

Semi-empirical Molecular Orbital Studies of Aromatic Hydrocarbons. I

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The Pariser—Parr—Pople approximation has been applied in a study of the electronic structures and electronic spectra of the molecules naphthalene, anthracene, and biphenylene. The molecular ground states are described by a single determinant wave function, whereas configuration interaction, including all the singly excited configurations has been invoked in the description of the electronically excited states. Predicted bond distances, ionization potentials, and electronic transitions are discussed in comparison with experimental observations.

1. INTRODUCTION

The semi-empirical molecular orbital method developed by Pariser and Parr^{1,2} and by Pople³ has shown to be a rather powerful tool for the description of the electronic structure and the electronic spectra of conjugated hydrocarbons. Its success is first of all due to the simplifications introduced in the unwieldy mathematical scheme making the purely theoretical methods unfeasible. In addition, the SCF-features retained in this method do make it superior to the still simpler Hückel approximation. This circumstance has been clearly demonstrated in a comparative study of the aniline molecule by Fischer-Hjalmars.⁴

Because of its semi-empirical nature, however, the merits and limitations of this method are intimately connected to the scheme according to which the values of the semi-empirical parameters are evaluated. The main problem in this context is to construct a single approach by which physical properties related to both the ground state and the electronically excited states of a molecule can be predicted with reasonable accuracy.

Recently Fischer-Hjalmars⁴ has scrutinized the different approximations in molecular orbital calculations on π -electron systems. She has suggested and thoroughly discussed a new, consistent method for the evaluation of semi-empirical parameter values in the Pariser—Parr—Pople approximation.⁵ Her

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approach is very general in the sense that it is not optimized for the description of any particular property of π -electron systems, and it may also be applied to conjugated molecules containing different kinds of heteroatoms.

In this investigation the approach developed by Fischer-Hjalmarsson will be applied in a study of some polynuclear aromatic hydrocarbons.

Numerous calculations of the electronic structure of aromatic molecules have previously been made. The majority of studies have been performed within the framework of the Hückel approximation which in most cases has shown to be satisfactory for a description of molecular ground state properties. For some molecules, however, the more elaborate Pariser—Parr—Pople method has been used in simultaneous discussions of the ground state and different electronically excited states. Here it is not intended to give any complete survey of previous studies. Only calculations of immediate interest for the present discussion will be referred to.

The main purpose of this work is to examine some aromatic molecules exhibiting carbon-carbon bond distances that are significantly longer than the normal aromatic bond. The most extreme examples of molecules in this class are the members of the perylene-series. Both in perylene⁶ and quaterrylene⁷ bond distances exceeding 1.50 Å have been observed. The molecules chrysene and phenanthrene, for which results of accurate X-ray measurements are available, show the same features, though to a less extent. In chrysene⁸ a bond distance of 1.465 Å has been found, and a value of 1.457 Å has been observed in phenanthrene.⁹

An attempt to describe the quasi-single *peri*-bonds in perylene has previously been made within the Hückel approximation, and it was concluded that this approximation fails in predicting π -electron densities that can account for these extremely long bonds.¹⁰

In the present paper results obtained for the molecules naphthalene, anthracene, and biphenylene will be presented and discussed. The first two molecules which have been studied extensively by experimental methods, are included in order to obtain a test on the approach applied in this study.

The molecule biphenylene, in which a carbon-carbon bond distance of 1.52 Å has been observed,¹¹ is not a benzenoid aromatic hydrocarbon. Because of the planarity¹¹ of the molecule, however, a description of its ground state within the π -electron approximation is expected to have some relevance. It is also of interest to compare the results obtained here with the previous studies based on the Hückel approximation.

In a forthcoming paper the electronic structure and spectra of the molecules chrysene, phenanthrene, and perylene will be discussed.

2. METHOD OF CALCULATION AND DETERMINATION OF PARAMETER VALUES

The mathematical and computational scheme for calculations within the Pariser—Parr—Pople approximation has previously been discussed by several authors.¹⁻⁵ Therefore only a brief presentation of the expressions defining the quantities treated as semi-empirical parameters in this approximation will be given. The particular semi-empirical approach used in this investigation has

recently been suggested and discussed in detail by Fischer-Hjalmars.⁵ Her notation will be applied in the following.

The matrix elements of the core-part of the π -electron Hamiltonian in the atomic orbital representation are of two different types:

$$\alpha_{\mu} = \int \chi_{\mu}^{*}(i) \overset{\text{core}}{H}(i) \chi_{\mu}(i) d\tau_i \quad (1)$$

and

$$\beta_{\mu\nu} = \int \chi_{\mu}^{*}(i) \overset{\text{core}}{H}(i) \chi_{\nu}(i) d\tau_i \quad (2)$$

In (1) and (2) χ_{μ} and χ_{ν} are atomic orbitals of $2p\pi$ -type centered at atoms μ and ν , respectively. By applying the decomposition of the molecular potential field suggested by Goepfert-Mayer and Sklar¹² the following relation is obtained:

$$\alpha_{\mu} = W_{\mu} - \sum_{\nu \neq \mu} (\mu\mu|\nu\nu) \quad (3)$$

where

$$W_{\mu} = \int \chi_{\mu}^{*}(i) [T(i) + V_{\mu}(i)] \chi_{\mu}(i) d\tau_i \quad (4)$$

and V_{μ} is the part of the core potential generated by nucleus μ and its σ -electrons. In (3) penetration integrals are neglected, and $(\mu\mu|\nu\nu)$ are matrix elements of the two-electron part of the Hamiltonian:

$$(\mu\mu|\nu\nu) = \iint \chi_{\mu}^{*}(i) \chi_{\nu}^{*}(j) (1/r_{ij}) \chi_{\mu}(i) \chi_{\nu}(j) d\tau_i d\tau_j \quad (5)$$

