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## A Simplified Version of the Pariser-Parr-Pople Treatment of $\pi$ -Electron Systems

By

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The semi-empirical configuration interaction treatment due to PARISER and PARR and to POPLÉ has been modified by reducing the set of electronic interaction integrals to  $\gamma'_{11}$  and  $\gamma'_{12}$  and by limiting the number of configurations to 10. HÜCKEL MOs are used as basis functions. The dependence of the resonance integral  $\beta'_{\mu\nu}$  on the interatomic distance  $R_{\mu\nu}$  is simulated by making  $\beta'_{\mu\nu}$  a quadratic function of the Hückel bond orders  $P_{\mu\nu}$ .

Le procédé semi-empirique de l'interaction de configuration selon PARISER, PARR et POPLÉ a été modifié en réduisant l'ensemble des intégrales d'interaction électronique à  $\gamma'_{11}$  et  $\gamma'_{12}$  et en limitant le nombre des configurations à 10. Les fonctions de base sont des orbitales moléculaires selon Hückel. La dépendance entre l'intégrale de résonance  $\beta'_{\mu\nu}$  et la distance interatomique  $R_{\mu\nu}$  est simulée en posant que  $\beta'_{\mu\nu}$  est une fonction quadratique des ordres de liaisons  $P_{\mu\nu}$  selon Hückel.

Eine Modifikation des semiempirischen CI-Verfahrens von PARISER, PARR und POPLÉ wurde zur Behandlung von  $\pi$ -Systemen herangezogen. Als Vereinfachung wurde der Grad der CI-Matrix auf zehn beschränkt und von den Elektronenwechselwirkungsintegralen nur  $\gamma'_{11}$  und  $\gamma'_{12}$  berücksichtigt. Hückel-MOs wurden als Basisfunktionen verwendet. Die Abhängigkeit des Resonanzintegrals  $\beta'_{\mu\nu}$  vom interatomaren Abstand  $R_{\mu\nu}$  wurde durch den Ansatz von  $\beta'_{\mu\nu}$  als quadratische Funktion der Hückel-Bindungsordnung  $P_{\mu\nu}$  angenähert.

### Introduction

The semi-empirical ASMO-CI treatment, due to PARISER and PARR [12, 13] and to POPLÉ [15, 16], is one of the most successful and versatile methods for the calculation of the energies of electronically excited states of  $\pi$ -electron systems. In these treatments the many-electron wave functions are written as linear combinations of Slater determinants involving one electron LCAO SMOs  $\Psi_{J(i)\alpha(i)}$  or  $\Psi_{J(i)\beta(i)}$ . The space part of these functions is given as a linear combination over atomic orbitals

$$\Psi_J = \sum_{\mu} c_{J\mu} \varphi_{\mu}$$

where the  $c_{J\mu}$  are assumed to be either the SCF-MO coefficients or those of any other ortho-normal set. Usually perimeter MOs or Hückel-MOs have been used as a basis.

The lowest closed shell configuration  $I_0$  for a  $\pi$ -electron system with  $2N$  electrons can be written as

$$I_0 = || \bar{1} \bar{1} \bar{2} \bar{2} \cdots J \bar{J} \cdots N \bar{N} ||$$

where the symbols  $J$  and  $\bar{J}$  have the following meaning

$$J \equiv \Psi_J(i) \alpha(i) \text{ and } \bar{J} \equiv \Psi_J(i) \beta(i)$$

and where the normalization factor is implied in the symbol  $||\dots\dots\dots||$ . A singly excited configuration  $\Psi_J^{-1} \Psi_T$  is defined as

$$\Psi_J^{-1} \Psi_T = 2^{-\frac{1}{2}} \{ ||1 \bar{1} 2 \bar{2} \dots J \bar{T} \dots N \bar{N} || \pm ||1 \bar{1} 2 \bar{2} \dots T \bar{J} \dots N \bar{N} || \},$$

the positive sign referring to singlet, the negative to triplet configurations.

Under the usual assumption of  $\sigma$ - $\pi$  separation the many electron Hamiltonian for the  $\pi$ -part takes the form

$$\mathcal{H} = \sum_i H_i^e + \sum_{i < j} G_{ij}$$

with  $G_{ij} = 1/r_{ij}$ .

