Of most significance is the fact that the bond-order relationships can be extended to include nonalternant hydrocarbons and annulenes without loss of correlative abilities.

The interrelations of certain physical properties and theoretical bond orders in benzenoid aromatic hydrocarbons are well-established. As examples, one finds that there are linear correlations of Coulson π bond orders¹ (Hückel molecular orbital method, HMO) with experimental bond lengths²⁻⁶ and with nmr spin-spin coupling constants of ortho hydrogen atoms, $J_{\text{HH}}^{\text{ortho}}$.⁷⁻¹² A theoretical rationale for empirical bond order-bond length relationships has been outlined by Salem,^{13,14} and the linear π bond order- J_{HH} relations are probably a consequence of dependence of J_{HH} on σ orbital overlap, and hence on bond length.¹⁵⁻¹⁸ More refined MO methods that have been used to correlate bond lengths and coupling constants do not lead to any appreciable better agreement of calculated and experimental values.^{17,19-25}

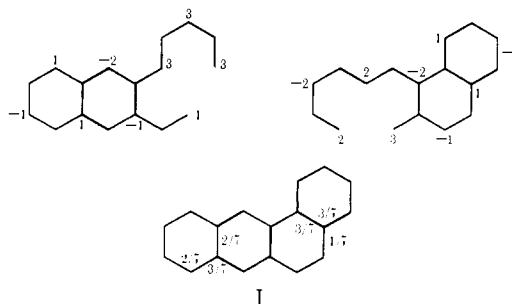
The applications of valence bond (VB) theory are less numerous and consider fewer systems. The VB theory of spin-spin coupling has been described in detail^{17,26} but has only been applied to benzene and methyl-substituted derivatives.¹⁷ The formulation of a VB bond order-bond length relation actually antedates MO treatments,^{27,28} but again has only been applied to a few benzenoid hydrocarbons.^{5,6,29-31} Nevertheless, it has been pointed out for particular molecules that Pauling bond orders are as successful in correlating bond lengths as any other kind of theoretical method.^{5,6,32}

Recently, it was demonstrated that a parameterized structure-resonance theory that uses only Kekulé structures^{33,34} gives resonance energies for many diverse kinds of π molecules that are in excellent agreement with the results of variable bond length SCF-LCAO-MO³⁵ calculations. Also, there is almost perfect correlation of resonance theory and SCF localization energies with Pauling bond orders.³⁶ These factors, along with extreme ease of calculation, mandate a complete comparison of Pauling bond orders with experimental bond lengths and coupling constants. A main

purpose is to show how the use of Pauling bond orders to correlate structural data can be extended to include π structures other than benzenoid hydrocarbons.

Calculations of Pauling Bond Orders

The least efficient way of finding Pauling bond orders is to draw all Kekulé structures, finally obtaining the ratio of structures in which a bond is double to the total number of structures. For alternant benzenoid systems many different techniques have been recently summarized.³⁷ The quickest method is to delete a vertex from the molecular graph of the π system under consideration, obtaining an odd alternant graph for which one can write a nonarbitrary set of coefficients that sum to zero around every vertex in the graph. The reader will recognize these coefficients as the unnormalized eigenvectors of a nonbonding (NB) MO for the deleted vertex system.³⁸ The sum of the coefficients at vertices adjacent to the deleted vertex is the structure count (SC)³⁹ for the parent system. Furthermore, these coefficients also enumerate the number of Kekulé structures in the parent system in which the bond to the deleted vertex position is double.⁴⁰ Graphs of deleted vertex systems of benz[*a*]anthracene are given in 1. The Pauling bond orders deter-



mined from the NBMO coefficients are also shown, and all

remaining bond orders in the molecule follow because the sum of Pauling bond orders around any vertex must equal unity.

One additional way of determining Pauling bond orders is of interest. In HMO theory the Coulson bond order¹ is defined according to eq 1, where the sum is over j occupied

$$P_{rs}^c = \sum_j n_j c_{jr} c_{js} \quad (1)$$

levels, n_j gives the number of electrons in level j , and c_{jr} and c_{js} are eigenvectors. Chemical intuition suggests that the quantity given in eq 1 should be a measure of electronic charge in a bonding region. However, the Coulson bond order cannot be considered as analogous to a bond population. The sum of all bond populations is the total number of electrons, whereas the sum of all Coulson bond orders is the total π energy of the delocalized π system. Ham and Ruedenberg⁴¹ state that the appropriate theoretical quantities for comparison with bond lengths are bond populations.

The Pauling bond order is analogous to the bond population in the above regard, and it is interesting that Pauling bond orders for all alternant systems can also be expressed within the HMO theory as shown in eq 2.⁴¹ The partial

$$P_{rs}^p = \sum_j n_j c_{jr} c_{js} / \epsilon_j \quad (2)$$

Coulson bond order of each level is weighted by the inverse of the eigenvalue so that less stable MO levels contribute to the bond order more than the lower levels. The point is that tables of HMO eigenvalues and eigenvectors can therefore be used to determine exact Pauling bond orders. The Pauling bond order has some of the characteristics of a bond population but also bears some resemblance to the Coulson bond order, although eq 1 and 2 show there cannot be an exact linear correspondence.

When one applies either of the two Pauling bond order methods described to π systems containing rings of $4n$ (n = integer) vertices, one finds that some bonds are found to have negative Pauling bond orders, and others have bond orders that are greater than unity. Neither of these two concepts have been discussed previously, although the occurrence of negative bond orders could be related to the fact that estimated resonance energies for cyclobutadienoid systems are negative, indicating antiaromatic character rather than a resonance stabilized system.⁴²⁻⁴⁵ A fuller discussion will be given in a later section.