Because of the formal neglect of differential overlap which is always assumed in this approximation, the only two-electron integrals having values different from zero are those defined by (5). They represent the electrostatic repulsion between the electrons i and j , in orbitals centered at atoms μ and ν , respectively. As a special case of (5) the one-center integrals $(\mu\mu|\mu\mu)$ also occur. A thorough discussion of the implications of the formal neglect of differential overlap has been given by Fischer-Hjalmars.¹³

The parameter W_{μ} defined by (4) is assumed to be the same for all atoms as only pure hydrocarbons are considered. For this parameter, $W_{2p,C}$, which has been determined from the ionization potential of ethylene, the value -9.594 eV has been adopted.⁵

The integrals $\beta_{\mu\nu}$ defined by (2) have been calculated from the general formula

$$-\beta_{\mu\nu} = S_{\mu\nu} \{k_1[(\mu\mu|\mu\mu) + (\nu\nu|\nu\nu)] + k_2(\mu\mu|\nu\nu)\} \quad (6)$$

developed by Fischer-Hjalmars.⁴ In this equation

$$S_{\mu\nu} = \int \chi_{\mu}^{*}(i) \chi_{\nu}(i) d\tau_i \quad (7)$$

The constants k_1 and k_2 have been determined by fixing the value of $\beta_{\mu\nu}$ for two different internuclear distances and by using values for the two-electron integrals obtained by a procedure also suggested by Fischer-Hjalmars.⁵ The compounds ethylene and benzene have been chosen, and the values obtained from an analysis of the spectra of these molecules are $\beta(\text{ethylene}) = -2.852$ eV and $\beta(\text{benzene}) = -2.390$ eV. See Ref.⁵ for a detailed discussion.

All resonance integrals between non-nearest neighbours are neglected in this method.

For the calculation of two-electron one-center integrals Fischer-Hjalmar⁴ has evaluated a formula which is general in the sense that it may be applied to *p*-electrons centered at any atom μ :

$$(\mu\mu|\mu\mu) = F_0 + 4F_2 \quad (8)$$

The Slater—Condon parameters F_0 and F_2 are determined from spectroscopic data for the atom in question. Her value for the carbon atom, 11.904 eV, has been adopted in this investigation.

For internuclear distances shorter than 2.6 Å the integrals $(\mu\mu|\nu\nu)$ have been computed from the relation:

$$(\mu\mu|\nu\nu) = 13.375 - 6.441R + 2.267R^2 - 0.384R^3 \text{ eV} \quad (9)$$

The formula (9) is a special form of a more general relation developed by Fischer-Hjalmar⁵; see Ref.⁵ for a detailed presentation. In (9) R is given in Å. It should be noted that (9) is not valid for $R = 0$.

For internuclear distances larger than 2.6 Å the two-electron integrals were calculated by use of the uniformly charged sphere approximation introduced by Parr.¹⁴ The effective nuclear charge of the carbon atom was assumed to be 3.12.

The iterative solution of the SCF equations was performed automatically on an IBM 7090 computer. The programme used in this investigation has been written by Dr. R. K. Nesbet, San José and kindly put at our disposal.

Eigenvectors from Hückel-type calculations were used as starting values by the iterative procedure, and the iterations went on until eight significant figures in the coefficients had been obtained. Eigenvalues and eigenvectors, electronic charges, mobile bond orders, matrix elements of H^{core} , and two-electron integrals in the molecular orbital representation were automatically printed out by the computer.

3. RESULTS AND DISCUSSION

In this paper results obtained for the molecules naphthalene (I), anthracene (II), and biphenylene (III) will be presented and discussed.

The discussion is divided into two main parts. In 3.a an examination of some ground state properties of the molecules will be given. Part 3.b is concerned with predictions made for the different electronically excited states of the molecules.

The calculations of the molecular ground states are based on a single determinant wave function, whereas configuration interaction, limited to inclusion of only singly excited configurations, has been incorporated in the description of the excited singlet and triplet states.

3. a. Ground state properties

The molecules studied in this investigation belong to the class of even alternant hydrocarbons. It has been shown by Pople³ that the Coulson—

Table 1. Mobile bond orders.

<i>Naphthalene</i>			<i>Anthracene</i>		
Bond	Order		Bond	Order	
	Present calc.	Hückel		Present calc.	Hückel
A—B	0.7939	0.725	A—B	0.8091	0.738
B—C	0.4939	0.555	B—C	0.4586	0.535
A—A'	0.5184	0.603	C—D	0.6258	0.606
C—C'	0.6130	0.518	A—A'	0.4976	0.586
			C—C'	0.5223	0.485

<i>Biphenylene</i>		
Bond	Order	
	Present calc.	Hückel
A—B	0.5344	0.621
B—C	0.7643	0.683
C—D	0.1090	0.263
A—A'	0.7867	0.691
C—C'	0.5535	0.565

Rushbrooke theorem¹⁵ for the distribution of π -electron charges in such systems is valid in the Pariser—Parr—Pople approximation used in SCF-calculations, provided that all the matrix elements W_{μ} in (4) are assumed to be equal. Accordingly, in the present calculation the π -electron charges on all carbon atoms are found to be equal to unity.

The mobile bond orders obtained by an SCF-calculation will usually differ from those given in the Hückel approximation. Since the former bond orders are selfconsistent, they are strictly related to the particular semi-empirical approach used in the calculations.

The bond orders obtained in this investigation are presented in Table 1 where also corresponding values given by standard Hückel-type calculations are included for comparison. See Fig. 1 for notation of the bonds.

The values in Table 1 clearly demonstrate that bond orders found to be high in the Hückel approximation are increased by an SCF-calculation. In the same way low bond orders are decreased. This implies that a structure containing pronounced single and double bonds is accentuated by an SCF-description. The same tendency is present in the modified Hückel approach allowing for a variation of the resonance integral, but to a less extent.