The energy is then a sum of one- and two-electron integrals over AOs:

$$H_{\mu\nu} = \langle \mu | H^e | \nu \rangle \quad \text{and} \quad \langle \mu(1) \nu(2) | G_{12} | \rho(1) \sigma(2) \rangle$$

where  $\mu$  etc. is used as a shorthand notation for  $\varphi_\mu$ .

If the approximation of zero differential overlap between the AOs is introduced then all two-electron integrals except those of the type

$$\gamma_{\mu\nu} = \langle \mu\nu | G | \mu\nu \rangle$$

vanish.

$H_{\mu\mu}$  corresponds to the ionization potential  $U_\mu$  of an electron in the AO  $\varphi_\mu$  corrected for the electrostatic interaction with the other positive centers  $\sigma \neq \mu$  of the core.  $H_{\mu\nu}$  ( $\mu \neq \nu$ ) is assumed to be different from zero only if the centers  $\mu$  and  $\nu$  are bonded in which case it takes the value  $\beta_{\mu\nu}$ . The interaction between two electrons occupying the same AO  $\varphi_\mu$  can be derived from spectroscopic data. The interaction  $\gamma_{\mu\nu}$  between two electrons in two different AOs  $\varphi_\mu$  and  $\varphi_\nu$  is a function of the interatomic distance  $R_{\mu\nu}$  between the two centers  $\mu$  and  $\nu$ . For intermediate distances the value of  $\gamma_{\mu\nu}$  is derived from a simplified model for the charge distributions  $\varphi_\mu^2$  and  $\varphi_\nu^2$ . For large distances  $\gamma_{\mu\nu}$  tends toward  $R_{\mu\nu}^{-1}$ .

Once the parameters  $\beta_{\mu\nu}$  and  $\gamma_{\mu\nu}$  and the one electron LCAO MOs  $\Psi_J$  have been specified for a particular  $\pi$ -electron system, then the calculation of the elements of the CI matrix proceeds according to simple rules. Therefore the method is specially well suited for digital computers.

### Outline of the simplified version of the PPP-treatment

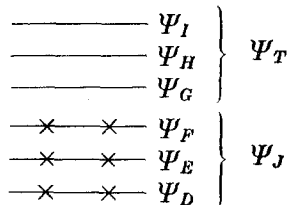
All integrals over AOs which do not involve either a single AO or a pair of bonded AOs are neglected, leaving only  $\beta_{\mu\nu}$ ,  $\gamma_{\mu\mu}$  and  $\gamma_{\mu\nu}$  ( $\mu$  and  $\nu$  bonded centers). Furthermore we are going to assume that for  $\pi$ -electron systems extending over carbon atoms only, the parameters  $\gamma_{\mu\mu}$  and  $\gamma_{\mu\nu}$  have fixed values:  $\gamma_{\mu\mu} = \gamma'_{11}$  and  $\gamma_{\mu\nu} = \gamma'_{12}$ . Such an approximation has been used before, by SALEM and LONGUET-HIGGINS [18], and in a critical discussion of the perimeter model for catacondensed  $\pi$ -electron systems [3].  $\gamma'_{11}$  and  $\gamma'_{12}$  are treated as empirical parameters whose values are taken to be the same for all carbon atoms and all carbon-carbon bonds in any  $\pi$ -electron system. They must be calibrated on the basis of spectroscopic data.

This simplification in itself, while limiting the number of terms contributing to each matrix element, does not lead to an important reduction in computing time. Such a reduction can only be achieved by cutting down the number of configurations that are taken into account. Extreme examples are the limitation

to  $\Gamma_0$ , the lowest closed shell configuration, and to the first four singly excited configurations  $\Psi_J^{-1}\Psi_T$  in the discussion of the long-wave length part of the electronic spectra of benzenoid aromatic systems by DEWAR and LONGUET-HIGGINS [1] and in the paper mentioned above [3]. A similar procedure has been described recently by KOUTECKY, PALDUS and ZAHRADNIK [5, 6]. In the present paper ten configurations, namely the lowest closed shell configuration  $\Gamma_0$  and nine singly excited configurations  $\Psi_J^{-1}\Psi_T$  have been used for the description of the ground state and the lowest excited states of  $\pi$ -electron systems:

$$\Psi = c_0 \Gamma_0 + \sum_{J,T} c_{JT} \Psi_J^{-1} \Psi_T$$

Hückel-MOs are used as the basis functions  $\Psi_J$ . This and the neglect of all two-center integrals between non-bonded pairs of AOs makes the energy associated with a linear combination insensitive to in-plane topological deformations of the system. According to a proposal by PLATT [14], the one electrons MOs are labeled as follows:



These six MOs define the nine singly excited configurations  $\Psi_J^{-1}\Psi_T$  which are used in our treatment:

$$\Psi_F^{-1}\Psi_G, \Psi_F^{-1}\Psi_H, \Psi_F^{-1}\Psi_I, \Psi_E^{-1}\Psi_G, \Psi_E^{-1}\Psi_H, \Psi_E^{-1}\Psi_I, \Psi_D^{-1}\Psi_G, \Psi_D^{-1}\Psi_H, \Psi_D^{-1}\Psi_I$$

The energy associated with a particular configuration  $\Psi_J^{-1}\Psi_T$  is taken relative to the energy of  $\Gamma_0$ : (for singlets)

$$\langle \Psi_J^{-1}\Psi_T | \mathcal{H} | \Psi_J^{-1}\Psi_T \rangle - \langle \Gamma_0 | \mathcal{H} | \Gamma_0 \rangle = F_{TT} - F_{JJ} + 2\langle JT | G | TJ \rangle - \langle JT | G | JT \rangle$$

with

$$F_{JK} = \langle J | F | K \rangle = \langle J | H^c | K \rangle + \sum_{l=1}^{u.o.} (2\langle LK | G | LJ \rangle - \langle LK | G | JL \rangle)$$

(u. o. = index of upper occupied MO).

The cross-terms between the configurations are calculated according to well known rules which, for singlet configurations, take the following form:

$$\langle \Psi_J^{-1}\Psi_T | \mathcal{H} | \Gamma_0 \rangle = \sqrt{2} F_{JT}$$

$$\langle \Psi_J^{-1}\Psi_T | \mathcal{H} | \Psi_K^{-1}\Psi_S \rangle = F_{TS} \delta_{JK} - F_{JK} \delta_{TS} + 2\langle KT | G | SJ \rangle - \langle KT | G | JS \rangle$$

For triplet configurations the relevant formulas are:

$${}^3\langle \Psi_J^{-1}\Psi_T | \mathcal{H} | \Gamma_0 \rangle = 0$$

$$\begin{aligned} {}^3\langle \Psi_J^{-1}\Psi_T | \mathcal{H} | \Psi_K^{-1}\Psi_S \rangle - \delta_{JK} \delta_{TS} \langle \Gamma_0 | \mathcal{H} | \Gamma_0 \rangle \\ = F_{TS} \delta_{JK} - F_{JK} \delta_{TS} - \langle KT | G | JS \rangle. \end{aligned}$$

For SCF-MOs all cross-terms  $F_{JK}$  ( $J \neq K$ ) vanish which leads to the consequence that all cross-terms between  $\Gamma_0$  and the singly excited configurations are zero.

The elements of the matrices  $G = (G_{\mu\nu})$ ,  $F = (F_{\mu\nu})$ ,  $P = (P_{\mu\nu})$  (generalized bond order) and  $H^c = (H_{\mu\nu}^c)$ , which have as a basis the set of AOs  $\varphi_\mu$  are defined as follows where  $b_J$  is the number of electrons occupying the MO  $\Psi_J$ :

$$\begin{aligned} G_{\mu\nu} &= \gamma_{\mu\nu} = \langle \mu\nu | G | \mu\nu \rangle \\ H_{\mu\nu}^c &= \langle \mu | H^c | \nu \rangle \\ F_{\mu\mu} &= U_\mu + \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\substack{\rho \\ \rho \neq \mu}} (P_{\rho\rho} - Z_\rho^c) \gamma_{\mu\rho} \\ F_{\mu\nu} &= H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \\ P_{\mu\nu} &= \sum_J b_J c_{J\mu} c_{J\nu} \end{aligned}$$

This set of rules leads, for a  $\pi$ -electron system of any size, to a CI matrix of degree 10, the eigenvalues and eigenvectors of which are considered, for most practical purposes, as sufficient approximations to the real eigenvalues and eigenfunctions of the system.