Polyenes and Benzenoid Hydrocarbons

The accurate optimum experimental values of bond lengths listed by Allinger and Sprague for benzene, ethylene, and butadiene were chosen to define a Pauling bond order-bond length relationship.⁴⁶ The bond orders and bond lengths are listed in Table I, and the data are fitted

Table I. Experimental and Calculated Bond Lengths (Å)

Compd	Bond order	Bond length		Calcd - exptl
		Exptl	Calcd	
Benzene	0.5	1.397 ^a	1.401	0.004
Ethylene	1.0	1.337 ^b	1.339	0.002
Butadiene	1.0	1.343 ^c	1.339	-0.004
Butadiene	0.0	1.466 ^c (1.464 ^d)	1.464	-0.002

^a A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).
^b L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, **42**, 2683 (1965).
^c W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966).
^d A. R. H. Cole, G. M. Mohay, and C. A. Osbourne, *Spectrochim. Acta, Part A*, **23**, 909 (1967).



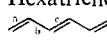



with high accuracy by the resulting linear eq 3. A linear

$$d_{rs} = 1.464 - 0.125p_{rs}^p \quad (3)$$

equation using Coulson HMO bond orders fits the data with average deviations three times larger. In addition, the bond length in graphite (exptl. 1.421 Å⁴⁷) is calculated to be 1.422 Å ($p^p = 0.333$) by eq 3, whereas the Coulson bond-order equation ($p^c = 0.535$) gives 1.438 Å.

For classical cyclic and acyclic olefins that can be represented by only a single Kekulé structure, the Pauling bond-order method makes a very straightforward prediction that all single bonds should be 1.464 Å in length and all double bonds 1.339 Å. Relevant experimental bond lengths are listed in Table II, and the differences between calculated and

Table II. Single and Double Bonds in Classical Polyenes (Å)

Compd	Bond	Bond length ^a (exptl)	Calcd - exptl
Cyclopentadiene 	a	1.342 ^b	-0.003
	b	1.469 ^b	-0.005
1,3-Cyclohexadiene 	a	1.346 ^c	-0.007
	b	1.467 ^c	-0.003
Hexatriene 	a	1.337 ^d	0.002
	b	1.457 ^d	0.007
	c	1.367 ^d	0.028
Dimethylfulvene 	a	1.347 ^e	-0.008
	b	1.476 ^e	-0.012
	c	1.340 ^e	-0.001
	d	1.462 ^e	0.002
Cycloheptatriene 	a	1.356 ^f	-0.017
	b	1.446 ^f	0.018
	c	1.356 ^f	-0.017
Cyclooctatetraene 	a	1.340 ^d	-0.001
	b	1.475 ^d	0.010

^a Electron diffraction values except for b (microwave). ^b L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965).
^c Averages from three investigations: G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 11 (1967); M. Traetteberg, *Acta Chem. Scand.*, **22**, 2305 (1968); O. Oberhammer and S. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).
^d M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724 (1966); **22**, 628 (1968).
^e J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 261 (1970).
^f M. Traetteberg, *ibid.*, **86**, 4625 (1964).

experimental values are given in the last column. Only the central double bond in hexatriene and the three bonds of cycloheptatriene show a deviation larger than the probable experimental error. The hexatriene molecule is quite flexible and it is possible that the experimental value of the central double bond is lengthened by torsional motions.²⁵ The cycloheptatriene results cannot be rationalized, but the near constancy of double bonds and single bonds in all of the other olefins in Tables I and II leads one to suspect that the experimental results may be incorrect.

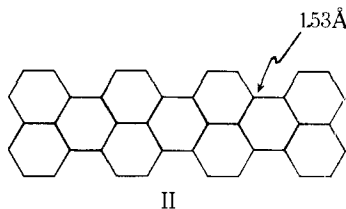
The bond lengths and Pauling bond orders of benzenoid hydrocarbons are listed in Table III. Also listed are average errors in the experimental bond lengths as given by the respective investigators and average differences of calculated and experimental bond lengths as determined with eq 3. Every benzenoid compound listed in the literature with quoted experimental errors of 0.010 Å or less was included in the table. Some of the larger structures illustrate a very useful aspect of Pauling bond orders, in that any interested

person can immediately check the calculated values. This is not possible for even the simplest of MO calculations.

Using eq 3, the average deviation of calculated and experimental values is $\pm 0.009 \text{ \AA}$, very slightly larger than the average estimated experimental error of $\pm 0.008 \text{ \AA}$. Presumably, a statistical fit of the bond lengths to Pauling bond orders would have yielded an even closer correlation, but the approach to using a few standard molecules has a particular advantage. If the correlation of data is generally good, as in the present work, one can then consider the exceptions as special cases for which *ad hoc* explanations may be necessary.

For example, there are 25 bonds listed in Table III which have bond orders larger than 0.500, and 19 of the calculated bond lengths are larger than the X-ray values. These are also the bonds where the calculated values have the largest errors, so if systematic experimental errors could be discovered characteristic of bonds with high bond orders, a great deal of the already small discrepancies could be removed. An examination of the available neutron and X-ray diffraction data^{48,49} suggests the possibility that bond lengths in bonds of high order are underestimated by X-ray diffraction. This is understandable since neutrons are scattered by atomic nuclei, whereas with X-rays the center of electronic charge clouds are determined. One can easily show that the shortening effect in the X-ray experiment should be an approximately linear function of bond order⁵⁰ with the correction in the experimental value being $+0.019 \text{ \AA}$ for a bond order of 0.800. Calculated bond lengths would then lie well within the limits of the experimental values.

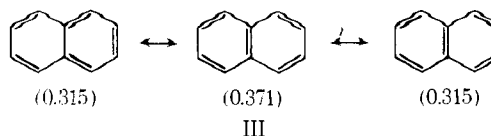
There is a variation of bond lengths found in Table III that could indicate a severe limitation of the use of Pauling bond orders to correlate bond lengths. In the worst case, bonds with bond order of 0.250 range in length from 1.420 (anthracene) to 1.468 \AA (chrysene). The average range for each bond order is *ca.* 0.02 \AA which is two to three times as large as the quoted experimental errors in Table III. However, I think it probable that experimental redeterminations of bond lengths in particular molecules might resolve these discrepancies. One notes that many of the supposed anomalies in bond order–bond length relationships have vanished when more accurate experimental data have become available. Bonds a and h in phenanthrene formerly were given as 1.457 and 1.390 \AA , respectively,⁵¹ values that were always troublesome to theorists. Bond f in pyrene was always calculated to be 0.02 to 0.03 \AA larger than the experimental value,⁴⁹ and bond e in perylene was always estimated by MO calculations to be much shorter than the length of 1.50 \AA from early data.⁵² For the latter case, a suggestion that overcrowding of 1,8-phenanthroid type hydrogen atoms would be relieved by a carbon–carbon extension of 0.03 to 0.04 \AA was widely accepted.^{5,6,53} This explanation is still advanced for the very long bonds (1.53 \AA) found in quarterylene⁵⁴ II, so a new determination of quarterylene bond



lengths may be in order. Recent force-field calculations generally agree that strain is relieved in aromatic systems by small adjustments in bond angles and out-of-plane deformations,^{46,55} rather than by bond length adjustments. The results given in Table III support this viewpoint.