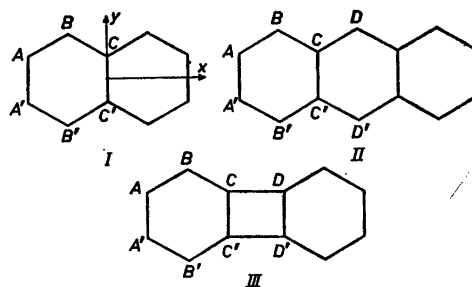


Fig. 1. Notation of bonds in naphthalene (I), anthracene (II), and biphenylene (III).

In order to establish a comparison between observed and predicted quantities, estimates of carbon-carbon bond distances from calculated bond orders are usually made. Such a comparison does, however, only give a limited test of the validity of the calculated bond orders as an additional relation has to be introduced to evaluate predicted bond distances.

Estimates of bond distances from mobile bond orders obtained by molecular orbital calculations are usually made by application of Coulson's formula¹⁶

$$R(p) = s - \frac{s - d}{1 + K[(1 - p)/p]} \quad (10)$$

In (10) s and d are the single and double bond distances between trigonally hybridized carbon atoms, respectively, and K is a constant the value of which is determined by requiring the $R(p)$ curve to pass through certain well defined ($R;p$) points. If one makes the reasonable choice of points, formal sp^2 - sp^2 single bond (1.517;0), the carbon-carbon bond in benzene (1.397;2/3), and the carbon-carbon bond in ethylene (1.337;1), then K will take a value equal to 1, and formula (10) reduces to the linear relation

$$R(p) = 1.517 - 0.18p \quad (11)$$

Coulson's formula is evaluated within the framework of the Hückel approximation, and it is not immediately obvious that it also is valid for estimates of bond distances from bond orders obtained by SCF-calculations. The expressions for the π -electron energy are different in these two methods because of different definitions of the Hamiltonian. Therefore a study of the relationship between p and R within the Pariser-Parr-Pople approximation has been undertaken.

In the atomic orbital representation the part of the π -electron energy depending on the internuclear distances is given by

$$E_{\pi}(R) = 2 \sum_{\mu < \nu} \sum_{\nu} p_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} \sum_{\mu < \nu} \sum_{\nu} [2 + p_{\mu\nu}^2] (\mu\mu|\nu\nu) \quad (12)$$

where the mobile bond orders for the ground state are defined by

$$p_{\mu\nu} = 2 \sum_i c_{i\mu} c_{i\nu} \quad (13)$$

In (13) the sum extends over all occupied molecular orbitals. The other symbols entering (12) are defined in Chapter 2. To obtain the total distance-dependent part of the molecular energy the compression energy of the underlying σ -core, $E_{\sigma}'(R)$, has to be included. For the simple considerations presented here a Hooke's law potential for $E_{\sigma}'(R)$ is assumed to be sufficiently accurate. This yields

$$E_{\sigma}'(R) = K_{\sigma}' \sum_{\mu < \nu} \sum_{\nu} [R_{\mu\nu} - R_s]^2 \quad (14)$$

In (14) R_s is the length of the sp^2 - sp^2 single bond, and K_{σ}' has the dimension of a force constant. In the π -electron Hamiltonian the electronic repulsion is taken explicitly into account. Accordingly a formal positive charge of unity is left on each carbon atom. This gives the effective nuclear interaction terms

$$E_N(R) = \sum_{\mu < \nu} \sum_{\nu} 1/R_{\mu\nu} \quad (15)$$

Because of incomplete information on σ -bonds in conjugated molecules, the constant $K_{\sigma'}$ in (14) has to be considered as a parameter the value of which is determined empirically. Therefore a redefinition of $K_{\sigma'}$ can be made in such a way as to allow for the inclusion of $E_N(R)$ in the compression energy $E_{\sigma'}(R)$ given by (14). In this way a resulting expression

$$E_{\sigma}(R) = K_{\sigma} \sum_{\mu < \nu} \sum [R_{\mu\nu} - R_s']^2 \quad (16)$$

is obtained. Strictly $R_s' > R_s$. The difference $R_s' - R_s$ is dependent on the magnitude of $K_{\sigma'}$, and therefore is difficult to estimate. It may in any case be expected to be small, and as an approximation R_s' is put equal to R_s . The R -dependent part of the total energy may then be expressed as

$$E(R) = 2 \sum_{\mu < \nu} \sum p_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} \sum_{\mu < \nu} \sum [2 + p_{\mu\nu}^2] (\mu\mu|\nu\nu) + K_{\sigma} \sum_{\mu < \nu} \sum [R_{\mu\nu} - R_s]^2 \quad (17)$$

The equilibrium conformation is determined by the conditions

$$\frac{\partial E(R)}{\partial R_{\mu\nu}} = 0 \text{ for each possible } R_{\mu\nu}. \quad (18)$$

By applying (6) and assuming that the variations of $S_{\mu\nu}$ and $(\mu\mu|\nu\nu)$ both are proportional to the variation of $\beta_{\mu\nu}$, the relations

$$\frac{\partial \beta_{\mu\nu}}{\partial R_{\mu\nu}} [2p_{\mu\nu} + \frac{1}{2}k(2 + p_{\mu\nu}^2)] + 2K_{\sigma}(R_{\mu\nu} - R_s) = 0 \quad (19)$$

are obtained, one for each bond in the molecule. In (19) k is a proportionality constant.

For non-bonded atoms $\beta_{\mu\nu}$ is approximated to zero. If $\partial(\mu\mu|\nu\nu)/\partial R_{\mu\nu} \approx R_{\mu\nu}^{-2}$ is neglected for non-bonded atoms, a series of equations like (19), one for each carbon-carbon bond in the molecule, will be obtained as the final result of the minimization of $E(R)$ given by (17).

To solve (19) a relation between $\beta_{\mu\nu}$ and $R_{\mu\nu}$ has to be established. An expansion of $\beta_{\mu\nu}$ in terms of deviations from the bond distance in benzene including only the linear term, leaves three parameters to be determined in eqns. (19). By applying the three $(R;p)$ points mentioned above, a relation identical to (11) is obtained.