#### Transition moments, dipole moments and charge densities

The hybrid ground state  $\Psi_0$  and the excited states  $\Psi_a$  of a  $\pi$ -electron system are described by the following linear combinations:

$$\begin{aligned} \Psi_0 &= C_{00} \Gamma_0 + \sum_{J,T} C_{0,JT} \Psi_J^{-1} \Psi_T \\ \Psi_a &= C_{a0} \Gamma_0 + \sum_{J,T} C_{a,JT} \Psi_J^{-1} \Psi_T. \end{aligned}$$

The transition moment between two arbitrary states  $\Psi_a$  and  $\Psi_b$  is defined as

$$\vec{M}_{ab} = \langle \Psi_a | \vec{M} | \Psi_b \rangle$$

For  $a = b$  the above integral yields the dipole moment  $\vec{D}_a = \vec{M}_{aa}$  for the system in the hybrid state  $\Psi_a$ . The moment operator  $\vec{M}$  takes the form

$$\vec{M} = e \left( \sum_i \vec{r}_i - \sum_\mu Z_\mu^c \vec{r}_\mu \right)$$

where  $\vec{r}_i$  and  $\vec{r}_\mu$  are the position vectors of the electrons and the positive charges in the core, respectively. Making use of the ortho-normality of the MOs  $\Psi_J$  the following types of integrals can be obtained:

$$\begin{aligned} \langle \Gamma_0 | \vec{M} | \Gamma_0 \rangle &= 2e \sum_{K=1}^{u.o.} \vec{m}_{KK} - e \sum_\mu Z_\mu^c \vec{r}_\mu \\ \langle \Gamma_0 | \vec{M} | \Psi_J^{-1} \Psi_T \rangle &= \sqrt{2} e \vec{m}_{JT} \\ &\quad \langle \Psi_J^{-1} \Psi_T | \vec{M} | \Psi_K^{-1} \Psi_S \rangle \\ &= e \left( 2 \sum_{L=1}^{u.o.} \vec{m}_{LL} - \sum_\mu Z_\mu^c \vec{r}_\mu \right) \delta_{JK} \delta_{ST} \\ &\quad - e \vec{m}_{JK} \delta_{ST} + e \vec{m}_{ST} \delta_{JK} \end{aligned}$$

In these formulae the symbols  $\vec{m}_{IJ}$  stand for the transition moments between the one electron basis functions  $\Psi_J$  and  $\Psi_I$ . Their components are:

$$m_{IJ}^\xi = \langle I | \xi | J \rangle = \sum_\mu \sum_\nu v_{I\mu} c_{J\nu} \langle \mu | \xi | \nu \rangle.$$

As a consequence of the zero differential overlap approximation these expressions reduce to

$$m_{IJ}^{\xi} = \sum_{\mu} c_{I\mu} c_{J\mu} \xi_{\mu}$$

where the  $\xi_{\mu}$  ( $\xi = x, y, z$ ) are the coordinates of the center  $\mu$ .

The integral  $Q_{a\mu}$  (where the integration extends only over the space occupied by the AO  $\varphi_{\mu}$ )

$$Q_{a\mu} = \int_{\mu} \Psi_a \sum_i e_i \Psi_a d\tau$$

yields the  $\pi$ -electron density at the center  $\mu$  when the system is in the state  $\Psi_a$ . It has been shown by PARISER, that in neutral alternant systems  $Q_{a\mu} = 1$  for all states and all centers. Such systems are therefore dipole free in all electronic states. This follows from the well known pairing properties of the basis functions  $\Psi_J$ . To retain this property in our reduced version of the CI treatment it is necessary that configurations which are degenerate in the one electron scheme are included by pairs.

#### Remarks concerning the parameters

In most cases the bond lengths in a particular  $\pi$ -electron system are not known. For this reason a constant value for the parameter  $\beta_{\mu\nu}$  is generally used. However, trial calculations have shown that this assumption, when introduced into the scheme described in the previous chapters, will lead to predictions which are in bad agreement with the corresponding experimental results if the system exhibits strong bond alternation. In such cases it is necessary to take the dependence of  $\beta_{\mu\nu}$  on  $R_{\mu\nu}$  into account. This can be done in an approximate way through the use of the close correlation between  $R_{\mu\nu}$  and the bond orders  $P_{\mu\nu}$  obtained from Hückel-MOs.

$$\beta_{\mu\nu} = \beta(R_{\mu\nu}) \approx \beta'(P_{\mu\nu}).$$

In the range of  $P_{\mu\nu}$  from 0.3 to 0.9 a quadratic approximation for this dependence may be used:

$$\beta'(P_{\mu\nu}) = k_2 P_{\mu\nu}^2 + k_1 P_{\mu\nu} + k_0.$$

The value of the constants  $k_2$ ,  $k_1$  and  $k_0$  has been obtained through a calibration procedure, using a selected set of spectroscopic data. Such a procedure is indicated, because the exact form of the AOs  $\varphi_{\mu}$  is not known. Indeed, if the function  $\beta(R_{\mu\nu})$  is assumed to be proportional to the overlap integral  $S(R_{\mu\nu})$  between  $2p$ -Slater-AOs with effective nuclear charge of 3.25 then the dependence of  $\beta$  on  $R_{\mu\nu}$  is much too small to yield satisfactory results.