The empirical structure-resonance theory mentioned in

the introductory section^{33,34} allows one to assign weights to the individual Kekulé structures, the weights being related to the eigenvectors of the Hamiltonian matrix. The results of such a calculation are illustrated in III, weights in paren-

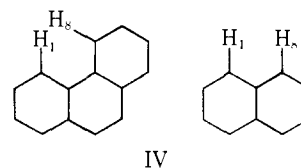


theses. Resulting calculated bond lengths differ from those given in Table III by an average of 0.004 \AA , some deviations negative and some positive, so that the average difference in experimental and calculated bond lengths remains approximately the same. With larger aromatic π systems the weights assigned by resonance theory calculations are even more uniform, so that one concludes that the Pauling bond order based on equivalent contributions of Kekulé structures is an adequate description for predictive purposes. In a few small nonalternant systems to be discussed, the relative weights of structures seems to be a more important factor.

It is not necessary to present a tabulation of bond orders, coupling constant data, and calculated coupling constants. The extensive previous work on the mutual correlations of Coulson bond orders with bond lengths and coupling constants,²⁻¹² in conjunction with the Pauling bond order–bond length relationship illustrated by the data in Table III, makes it apparent that a good Pauling bond order–coupling constant correlation will exist. The ortho proton coupling constants for 50 sets of positions in 14 polynuclear aromatic hydrocarbons^{12,18,56} fit eq 4 with a correlation coefficient of 0.984, and an average deviation of $\pm 0.1 \text{ Hz}$. In exact corre-

$$J_{\text{HH}}^{\text{ortho}} = 5.27 + 4.34p^{\rho} + 0.54S \quad (4)$$

spondence to the former work with Coulson bond orders, one finds that it is necessary to include a term for enhanced magnitude of a coupling constant if one of the coupled protons is in an overcrowded environment.^{12,18,57,58} The term *S* in eq 4 refers to the 1,8 pair of protons in phenanthrene IV and is a correction to be applied to $J_{\text{HH}}^{\text{ortho}}$. The statistically determined enhancement, 0.54 Hz, is larger than *ca.* 0.3 Hz found previously.⁵⁸ No statistically meaningful correction is necessary for the 1,8 protons in naphthalene where a value of *ca.* 0.1 Hz has been used.⁵⁸



Theoretically, the enhancement effect is probably due to several factors. The buttressing effect of the overcrowded protons which shortens the coupled proton–proton distance and the resulting decreases in HCC angles would lead to increased coupling constant, whereas out-of-plane distortion of the molecular framework would give a diminution.^{15,58} The resulting change in coupling constant does seem remarkably constant from molecule to molecule considering the widely varying geometries of aromatic hydrocarbons (see Table III for references). One concludes that the various kinds of distortion from ideal geometry accidentally cancel to a large degree in their net effect on ortho coupling constants.⁵⁹

An interesting application of eq 4 is to use nmr data to calculate bond orders in compounds with unusual structural features for comparison with theory. Agreement should be no more than semiquantitative considering the sensitivity of coupling constants to bond angle changes. When applied to

Table III. Bond Lengths in Benzenoid Hydrocarbons (Å)