This result is not unexpected in view of the assumptions involved in the deduction given above. The neglect of variation of the two-electron integrals for non-bonded atoms leading to eqns. (19), reduces the variational problem to one closely related to that on which Coulson's formula is based. Also the numerical values of the parameters in the linear $R(p)$ functions are identical. This is merely due to the fact that the same reference points have been applied in both cases.

Thus the linear relationship given by Coulson's formula in the Hückel approximation should be applicable for estimates of bond distances from bond orders calculated by an SCF procedure.

In this connection it should be pointed out that the values assumed for the three reference points give relation (11) directly. The difference between the lengths of the formal sp^2 - sp^2 single bond and the carbon-carbon bond in

benzene is exactly twice the difference between the carbon-carbon bond lengths in benzene and ethylene. If these differences are combined with the appropriate bond order values for the three bonds an expression identical to (11) is obtained. This circumstance demonstrates that not too much theoretical significance should be put into this relation. First of all it should be considered as a useful interpolation formula.

A formula similar to (11) was suggested by Longuet-Higgins and Salem some years ago.¹⁷ More recently such a linear relation has been applied in several discussions of bond distances in conjugated molecules.¹⁸⁻²¹

The carbon-carbon bond lengths in benzene and ethylene have been determined experimentally with very high precision. The values used in this study, 1.397 Å²² and 1.337 Å,²³ respectively, have been obtained by electron diffraction investigations. Several independent measurements have given results that are in close agreement with these values. The formal sp^2-sp^2 single bond for which the mobile bond order in the molecular orbital formalism is equal to zero, is hardly existent in any molecule. The value 1.517 Å applied here is a result of theoretical studies in hybridization made by Coulson.²⁴ This value does agree rather well with the observed value of 1.515 Å for the length of the bridge-bond linking together two mutually orthogonal phenyl rings in hexaphenylbenzene.²⁵

Bond distances estimated from calculated bond orders by means of relation (11) are presented in Table 2 where also experimental values are included for the purpose of comparison.

Table 2. Calculated and observed bond distances (R in Å).

<i>Naphthalene</i>						
Bond	$R_{\text{calc.}}$	$R_{\text{E.D.}}$	R_{X}	$\Delta_{\text{E.D.}}$	Δ_{X}	
A-B	1.374	1.371 (0.009)	1.364	+ 0.003	- 0.010	
B-C	1.428	1.422 (0.004)	1.421 (0.005)	- 0.006	- 0.007	
A-A'	1.424	1.412 (0.014)	1.415	- 0.012	- 0.009	
C-C'	1.407	1.420 (0.007)	1.418	+ 0.013	+ 0.011	
<i>Anthracene</i>						
Bond	$R_{\text{calc.}}$	$R_{\text{E.D.}}$	R_{X}	$\Delta_{\text{E.D.}}$	Δ_{X}	
A-B	1.371	1.390	1.368	+ 0.019	- 0.003	
B-C	1.435	1.420	1.436	- 0.015	+ 0.001	
C-D	1.404	1.404	1.399 (0.004)	0	- 0.005	
A-A'	1.427	1.419	1.419	- 0.008	- 0.008	
C-C'	1.423	1.425	1.428	+ 0.002	+ 0.005	
<i>Biphenylene</i>						
Bond	$R_{\text{calc.}}$		R_{X}	Δ_{X}		
A-B	1.421		1.42	0		
B-C	1.379		1.38	0		
C-D	1.509 (1.497)		1.52	+ 0.011 (+ 0.023)		
A-A'	1.375		1.35	- 0.025		
C-C'	1.417		1.38	- 0.037		

The molecular structures of naphthalene and anthracene have been studied in detail by experimental methods, and rather precise information on the carbon-carbon bond distances in these molecules is available. Two sets of experimentally obtained values are included in the table. The first one refers to results reported by Bastiansen *et al.*²⁶ who have performed electron diffraction studies of the free molecules. The second set gives the values obtained by Cruickshank and Sparks²⁷ in a very detailed X-ray crystallographic investigation. These two sets of bond lengths are labelled $R_{E.D.}$ and R_X , respectively, and are given in the third and fourth columns of the table.

Formal averages of 0.005 and 0.004 Å are reported as standard deviations of the R_X values for naphthalene and anthracene, respectively. For naphthalene estimates of individual deviations of the $R_{E.D.}$ values have been given and the resulting figures are included in the $R_{E.D.}$ column in the table. In the case of anthracene the electron diffraction studies have led to an ambiguity in the determination of structure parameters, and consequently no standard deviations were reported.

Except for the A—B and B—C bonds in anthracene, the agreement between the two sets of experimental values must be considered as convincing. Accordingly, the experimental material available should make these two molecules suitable as test compounds for the procedure applied in this study.

The differences between the experimental and calculated values are given in columns 5 and 6 in the table.

For naphthalene a comparison between the predicted values and those obtained by electron diffraction is particularly interesting as estimates of standard deviations have been made individually for each observed bond distance. Except for the C—C' bond the predicted lengths deviate from the $R_{E.D.}$ values by amounts equal to or smaller than the reported standard deviations. For this bond the discrepancy is twice the estimated standard deviation.

The differences between the predicted values and those observed by X-ray studies are all within twice the reported average standard deviation of 0.005 Å.

This implies that the predicted values are in accordance with the two sets of observed ones, the differences being hardly significant.

Calculated r.m.s. differences between the predicted and the two sets of bond distances are 0.008 Å and 0.009 Å for the $R_{E.D.}$ and R_X values, respectively. A substantial contribution to these differences comes from the bond C—C' which is predicted to be too short by an amount comparable to the experimental uncertainties.