As the basis functions  $\Psi_J$  have been calculated in the Hückel approximation with a constant value of  $\beta$  for all bonds, the assumption of a  $\beta$  dependent on  $P_{\mu\nu}$  will have as a consequence that all cross-terms between configurations containing one electron integrals will depend on the choice of  $k_2$ ,  $k_1$  and  $k_0$ .

Different approximations for  $\gamma_{\mu\nu}$  have been proposed in the past. As mentioned above we are restricting the set of  $\gamma$ 's to the two constant parameters  $\gamma'_{11}$  and  $\gamma'_{12}$  following a suggestion by LONGUET-HIGGINS and SALEM. This is the minimum set necessary to yield a qualitatively correct sequence of the low-lying electronic states of  $\pi$ -electron systems. That the reduction to only two parameters will also

yield a reasonable quantitative result can be rationalised by the following argument due to RUEDENBERG [17] and to SALEM and MURRELL [10]: It can be shown that only the differences between consecutive  $\gamma$ -terms, that is  $\gamma_{1\mu} - \gamma_{1\mu+1}$  enter the calculation of the numerical values of the matrix elements. These differences die out faster with increasing  $\mu$  than do the  $\gamma_{1\mu}$  themselves. Our parameters  $\gamma'_{11}$  and  $\gamma'_{12}$  can be considered as the first two members of the series of such differences and therefore the neglect of higher terms is not expected to change the numerical results in a fundamental way.

### Results

Tab. 1 contains the results obtained with the following set of parameters (see appendix II):

$$\begin{aligned} \beta'(P_{\mu\nu}) &= -1.35 P_{\mu\nu}^2 - 0.45 P_{\mu\nu} - 1.60 \text{ (eV)} \\ \gamma'_{11} &= 7.0 \text{ eV} \\ \gamma'_{12} &= 1.7 \text{ eV} \end{aligned}$$

$E_i$  are the eigenvalues of the CI matrix of degree 10. All values have been quoted, even though the higher ones are certainly without physical meaning in view of the approximations introduced into the model.  $\Delta E_i = E_i - E_0$  is the transition energy,  $f$  the calculated oscillator strength and  $D_i$  the dipole moment of the state.

Table 1

Hexatriene				Octatetraene				Decapentaene				
$\Gamma$	$E_i$	$\Delta E_i$	exp. [9, 19]	$\Gamma$	$E_i$	$\Delta E_i$	exp. [9, 19]	$\Gamma$	$E_i$	$\Delta E_i$	exp. [9, 19]	
0		-0,30				-0,33				-0,31		
1	B B <sup>0</sup>	4,73	5,04	4,64	B B <sup>0</sup>	3,73	4,06	4,08	B B <sup>0</sup>	3,07	3,39	3,71
2	A	5,95	6,25		A C	4,81	5,14	5,32	A C	4,03	4,34	5,12
3	B	7,20	7,50		A	5,96	6,29		A	5,00	5,31	
4	A	7,32	7,63		B	6,08	6,40		B	5,20	5,51	
5	B	7,95	8,26		B	6,59	6,92		B	5,59	5,91	
6	B	9,11	9,41		B	7,76	8,09		B	6,67	6,99	
7	A	9,57	9,88		A	8,08	8,41		A	6,91	7,23	
8	A	9,85	10,15		A	8,65	8,98		A	7,56	7,87	
9	B	10,74	11,04		B	9,61	9,94		B	8,48	8,79	