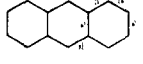
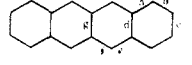
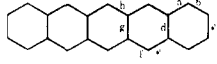
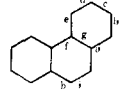
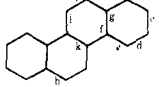
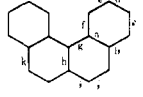
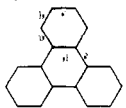
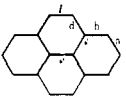
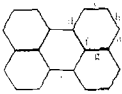
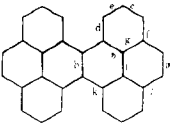
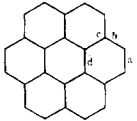
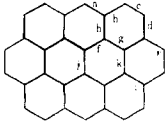
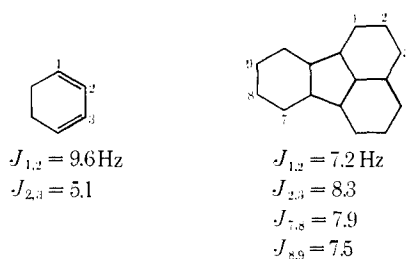
Compd	Bond	Bond order	Length		Calcd - exptl
			Exptl	Calcd	
Naphthalene (1961) ^a 	a	0.333	1.422	1.422	0.0
	b	0.667	1.371	1.381	0.010
	c	0.333	1.412	1.422	0.010
	d	0.333	1.420	1.422	0.002
			±0.008		±0.005
Anthracene (1964) ^b 	a	0.250	1.444	1.433	-0.011
	b	0.750	1.375	1.370	-0.005
	c	0.250	1.418	1.433	-0.015
	d	0.500	1.405	1.401	-0.004
	e	0.250	1.433	1.433	0.0
			±0.008		±0.007
Tetracene (1961) ^c 	a	0.200	1.420	1.439	0.019
	b	0.800	1.381	1.364	-0.017
	c	0.200	1.459	1.439	-0.020
	d	0.200	1.420	1.439	0.019
	e	0.600	1.390	1.389	-0.001
	f	0.400	1.404	1.414	0.010
	g	0.200	1.460	1.439	-0.021
			±0.010		±0.015
Pentacene (1961) ^d 	a	0.167	1.43	1.443	0.01
	b	0.833	1.36	1.360	0.0
	c	0.167	1.44	1.443	0.0
	d	0.167	1.45	1.443	-0.01
	e	0.667	1.38	1.381	0.0
	f	0.333	1.41	1.422	0.01
	g	0.167	1.46	1.443	-0.02
	h	0.500	1.40	1.401	0.0
			±0.01		±0.006
Phenanthrene (1971) ^e 	a	0.400	1.423	1.414	-0.009
	b	0.600	1.386	1.389	0.003
	c	0.400	1.394	1.414	0.020
	d	0.600	1.401	1.389	-0.012
	e	0.400	1.409	1.414	0.005
	f	0.200	1.465	1.439	-0.026
	g	0.400	1.420	1.414	-0.006
	h	0.200	1.453	1.439	-0.014
	i	0.800	1.350	1.364	0.014
			±0.008		±0.012
Chrysene (1960) ^f 	a	0.375	1.428	1.417	-0.011
	b	0.625	1.363	1.386	0.023
	c	0.375	1.394	1.417	0.013
	d	0.625	1.381	1.386	0.005
	e	0.375	1.409	1.417	0.008
	f	0.250	1.468	1.433	-0.025
	g	0.375	1.409	1.417	0.008
	h	0.250	1.421	1.433	0.012
	i	0.750	1.369	1.370	0.001
	j	0.250	1.428	1.433	0.005
	k	0.500	1.401	1.401	0.0
			±0.010		±0.010
Benzphenanthrene (1963) ^g 	a	0.375	1.431	1.417	-0.014
	b	0.375	1.391	1.417	0.026
	c	0.625	1.374	1.386	0.012
	d	0.375	1.409	1.417	0.008
	e	0.625	1.378	1.386	0.012
	f	0.375	1.433	1.417	-0.016
	g	0.250	1.446	1.433	-0.013
	h	0.500	1.412	1.401	-0.011
	i	0.250	1.430	1.433	0.003
	j	0.750	1.342	1.370	0.028
	k	0.250	1.443	1.433	-0.010
			±0.010		±0.014
Triphenylene (1963, 1973) ^h 	a	0.444	1.410	1.409	-0.001
	b	0.556	1.381	1.395	0.014
	c	0.444	1.347	1.409	0.012
	d	0.444	1.413	1.409	-0.004
	e	0.111	1.458	1.450	-0.008
			±0.006		±0.008
Pyrene (1972) ⁱ 	a	0.500	1.395	1.401	0.006
	b	0.500	1.406	1.401	-0.005
	c	0.333	1.425	1.422	-0.003
	d	0.167	1.438	1.433	0.005
	e	0.333	1.430	1.422	-0.008
	f	0.833	1.367	1.360	-0.007
			±0.004		±0.006

Table III (Continued)

Compd	Bond	Bond order	Length		Calcd - exptl
			Exptl	Calcd	
Perylene (1964) ^j 	a	0.333	1.400	1.422	0.022
	b	0.667	1.370	1.381	0.011
	c	0.333	1.418	1.422	0.004
	d	0.667	1.397	1.381	-0.016
	e	0.0	1.471	1.464	-0.007
	f	0.333	1.425	1.422	-0.003
	g	0.333	1.424	1.422	-0.002
			±0.004		±0.009
Pyrenopyrene (1972) ^k 	a	0.829	1.339	1.360	0.021
	b	0.714	1.380	1.375	-0.005
	c	0.514	1.374	1.399	0.025
	d	0.514	1.399	1.399	0.0
	e	0.486	1.383	1.403	0.020
	f	0.486	1.387	1.403	0.016
	g	0.343	1.424	1.421	-0.003
	h	0.343	1.415	1.421	0.006
	i	0.314	1.424	1.425	0.001
	j	0.171	1.435	1.443	0.008
	k	0.143	1.464	1.446	-0.018
			±0.008		±0.011
Coronene (1966) ^l 	a	0.700	1.347	1.377	0.031
	b	0.300	1.415	1.427	0.012
	c	0.400	1.433	1.414	-0.019
	d	0.300	1.425	1.427	0.002
			±0.009		±0.015
Ovalene (1973) ^m 	a	0.500	1.401	1.401	0.0
	b	0.200	1.445	1.439	-0.006
	c	0.800	1.354	1.364	0.010
	d	0.200	1.432	1.439	0.007
	e	0.400	1.411	1.414	0.003
	f	0.400	1.419	1.414	-0.005
	g	0.300	1.429	1.423	-0.006
	h	0.300	1.425	1.423	-0.002
	i	0.400	1.429	1.414	-0.015
	j	0.200	1.435	1.432	0.004
	k	0.300	1.424	1.423	0.001
	l	0.600	1.366	1.389	0.023
			±0.005		±0.007

^a A. Allmeningen, O. Bastiansen, and F. Dyvik, *Acta Crystallogr.*, **14**, 1056 (1961). ^b R. Mason, *ibid.*, **17**, 547 (1964). ^c R. B. Campbell, J. M. Robertson, and J. Trotter, *ibid.*, **15**, 289 (1961). ^d R. B. Campbell, J. M. Robertson, and J. Trotter, *ibid.*, **14**, 705 (1961). ^e Average of X-ray and neutron diffraction data, M. I. Kay, Y. Okaya, and D. E. Cox, *Acta Crystallogr., Sect. B*, **27**, 26 (1971). ^f D. M. Burns and J. Iball, *Proc. Roy. Soc., Ser. A*, **257**, 491 (1960). ^g F. L. Hirshfeld, S. Sandler, and G. M. J. Schmidt, *J. Chem. Soc.*, 2108 (1963). ^h Average of X-ray and neutron diffraction data, F. R. Ahmed and J. Trotter, *Acta Crystallogr.*, **16**, 503 (1963); G. Ferraris, D. W. Jones, and J. Yerkess, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallechem.*, **138**, 113 (1973). ⁱ Neutron diffraction: A. C. Hazell, F. K. Larsen, and M. S. Lehmann, *Acta Crystallogr., Sect. B*, **28**, 2977 (1972). ^j A. Camerman and J. Trotter, *Proc. Roy. Soc., Ser. A*, **279**, 129 (1964). ^k K. W. Muir and J. M. Robertson, *Acta Crystallogr., Sect. B*, **28**, 879 (1972). ^l J. K. Fawcett and J. Trotter, *Proc. Roy. Soc., Ser. A*, **289**, 366 (1966). ^m R. G. Hazell and G. S. Pawley, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallechem.*, **137**, 159 (1973).