In the case of anthracene the predicted bond lengths should primarily be compared to those observed by the X-ray investigation because of the ambiguity reported in the results obtained by electron diffraction. This ambiguity has first of all affected the $R_{E.D.}$ values for the bonds A—B and B—C, and it is gratifying to notice that the predicted values agree closely with the R_X values for these two bonds as well as for all the others. The largest difference is exactly twice the reported average standard deviation, the other discrepancies being of the same order of magnitude as this deviation of 0.004 Å. The calculated r.m.s. difference between the predicted bond lengths and the R_X values is 0.005 Å.

It is interesting to notice that the bond C—C' for which the predicted value is too short in both of the molecules, is a bond connecting two tertiary carbon atoms. In the case of anthracene the deviation is negligible, and therefore it would be inconsistent to search for a partial interpretation of this discrepancy for naphthalene by considering a correction of the W_μ values for the tertiary carbon atoms.

Another point of interest ought to be mentioned. The bond orders obtained for these two molecules are based on parameter values calculated from the internuclear distances given by the electron diffraction investigation. In spite of this predicted bond distances for anthracene are in much better agreement with the more reliable X-ray results. This fact indicates that the final π -electron distribution obtained by the iterative solution of the SCF-equations is not solely dependent on the particular molecular model chosen for the calculations.

The third molecule included in this investigation, biphenylene, cannot be considered as a normal aromatic hydrocarbon on account of the particular hybridization that obviously must be present at the tertiary carbon atoms. It may be regarded as a derivative of the hypothetical cyclobutadiene, and a detailed theoretical study of its electronic structure would require a consideration of the specific effects arising from changes in hybridization, and from internal strain in the four-membered ring.

The molecule is observed to have a planar carbon skeleton in the crystal.¹¹ Consequently an approximate description of its π -electron structure may be given by the method applied in this study. A strict formulation of the problem would require a revised model of the underlying σ -core to take into account the particular σ -electron distribution around the tertiary carbon atoms. This in turn would lead to changes in the values of the matrix elements of H^{core} in the atomic orbital representation. SCF-calculations on atoms have demonstrated that the form of the individual orbitals characterized by the orbital exponent is not very sensitive to the particular state of the free atom.²⁸ If the valence state of an atom in a molecule may be thought of as a superposition of different atomic states, one should not expect any substantial changes in the matrix elements of H^{core} . Hence a description of the π -electron distribution in the ground state of this molecule given by the approximation applied for naphthalene and anthracene should be acceptable, and the bond orders given in Table 1 should have the same relevance as in the case of benzenoid systems.

The mobile bond orders obtained for this molecule reveal some interesting features. First of all the value found for the bond C—D is extremely low. Consequently the π -electrons should influence the length of this bond to a rather small extent. From the linear relation (11) the shortening due to the π -electrons is found to be 0.020 Å. It is very difficult to make an accurate estimate of the length of a formal single bond between two carbon atoms in valence states adequate for the description of the core electrons of the tertiary atoms in this molecule. For an approximate analysis, however, information available for the cyclobutane molecule will be applied.

The carbon-carbon bond distance in cyclobutane is observed to be 1.548 Å.²⁹ The normal sp^3 - sp^3 single bond in open chain paraffins is shorter by an amount

of 0.012 Å.³⁰ It has been suggested that this stretch of the bond distance in cyclobutane is due to the fact that the repulsion between the non-bonded atoms in the ring overcompensates the shortening expected because of bent bonds.³¹

Cyclobutane is formally a saturated molecule having a non-planar ring structure. Thus the localized bond orbitals forming the bent carbon-carbon bonds in this ring will be of a tetrahedral type whereas those appropriate for a description of the σ -bonds in the four-membered ring of biphenylene have to be distorted sp^2 hybrids. Without detailed calculations it is impossible to decide to what extent the σ -bond C—D is bent. Tentatively it is suggested that the net effect of bending and non-bonded repulsion in this region will be of the same order of magnitude as in cyclobutane. This yields a value of 1.529 Å for the formal single bond between atoms C and D, and a prediction of a length of 1.509 Å for the bond C—D. The experimental value reported is 1.52 Å.¹¹ Thus the agreement between the observed and predicted value is satisfactory, but in view of the assumptions involved in the calculations this accordance may be considered as partly fortuitous; see, *e.g.*, Ref.³²

In Table 2 a value predicted for the bond C—D by means of formula (11) also is included in parenthesis. The same formula has been used for estimates of the other bond distances in the molecule. As demonstrated in the table none of the discrepancies between predicted and observed values are significantly larger than the estimated standard deviation of 0.031 Å for the measured bond distances. The experimental values quoted in the table are reported by Mak and Trotter who have made an X-ray investigation of the crystal and molecular structure of the compound.¹¹ Their data have been used for the evaluation of semi-empirical parameter values in this study.

It is interesting to notice that the bond orders obtained in this investigation give predominance to a Kekulé bond diagramme exhibiting double bonds in the positions A—A' and B—C. Consequently biphenylene may be regarded as a derivative of cyclobutane. This result is in contrast to conclusions drawn from some previous studies claiming the presence of a cyclobutadiene-type structure.^{33,34} On the other hand Baker *et al.*³⁵ have demonstrated that the chemical reactivity of biphenylene can be well interpreted on the basis of the structure supported here.

The ionization potential is another typical ground state property of a molecule. To obtain a test on the intrinsic consistency of the particular approach used in this investigation, ionization energies have been calculated and compared with experimental values.

According to Koopmans' theorem³⁶ applied to molecules having closed shell configurations, the ionization potential is approximated by the negative of the Hartree—Fock energy for the highest filled shell in the ground state of the molecule. From a purely theoretical viewpoint this theorem is based on several drastic assumptions. Recently the consequences of these assumptions have been studied by Hoyland and Goodman^{37,38}, and also by I'Haya for the case of ethylene.³⁹ The conclusion reached by Hoyland and Goodman is that Koopmans' theorem is invalid for conjugated hydrocarbons by an amount of 2—4 eV, the predicted values being always too high.³⁸

Table 3. Calculated and observed ionization potentials (eV).