Benzene			Naphthalene				Anthracene				
$\Gamma$	$E_i = \Delta E_i$	$f$	$\Gamma$	$E_i$	$\Delta E_i$	$f$	$\Gamma$	$E_i$	$\Delta E_i$	$f$	
0	$A_{1g}^-$		$A_{1g}^-$	-0,05			$A_{1g}^-$	-0,06			
1	$B_{2u}^- L_b$	5,28	$B_{3u}^- L_b$	4,34	4,39		$B_{2u}^+ L_a$	3,37	3,43	0,33	
2	$B_{1u}^+ L_a$	5,90	$B_{2u}^+ L_a$	4,44	4,49	0,20	$B_{3u}^- L_b$	3,75	3,80		
3	$E_{1u}^+ B_{a,b}$	7,30	2,50	$B_{3u}^+ B_b$	5,46	5,50	2,07	$B_{2u}^+ B_b$	4,43	4,49	2,58
4			$B_{1g}^-$	5,82	5,86		$B_{3u}^-$	4,45	4,50		
5	$E_{2g}^+$	8,92	$B_{2u}^+ B_a$	6,00	6,05	0,55	$B_{1g}^+$	5,11	5,17		
6			$A_{1g}^-$	6,13	6,18		$A_{1g}^-$	5,40	5,46		
7	$E_{2g}^-$	9,55	$B_{1g}^+$	6,83	6,88		$B_{2u}^+$	5,58	5,63	0,29	
8			$A_{1g}^+$	7,54	7,59		$A_{1g}^+$	6,36	6,41		
9	$B_{1u}^+$	11,76	$B_{2u}^+$	7,64	7,69	1,06	$B_{2u}^+$	6,56	6,62	1,12	

Table 1 (continuation)



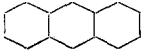
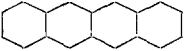
	Tetracene				Phenanthrene			
	$\Gamma$	$E_i$	$\Delta E_i$	$f$	$\Gamma$	$E_i$	$\Delta E_i$	$f$
0	$A_{1g}^-$	-0,05			$A^-$	-0,01	-	-
1	$B_{2u}^+ L_a$	2,61	2,66	0,35	$A^- L_b$	3,98	4,00	-
2	$B_{3u}^- L_b$	3,37	3,42		$B^+ L_a$	4,13	4,15	0,30
3	$B_{1g}^-$	3,45	3,49		$B^+ B_b$	4,72	4,73	1,78
4	$B_{3u}^+ B_b$	3,82	3,87	2,90	$A^+$	5,02	5,04	1,09
5	$B_{1g}^+$	4,13	4,18		$A^-$	5,15	5,17	-
6	$A_{1g}^-$	4,80	4,85		$B^-$	5,22	5,23	-
7	$B_{2u}^+$	4,93	4,98	0,07	$A^+$	5,84	5,85	0,24
8	$A_{1g}^+$	5,50	5,54		$B^+$	6,31	6,32	0,26
9	$B_{2u}^+$	5,70	5,75	1,26	$B^+$	6,72	6,74	0,47

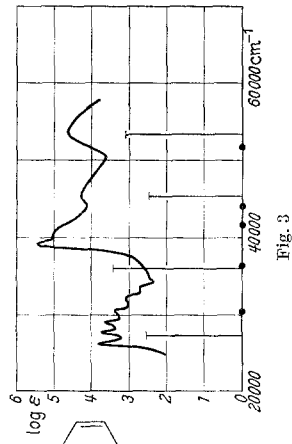
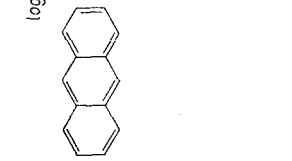
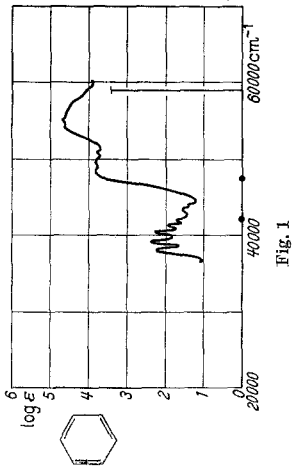
  

	Fulvene					Azulene				
	$\Gamma$	$E_i$	$\Delta E_i$	$f$	$D$	$\Gamma$	$E_i$	$\Delta E_i$	$f$	$D$
0	A	-0,66	-		0,65	A	-0,15	-		2,38
1	B	2,53	3,19	0,03	-2,78	B	1,76	1,92	0,02	-0,65
2	A	4,78	5,44	1,08	1,88	A	3,23	3,38	0,007	-0,48
3	A	6,67	7,33	0,38	3,46	A	3,89	4,04	1,65	3,15
4	B	7,21	7,87	0,23	1,73	B	4,26	4,41	0,18	-0,01
5	A	7,52	8,18	0,22	4,16	B	5,80	5,95	0,99	5,71
6	B	8,82	9,48	0,29	8,33	B	6,69	6,84	0,06	7,35
7	A	9,10	9,76	0,24	3,36	A	6,69	6,84	0,32	6,39
8	A	10,76	11,42	0,01	2,75	A	7,62	7,78	0,05	7,44
9	B	11,08	11,75	0,02	9,86	B	9,53	9,69	0,06	14,31