1,3-cyclohexadiene⁶⁰ and fluoranthene, V,⁶¹ the calculated



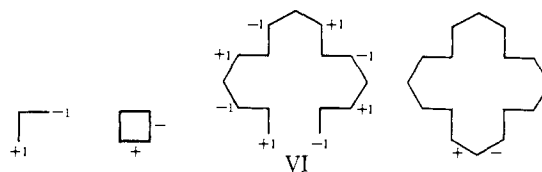
V

bond orders are cyclohexadiene, $p_{12} = 1.00$ (1.00), $p_{23} = -0.04$ (0.00), fluoranthene, $p_{12} = 0.32$ (0.33), $p_{23} = 0.70$ (0.67), $p_{78} = 0.48$ (0.50), and $p_{84} = 0.51$ (0.50), where the Pauling bond orders are in parentheses. Application of the Coulson bond orders (four-parameters) linear correlation⁵⁸ with coupling constants gives the same kind of good agreement. Within the limits of generally planar structures and six-membered rings with bond angles close to 120° , it seems that ortho coupling constant data can be used to obtain in-

formation about bond orders, and hence about bond lengths and π -electron delocalization. This approach has been already useful in discussions of the structures of strained benzocycloalkenes⁵⁹ and benzo-substituted annulenes.^{62,63} A further use will be to assess the validity of Pauling bond orders in the subsequent discussion of nonalternant systems and annulenes.

Cyclobutadiene Derivatives

A naive use of the NBMO coefficients of deleted vertex structures for $4n$ ($n = \text{integer}$) monocyclic annulenes leads to a prediction of alternating positive and negative bond orders in the parent annulene, as for example in cyclobutadiene or [16]annulene VI. This prediction is in some agree-

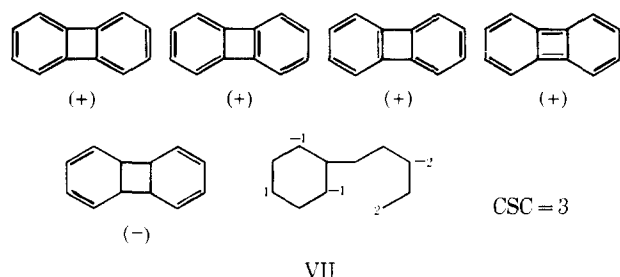


ment with experimental facts and theoretical work. Bond alternation in parent cyclobutadiene is found as a result of either MO^{44,64,65} or VB⁶⁵⁻⁶⁷ calculations, and some good experimental data on the reactions of 1,2-diphenylcyclobutadiene are best explained on the basis of a short-long bond-switching molecule.⁶⁸ An alternation of bond lengths in [16]annulene is even more firmly established from X-ray data.⁶⁹

However, the agreement is no more than very roughly qualitative. Experimental bond lengths in [16]annulene⁶⁹ and the calculated bond lengths in cyclobutadiene⁴⁴ are the lengths expected for normal double and single bonds, inferring alternating Pauling bond orders of one and zero, respectively. Furthermore the HMO definition of Pauling bond order, eq 2, gives indeterminate values since there are occupied π levels with an eigenvalue of zero. This is consistent with the corrected structure count (CSC),⁷⁰ a concept defined in an earlier paper,³⁹ for cyclobutadiene being zero, qualitatively indicating an unstable and reactive system.

The indeterminate bond orders, the CSC of zero, and the positive and negative characters of the bond orders given by the coefficients of the NBMO in VI are all consequences of the fact that two Kekulé structures in cyclobutadiene have opposite parities or signs,^{40,71} so that they enter the VB wave equation for the ground state of cyclobutadiene with opposite signs,^{34,40} giving rise to a nontotally symmetric ground state.⁷² The parities of the structures can be determined in several different ways,^{34,40,71,73} but the simplest is to use the NBMO coefficients of a structure with a deleted vertex, *e.g.*, VI. If the signs of the adjacent coefficients differ, parent structures with double bonds to positions of differing signs will differ in parity.

There are many π systems that are composed of structures that have different parities, but which still possess a finite CSC and a closed shell by an HMO calculation.³⁹ Biphenylene, VII, has five Kekulé structures, four of one parity and one with opposite sign, resulting in a CSC of 3. The



correct interpretation of this structure count is not that only three of the five structures contribute to the resonance hybrid,⁷⁴ but is that four structures contribute in a positive way and one structure contributes in a negative sense. This interpretation is consistent with the HMO definition of Pauling bond order, eq 2, which gives for example a negative bond order of $1/3$ to each of the bonds connecting the six-membered rings, and positive Pauling bond orders for all of the other bonds, exactly as calculated from the NBMO structure in VII. All of this is reinforced when one considers that resonance theory calculations of the resonance energy³⁴ based on a four positive structures—one negative structure wave function are in excellent agreement with LCAO-MO-SCF estimates.^{35,75}

Pauling bond orders for biphenylene, calculated values of bond lengths and $J_{\text{HH}}^{\text{ortho}}$, and the experimental data are given in Table IV. Agreement between experiment and theory is remarkable, especially for the long interring bond *e* usually calculated by SCF-MO theories to be of the order of 1.48 to 1.49 Å.^{25,75} However, the MO calculations repro-

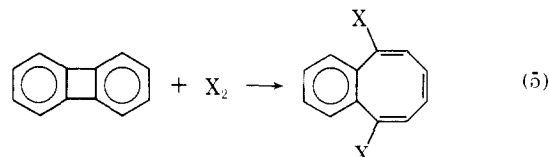
Table IV. Biphenylene Bond Orders, Bond Lengths, and Coupling Constants