Molecule	(IP) _{calc.}	(IP) _{obs.}	Method	Reference
Naphthalene	8.54	8.12 ± 0.01	Photoioniz.	42
		8.2 _a	El. impact	40
		8.46	»	41
Anthracene	7.62	7.5 _b	El. impact	40
		7.85	»	41
Biphenylene	8.84	—	—	—

In column 2 of Table 3 ionization potentials obtained by the use of Koopmans' theorem are given. For naphthalene and anthracene several experimental values are reported in the literature. Results obtained by the electron impact method^{40,41} and by photoionization⁴² are included in the table. No experimental value for biphenylene has been found in the literature.

The agreement between the predicted values and those obtained by the electron impact method is satisfactory. The ionization potential for naphthalene obtained by the photoionization technique is significantly lower than the calculated one. This difference is to be expected since the values given by Koopmans' theorem refer to vertical ionization whereas the experimental value represents an adiabatic potential characterized by a 0-0 transition.⁴²

Hedges and Matsen⁴³ have estimated the ionization potentials of a series of aromatic molecules by assuming a linear relation between the ionization energy and the long wavelength absorption band in the UV region. By this method they have estimated the difference between the potentials of naphthalene and anthracene to 0.89 eV. The corresponding difference obtained in this investigation is 0.92 eV.

The explanation of the accordance between the observed values and those predicted in the present investigation is to be found in the particular semi-empirical approach used for the evaluation of the parameter values. The parameter most important for the prediction of ionization potentials on an absolute scale is W_μ defined by (4). As mentioned in Chapter 2 the value of this parameter has been determined from the ionization potential of ethylene. Thus a molecular ionization potential is included in the procedure. It is, however, gratifying to notice that the experimental value used is one for a non-aromatic molecule, and its actual value, 10.515 eV,⁴² is about 3 eV higher than the observed ionization potential for naphthalene.

3. b. Excited states and electronic transitions

In order to give a quantitative description of the electronically excited states of a molecule by using molecular orbitals obtained from the solution of the ground state problem, superposition of configurations has to be invoked.

Because of the semi-empirical nature of the Pariser—Parr—Pople approximation, the number of configurations necessary for reproducing the main features of the electronic spectrum of a molecule can be limited. Results ob-

tained by previous studies within this approximation demonstrate that for aromatic hydrocarbons reliable predictions can be made by including only some of the lowest singly excited configurations.^{44,45} The extent to which superposition of configurations has to be included does of course depend on the scheme applied for the evaluation of the basic semi-empirical parameters. The particular approach used in this investigation does not give parameter values that are optimized for a description of the electronic transitions in aromatic molecules. Some of the details in the benzene spectrum are not accurately reproduced,⁵ and the same situation should be reflected in the description of condensed aromatic hydrocarbons. To compensate for this deficiency all the singly excited configurations have been included in the description of the excited states of each of the molecules considered in this study.

For alternant hydrocarbons there is always degeneracy between the excited configurations $\Psi(i \rightarrow k')$ and $\Psi(k \rightarrow i')$ in the Hückel approximation.¹⁵ It has been shown by Pople⁴⁴ that the same degeneracy occurs for both singlets and triplets in an SCF description. This yields the important relations

$${}^1E(i \rightarrow k') = {}^1E(k \rightarrow i'), \text{ and } {}^3E(i \rightarrow k') = {}^3E(k \rightarrow i') \quad (20)$$

The notation used for the molecular orbitals is the following. The filled orbitals in the ground state are labelled 1, 2,, i, j, \dots in order of increasing energy, and the empty orbitals are labelled j', i', \dots , 2', 1' in the same order.

Some further important rules valid for alternant hydrocarbons have been stated and proved by Pariser.⁴⁵ If the linear combinations

$${}^1\Psi_{ik}^{\pm} = 2^{-1/2} [{}^1\Psi(i \rightarrow k') \pm {}^1\Psi(k \rightarrow i')] \quad (21)$$

and

$${}^3\Psi_{ik}^{\pm} = 2^{-1/2} [{}^3\Psi(i \rightarrow k') \pm {}^3\Psi(k \rightarrow i')] \quad (22)$$

are constructed, each configurational determinant, singlet and triplet, will split into two determinants, where plus states do not mix with minus states. Formally the single configuration describing the ground state of the molecule behaves as a minus state interacting only with ${}^1\Psi_{ik}^{-}$. In the present investigation self-consistent molecular orbitals are used for the construction of the configurations, and consequently, by Brillouin's theorem, there will be no interaction between the ground configuration and any of the singly excited configurations. For the sake of consistency the ground configuration is still labelled as a minus state (${}^1A_{1g}^{-}$). The excited configurations ${}^1, {}^3\Psi(i \rightarrow i')$ behave like plus states since they interact only with ${}^1, {}^3\Psi^{+}$ states.

The dipole transition moment between any two plus states or between any two minus states is zero. Accordingly, only transitions between plus and minus states are allowed.

All the molecules included in this investigation belong to the symmetry group D_{2h} and the molecular orbitals belong to the irreducible representations a_{1u} , b_{1u} , b_{2g} , and b_{3g} . Furthermore the possible symmetries for the configurations are A_{1g} , B_{1g} , B_{2u} , and B_{3u} . The coordinate system chosen is shown in Fig. 1. From the character table of the group one finds that the coordinates x and y belong to the irreducible representations B_{3u} and B_{2u} respectively.

This implies that the only dipole transitions from the ground state are those to ${}^1B_{3u}^+$ and ${}^1B_{2u}^+$. The first of these will be polarized along the long axis of the molecule, and the second along the short one.

To estimate the shifts in the energies of the excited states introduced by superposition of configurations, the off-diagonal matrix elements of the π -electron Hamiltonian have to be calculated.

The calculations of the excited state energies were made in two steps. First only the interaction between the degenerate configurations was considered.

The next step in the calculations was to consider further interaction among plus and minus states, all states included. Because of the rather high symmetry of the molecules, extensive factorization of the secular determinant could be made. Thus a series of independent secular problems of low order was obtained. For anthracene, the largest of the molecules considered here, the inclusion of all configurations did eventually lead to 8 independent secular equations for the singlet states, one of order 3, 6 of order 6, and one of order 10.

For the triplets only the plus states were calculated as the energies of singlet and triplet minus states will be the same before as well as after superposition of singly excited configurations.

It is interesting to study the changes introduced in the energy level spectrum by each of the two steps in the calculation. Fig. 2 gives a picture of the effects on the ${}^1B_{1g}$ states of naphthalene. The figure demonstrates clearly that the major changes in the energy level spectrum are introduced by the interaction between the degenerate configurations. Further mixing of configurations only give small adjustments to the energy levels. The same picture is valid for all the molecules studied in the present investigation irrespective of the state symmetries. The importance of this fact has been pointed out previously by

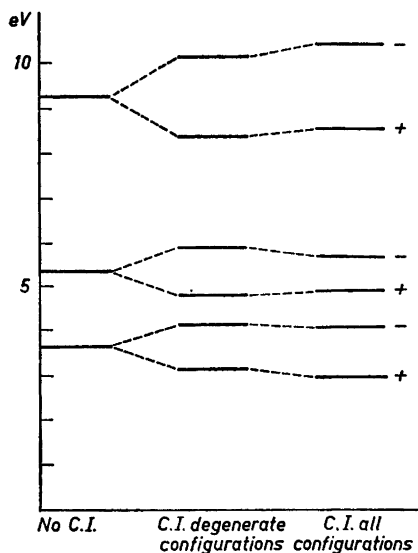


Fig. 2. Effect of configuration interaction (C.I.) on the ${}^1B_{1g}$ states of naphthalene.

several authors, and Moffit⁴⁶ has introduced the name first order configuration interaction for the superposition of degenerate configurations.

To provide a test on the predictions made for the excited state energies relative to the energy of the ground state, a comparison with observed electronic transitions is made. In making such a comparison one should bear in mind the uncertainties in the experimental data as well as the approximations underlying the theoretical calculations. The measured transition frequencies are perturbed by vibrational excitations, and in general it is difficult to locate the pure electronic transition. The measured oscillator strengths are influenced by vibronic couplings and are in most cases very uncertain. Rather few experimental polarizations are known.

The predicted oscillator strengths have been obtained from the formula

$$f = 1.085 \times 10^{11} \times \omega \times |\mathbf{M}|^2 \quad (23)$$

given by Mulliken and Rieke.⁴⁷ In (23) ω is the frequency of the transition in cm^{-1} , and $|\mathbf{M}|$ is the modulus of the off-diagonal matrix element of the dipole moment.

Table 4. Naphthalene. Calculated and experimental spectrum.

Transition	ω (cm^{-1})		f		polarization	
	calc.	obs.	calc.	obs.	calc.	obs.
${}^1A_{1g}^- \rightarrow {}^1B_{3u}^-$	35 037	32 020	0	2×10^{-4}	forb.	x
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	38 167	35 000	0.05	0.02	y	y
${}^1A_{1g}^- \rightarrow {}^1B_{3u}^+$	51 761	45 400	2.14	1.21	x	x
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	53 778	59 800	0.87	0.6?	y	—
${}^1A_{1g}^- \rightarrow {}^3B_{2u}^+$	21 798	21 300	0	—		
${}^1A_{1g}^- \rightarrow {}^3B_{3u}^+$	31 189	—	0	—		
${}^3B_{2u}^+ \rightarrow {}^3A_{1g}^-$	25 878	—	0.10	—	y	
		24 200		—		x
${}^3B_{2u}^+ \rightarrow {}^3B_{1g}^-$	26 919	—	0.39	—	x	
		25 660		—		x
${}^3B_{2u}^+ \rightarrow {}^3B_{1g}^+$	27 532	—	0	—	forb.	
		26 950		—		x

Tables 4, 5, and 6 give a comparison between calculated and experimental spectra for naphthalene, anthracene, and biphenylene respectively. Only the lowest transitions are included as these are the ones for which comparatively reliable interpretations of the observed spectra are available. Furthermore the method applied in the present study cannot be expected to yield any satisfactory description of the higher electronic transitions. Even for the lowest excited states one cannot require any accurate reproduction of the experimental data. This is first of all due to the assumption of a fixed σ -core potential common to all the different electronic states of the molecule, excluding the possibility for substantial shifts in the minimum positions of the potential energy surface by electronic excitations. Moreover the calculated oscillator strengths rest on the assumption of an orthogonal set of $2p\pi$ basic functions.

Table 5. Anthracene. Calculated and experimental spectrum.

Transition	ω (cm ⁻¹)		f		polarization	
	calc.	obs.	calc.	obs.	calc.	obs.
${}^1A_{1g}^- \rightarrow {}^1B_{3u}^-$	29 718		0		forb.	—
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	30 992	27 400	0.20	0.10	<i>y</i>	<i>y</i>
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	44 706	40 000	8×10^{-4}	—	<i>y</i>	—
${}^1A_{1g}^- \rightarrow {}^1B_{3u}^+$	45 270	42 270	3.23	1.56	<i>x</i>	<i>x</i>
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	49 772	45 200	0.54	0.21	<i>y</i>	<i>y</i>
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	64 040	54 000	1.18	0.41	<i>y</i>	<i>y</i>
${}^1A_{1g}^- \rightarrow {}^3B_{2u}^+$	14 044	14 927	0	—	forb.	—

In view of these approximations a reproduction of the main patterns of the electronic spectra should be considered as satisfactory.