Bond	Order	Bond length, Å		$J_{\text{HH}}^{\text{ortho}}$, Hz	
		Calcd ^a	Exptl ^b	Calcd ^c	Exptl
a	0.333	1.422	1.423	7.2	7.1, ^d 6.9 ^e
b	0.667	1.381	1.385	8.2	8.1, 8.3
c	0.667	1.381	1.372		
d	0.667	1.381	1.426		
e	-0.333	1.506	1.514		

^a Equation 3. ^b X-Ray, ref 76. ^c Equation 4. ^d Reference 77. ^e Reference 59.

duce the bond length of bond *d* more accurately, giving values of 1.41 to 1.42 Å. It is noteworthy that an earlier X-ray study gave the length of bond *d* as 1.38 Å,⁷⁴ but the longer value has been recently confirmed by an electron diffraction study (1.432 ± 0.018 Å).⁷⁸ For the coupling constants HMO theory¹⁸ gives $J_{\text{HH}}^{\text{ortho}} = 7.4$, and $J_{\text{HH}}^{\text{ortho}} = 7.9$ Hz, less accurate than the Pauling bond-order results.

One additional experimental fact may be pertinent to judging the results of the bond-order calculations. Nearly all addition reactions of biphenylene give products derived from attack at bond *d* as shown in eq 5.⁷⁹⁻⁸¹ It is well

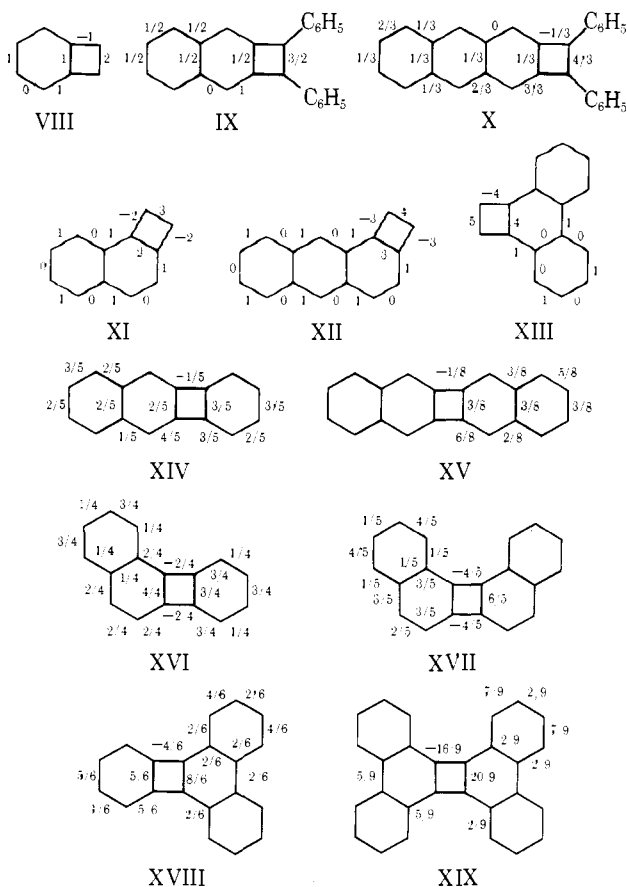


known that addition reactions generally take place at the regions of highest bond order or lowest localization energy as calculated by HMO theory,^{82,83} which would predict reaction of bond *b* or at *c*, respectively. The reaction at *d* is at least consistent with the Pauling bond-order calculation. Overall, the Pauling method seems to have a greater predictive power than the HMO method.

The negative Pauling bond order calculated for bond *e* in biphenylene by eq 2 and the NBMO method is an unusual concept that prompted a survey of Pauling bond orders in other compounds containing four-membered rings. The results are given in VIII to XIX, in which it can be seen that Pauling bond orders of greater than unity are also possible for π systems. The large negative and positive bond orders may point to a further deficiency of the Pauling bond order-bond length relationship. Using eq 3 bond lengths as low as 0.839 Å and as high as 1.964 Å would result for phenanthrocylobutadiene, XIII. Such bond lengths would seem to be very unlikely.

The unusual bond orders can be correlated with chemical and physical properties of the compounds. The alternating bond orders for the unknown structures VIII, XI, XII, and XIII infer that they should be represented as polyolefins with extraordinarily distorted and reactive cyclobutadiene moieties. The four-membered rings in each compound have alternating negative and positive bond orders, both larger than one. The only other compound in the group with the same kind of cyclobutadiene ring is XIX, which has also been the object of some unsuccessful synthetic attempts.⁸⁴

The remaining structures are all known compounds. They all have bond orders more comparable to those in biphenylene except that IX, X, XVII, and XVIII have a bond in the four-membered ring with bond order greater than unity, ranging from 1.50 to 1.20. Each compound undergoes its principal addition reactions at those bonds,^{85,87} so



the calculations are in qualitative agreement with experiment. Also, the relative stabilities of pairs IX, XI; X, XII; XV, XVII; and XIV, XVI⁸⁵⁻⁸⁷ are correlated by the calculations. The isomer with the more uniform bond order is more stable in each case. This always corresponds to the more linear compound, and this order of stabilities is also predicted by MO calculations.⁸⁸ Finally, the nmr spectrum of 1,2-diphenylnaphtho[*b*]cyclobutadiene, IX, has a sharp singlet at δ 6.50,⁸⁷ characteristic of olefinic protons. The assigned bond orders of 1.00 and 0.0 for the adjacent bonds to position 3 are consistent. Unfortunately no additional nmr spectral data have been published for any of these compounds. A comparison of coupling constants with the predicted values from eq 4 would help to judge the usefulness of this approach.

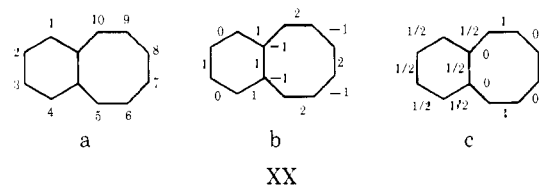
Annulenes

The synthetic efforts directed toward annulenes and studies of their properties have been primarily associated with investigations of the concept of aromaticity.⁸⁹ The various definitions of aromaticity (and antiaromaticity⁹⁰) include criteria based on bond lengths, magnetic properties, and calculated bond orders,⁹¹ and the establishment of a uniform bond length around the perimeter of an annulene is held to be particularly diagnostic of aromaticity.