The three distinct band systems characterizing the naphthalene absorption spectrum in the UV region have been studied in detail by spectroscopic methods. Craig *et al.*⁴⁸ have examined the first band system very closely, and they report a vapour frequency at 32 020 cm⁻¹ for the 0—0 transition. The electronic contribution to the oscillator strength for this transition has been estimated⁴⁹ to 2×10^{-4} . The assignment of this transition as long-axis polarized first made by McClure⁵⁰ has later been confirmed.^{51,52} Thus the observations made for this transition strongly support the result of the present calculations.

The two subsequent band systems for naphthalene have been studied experimentally by Bree and Thirunamachandran.⁴⁹ The first of these transitions is found to be short-axis polarized in agreement with previous observations.⁵⁰ They have estimated the oscillator strength for the 0—0 transition in this band to 0.02. For the next system at around 45 400 cm⁻¹ they report a long-axis polarized transition with a total f -value of 1.21. The fourth transition predicted is compared with observations made by Klevens and Platt.⁵³ The calculated and observed f -values are in accordance. For the polarization of this transition no experimental information is available.

Recent experimental studies have provided some interesting information on the triplet states of naphthalene. Paramagnetic resonance absorption measurements⁵⁴ on solid solution of naphthalene in durene have led to the conclusion that the symmetry of the lowest triplet state is ${}^3B_{2u}$, in complete agreement with the present calculations. The position of the observed⁵⁵ band corresponding to the symmetry-forbidden transition from the ground state is also in close agreement with the prediction made here.

The triplet-triplet absorption spectrum of naphthalene has been studied experimentally by El-Sayed and Pavlopoulos.⁵⁶ From the results obtained for the polarizations they conclude that the three triplet-triplet absorption bands in the visible region all correspond to the allowed transitions from the lowest triplet state to states of symmetry ${}^3B_{1g}^-$. These transitions are polarized along the long molecular axis.

These observations are not consistent with the predictions made here. According to the calculations the band of lowest energy arises from a transi-

Table 6. Biphenylene. Calculated and experimental spectrum.

Transition	ω (cm ⁻¹)		f		polarization	
	calc.	obs.	calc.	obs.	calc.	obs.
${}^1A_{1g}^- \rightarrow {}^1B_{1g}^+$	37 099	25 467	0	<10 ⁻³	forb.	forb.
${}^1A_{1g}^- \rightarrow {}^1B_{3u}^+$	47 981		1.94		x	
		28 200		—		x
${}^1A_{1g}^- \rightarrow {}^1B_{2u}^+$	46 763		0.08		y	
		40 250		—		—

tion to ${}^3A_{1g}^-$. The second band of rather high intensity is predicted to correspond to a transition to ${}^3B_{1g}^-$. It is here suggested that the third weak band in this region arises from the forbidden transition to ${}^3B_{1g}^+$. The same assignments have previously been made by Pariser.⁴⁵

The discrepancies between observations and predictions on interrelations among excited states is not unexpected. Superposition of configurations has been limited, and, as mentioned above, the semi-empirical parameters are not optimized for a description of excited states. On the other hand, the experimental results for the triplet-triplet transitions cannot be regarded as conclusive. Three close-lying states of the same symmetry should be expected to mix strongly and give rise to large splittings in the energy-level spectrum.

A comparison between the observed and calculated spectrum of anthracene (Table 5) shows a situation similar to that one for naphthalene. The main features of the spectrum are accounted for, and it is gratifying to notice that the predicted polarizations and the sequence of intensities for transitions from the ground state are in agreement with the experimental results.

The observed values quoted in the table are reported by Lyons and Morris⁵⁷ who also have given a survey of previous measurements.

The four main systems of the spectrum observed in solution are well reproduced by the present calculations. The polarizations are in complete agreement and the relative intensities are in accordance. The absolute values of the predicted oscillator strengths, however, are all too high.

The lowest, symmetry-forbidden, transition predicted is very close to the strong absorption band of the first main system, and is most likely submerged in this. An allowed, but extremely weak transition giving rise to absorption at around 44 700 cm⁻¹ is predicted. This transition may be related to the weak absorption at around 40 000 cm⁻¹ observed in the crystal spectrum.⁵⁷

The lowest triplet state of anthracene has also been studied experimentally. The 0—0 transition from the ground state is found⁵⁸ to give absorption at 14 900 cm⁻¹ in nice agreement with the calculated value. The predicted symmetry of the state is also in accordance with experimental observation.⁵⁸

It is encouraging to see that the particular approach used in the present molecular orbital study is able to account for both the energy and symmetry of the excited states in naphthalene and anthracene.

Biphenylene which belongs to the same point group as naphthalene and anthracene exhibits an excited energy-level spectrum that deviates appreciably

from that of the polyacenes. The symmetry predicted for the lowest excited singlet state is B_{1g}^+ . Recent experimental studies strongly support this prediction. From an investigation of the weak low-energy band in vapour and solution Hochstrasser⁵⁹ has concluded that the spectrum shows a vibrational structure typical for a $g-g$ forbidden excitation. The predicted transition frequency, however, is substantially higher than the measured value for the 0—0 transition. The symmetry of the second excited level has been determined from studies of the crystal spectrum,^{59,60} and the assignment suggested is B_{3u} . Furthermore it has been concluded that a transition to this state absorbs at 28 200 cm^{-1} . These observations suggest the allowed transition from the ground state to the lowest state of symmetry B_{3u}^+ .

The predicted f -value for this transition is rather high, but the calculated frequency prevents any decisive assignment. Another strong band at 40 250 cm^{-1} has been observed,⁶¹ but the polarization of the corresponding transition has not been determined. This band could be connected to the predicted short axis polarized transition at around 46 700 cm^{-1} .

The main conclusion to be drawn from the comparison presented in Table 6 is that the particular approach applied in the present investigation is not adequate for a quantitative discussion of the excited states of this molecule. This result is not unexpected. The calculated frequencies refer to vertical excitations, and the assumption of a fixed σ -core potential common to all the different electronic states of the molecule has to be considered as unrealistic in this case where appreciable internal strain is present.

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