For monocyclic annulenes the inference from Pauling bond orders regarding bond lengths is that $4n$ π systems will possess alternating bond lengths (see the previous section) and $4n + 2$ systems will have uniform bond lengths close to 1.401 Å in length, eq 3. X-Ray crystallographic data are generally in agreement. In [10]-, [14]-, and [18]annulenes⁹²⁻⁹⁴ the bond lengths vary between 1.382 and 1.419 Å which is less than the variation found in naphthalene. MO theory predicts extreme alternation in bond lengths for [18]annulene.^{46,91}

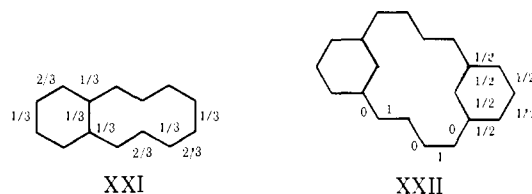
Many annulenes have been synthesized in which the an-

nulene periphery is incorporated into benzene rings or larger aromatic moieties. In these cases coupling constant data for the aromatic protons can be used to ascertain the bond orders in the aromatic rings, and the values of the aromatic ring bond orders allow one to infer the annulene bond orders. This approach has been used in conjunction with PPP-type SCF calculations to examine benzo-annulated annulenes,^{62,63} but the formulation of the idea in terms of Pauling bond orders is especially simple. For example, consider benzocyclooctatetraene, a benzolated [8]annulene, XX. The predicted Pauling bond order for a delocalized

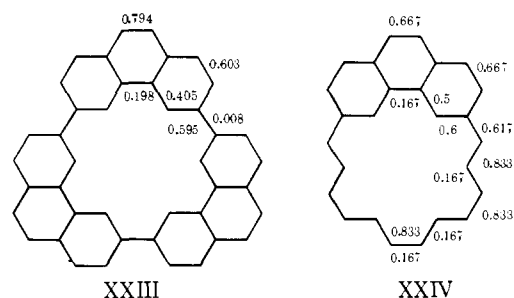


planar structure is given in XXb, and the structure is characterized by bond order alternation in both six- and eight-membered rings. From eq 4 the ratio of J_{HH}^{12}/J_{HH}^{23} should be 0.55. However, the experimental ratio is 1.06⁶³ which could be interpreted to imply the bond orders shown in XXc. Structure XXc is also in agreement with the nmr chemical shifts of the double bond protons,⁹⁵ and the highly likely nonplanar tub shape of the eight-membered ring.⁹⁶

In XX, the delocalization of electrons that results in antiaromatic destabilization³⁴ is mitigated by distortion to a more stable structure, and this is accompanied by a change to more evenly distributed bond orders in the aromatic ring. The delocalized annulene would have alternating bonds in the aromatic moiety, while normal alternating single and double bonds in the annulene give rise to more uniform bonds in the benzene portion. The same kind of result is found in $[4n + 2]$ annulenes, with of course the proviso that distortion of the molecule away from planarity will probably not occur. Two examples are shown in XXI and XXII, where the more delocalized structure, XXI, has the greater alternation in the benzene moiety.


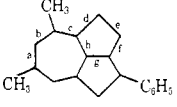
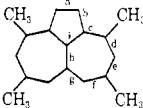
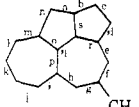
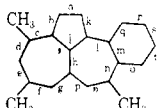
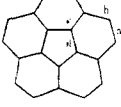


The small amount of experimental data on bond lengths and magnetic properties which is available is well-correlated with Pauling bond orders. In XXIII the calculated bond orders of the inner [18]annulene vary from 0.008 to 0.595, in agreement with the fact that the H-nmr spectrum does not indicate a diamagnetic ring current for the macrocyclic system. The bond order for the bond between the phenanthrene units is practically zero so a spectrum characteristic



of essentially isolated phenanthrene units should be obtained. A diamagnetic ring current would not be damped in

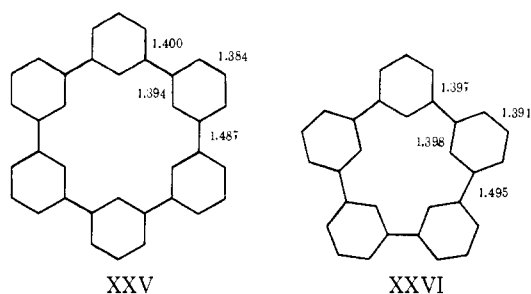
Table V. Bond Lengths in Nonalternant Hydrocarbons

Compd	Bond	Length, Å (exptl)	This work, Å (calcd)	SCF-MO, Å (calcd)
Azulene 	a	1.394 ^a	1.401	1.398 ^b
	b	1.398	1.401	1.413
	c	1.391	1.401	1.406
	d	1.400	1.401	1.401
	e	1.392	1.401	1.385
	f	1.498	1.464	1.469
Cyclopent[cd]azulene 	a	1.394 ^c	1.400	1.398 ^d
	b	1.398	1.400	1.400
	c	1.378	1.400	1.400
	d	1.435	1.432	1.428
	e	1.373	1.369	1.376
	f	1.444	1.432	1.436
	g	1.378	1.400	1.394
	h	1.419	1.432	1.440
Aceheptylene 	a	1.393, ^e 1.393 ^f	1.400	1.395 ^d
	b	1.412, 1.396	1.400	1.414
	c	1.437, 1.436	1.432	1.425
	d	1.380, 1.358	1.369	1.388
	e	1.434, 1.418	1.432	1.416
	f	1.367, 1.368	1.369	1.388
	g	1.449, 1.446	1.432	1.426
	h	1.429, 1.399	1.400	1.429
	i	1.472, 1.470	1.432	1.434
	Pentalenoheptalene 	a	1.409 ^g	1.422
b		1.441	1.443	1.435
c		1.382	1.360	1.378
d		1.454	1.443	1.432
e		1.345	1.381	1.399
f		1.444	1.422	1.410
g		1.365	1.381	1.389
h		1.450	1.422	1.422
i		1.430	1.443	1.442
j		1.378	1.360	1.382
k		1.419	1.443	1.421
l		1.379	1.360	1.383
m		1.399	1.443	1.429
n		1.405	1.381	1.398
o		1.503	1.443	1.452
p		1.406	1.401	1.418
q		1.388	1.422	1.419
r	1.404	1.401	1.416	
s	1.431	1.443	1.451	
Benzo[c]aceheptylene 	a	1.38 ^h	1.39	
	b	1.40	1.41	
	c	1.43	1.41	
	d	1.38	1.39	
	e	1.39	1.41	
	f	1.38	1.39	
	g	1.39	1.41	
	h	1.40	1.41	
	i	1.44	1.44	
	j	1.47	1.41	
	k	1.36	1.41	
	l	1.44	1.44	
	m	1.39	1.41	
	n	1.48	1.44	
	o	1.35	1.36	
	p	1.45	1.44	
	q	1.41	1.41	
r	1.33	1.39		
s	1.36	1.41		
t	1.38	1.39		
u	1.43	1.41		
Corannulene 	a	1.402 ⁱ	1.373	
	b	1.440	1.430	
	c	1.391	1.407	
	d	1.413	1.430	

^a Reference 104. ^b Reference 101. ^c Reference 106 and 107. ^d Reference 102 and 106. ^e Reference 108. ^f Reference 109. ^g Reference 110. ^h Reference 111. ⁱ Reference 105.

XXIV, and the nmr spectrum does have many features that can be explained on this basis.⁹⁷ In addition, $J_{\text{HH}}^{1,2}$ in the phenanthrene moiety is 8 Hz which gives a bond order of 0.630 for the 1,2 bond according to eq 4, to be compared with the calculated bond order of 0.667.

The bond lengths in XXV and XXVI have been determined by X-ray crystallography.⁹⁸ Calculated bond orders



of 0.500 for the benzene rings and zero for the interring bonds are consistent with the experimental lengths. The connecting bands are longer than the value given by eq. 3 but are very similar to the experimental biphenyl interring bond length, 1.497 Å.⁹⁹ Biphenyl and both XXV and XXVI obtain relief from overcrowding by deformation from planarity, and there may be an effect on the bond length from this source that cannot be discussed in the context of Pauling bond orders.

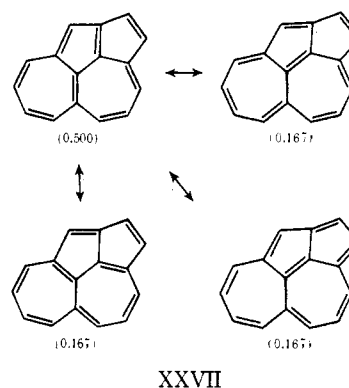
Nonalternant Hydrocarbons

The molecular geometries of nonalternant hydrocarbons have been calculated by several different variants of semiempirical SCF-MO methods, the most successful of which has been the variable bond length procedure¹⁹ in which the two-center integrals are adjusted at each iteration by making use of a linear bond order-bond length relation.¹⁰⁰⁻¹⁰³ The only verification of these theories must be a comparison with experimental structural data, and unfortunately there are not very many nonalternant molecules for which such data are available. In Table V predicted bond lengths and the extant X-ray data are compared with bond lengths calculated by the Pauling method using eq 3 and by the SCF-MO method. Except for azulene¹⁰⁴ and corannulene,¹⁰⁵ the structures of alkyl derivatives rather than the parent π systems were analyzed experimentally.¹⁰⁶⁻¹¹¹ The effect of the substituents is not expected to be large, and the calculations¹⁰¹⁻¹⁰³ are for the unsubstituted structures.

The agreement of calculations and experiment is good. The average deviation of the difference is ± 0.016 Å for the Pauling method based on Kekulé structures and ± 0.017 Å for the SCF calculations. The more symmetrical the molecule, the better the calculations agree with experiment, e.g., azulene and aceheptylene, average deviations ± 0.010 and ± 0.014 Å respectively. In the last two molecules, benzo[*e*]aceheptylene and corannulene, the relative variations in bond lengths from bond to bond are correlated quite accurately by the Pauling method. The average deviation for benzo[*c*]aceheptylene is ± 0.021 Å to be compared with the standard deviation in the experimental lengths of ± 0.015 Å. One-half of the total variation is associated with only four bonds j, k, r, and s. Bonds r and s especially have unusual lengths for a benzene ring, and it is likely that the experimental values are not accurate. An anomalous long bond is found in the five-membered rings at the annelation points in azulene, aceheptylene, pentalenoheptalene, and benzoaceheptylene. It seems likely that the lengthening of these bonds can be ascribed to the result of strain in the σ bond skeletons of the molecules. Also, the reasonably good correlation found for the corannulene bonds may be fortuitous,

since the corannulene molecule is nonplanar and might not be expected to conform to a theory that assumes planar π -electron structures.

One final aspect of the Pauling bond length calculations for these nonalternant molecules needs to be discussed. If one examines the graphs³⁴ for the resonance interactions of the Kekulé structures of cyclopentazulene (three structures), aceheptylene (three structures), and pentalenoheptalene (four structures) one finds that in each case a central structure that undergoes stabilizing resonance interactions with all other structures. This is illustrated in XXVII for



pentalenoheptalene, and the relative weight of the central structure is three times as large as the other structures as can be determined from the relevant secular equations. The calculated weights are 2:1:1 for the Kekulé structures of the other two molecules.³⁴ In this treatment the resonance interaction characteristic of pentalene is assumed not to contribute to stabilizing the resonance hybrid. The bond lengths summarized in Table V incorporate these calculated weights. The effect is significant for these nonalternants with a small number of structures in contrast to the calculations on alternant systems, as illustrated previously for naphthalene. With this caveat, it can be seen that the simplified concepts embodied in resonance theory and Pauling bond orders can be usefully extended to nonalternant systems.

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