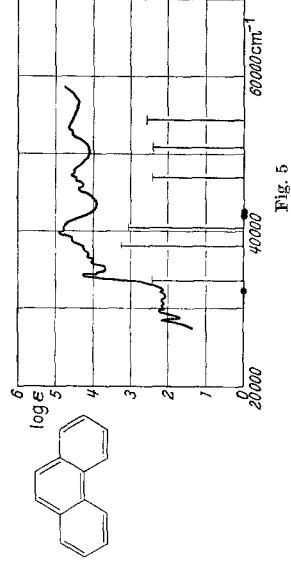
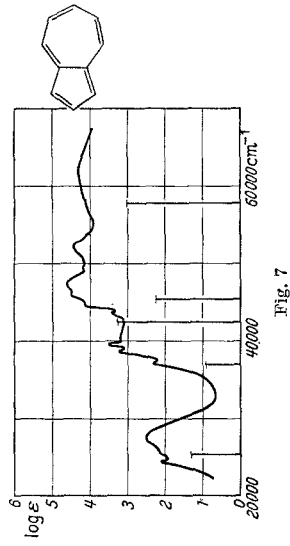
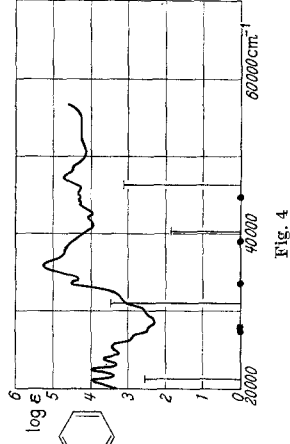
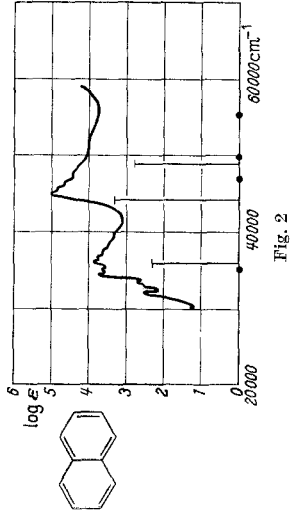
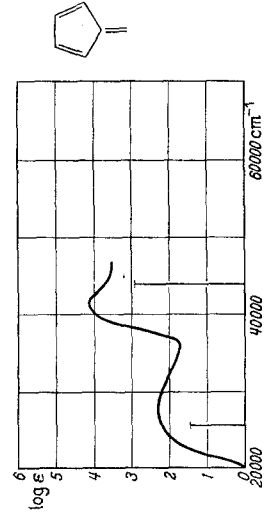
These results have been matched with the experimental data in Fig. 1 to 7. Allowed transitions are indicated by vertical bars of length  $\log f$ , forbidden transitions by points. In Tab. 2 we have compared our results for the first four members of the acene family with those obtained by PARISER [12] according to the complete PPP method and with the experimental values for both the singlet [4] and the triplet states [2, 7, 8].

Table 2

													
	$\Delta E_i$	PPP [12,13]	exp.	$\Delta E_i$	PPP [12,13]	exp.	$\Delta E_i$	PPP [12,13]	exp.	$\Delta E_i$	PPP [12,13]	exp.	
Singlet [2]			[4]			[4]			[4]			[4]	
$^1B_{2u}^+$	( $^1E_{1u}^+$ )	7,30	6,55	6,76	6,05	6,31	6,11	5,63	5,25	5,65	4,98	4,69	4,1
$^1B_{3u}^+$					5,50	5,94	5,58	4,49	5,50	4,86	3,87	5,09	4,6
$^1B_{2u}^+$	( $^1B_{1u}^+$ )	5,90	5,96	6,12	4,49	4,49	4,49	3,43	3,65	3,42	2,66	3,11	2,65
$^1B_{3u}^-$	( $^1B_{2u}^-$ )	5,28	4,71	4,90	4,39	4,02	4,08	3,80	3,72	3,72	3,42	3,57	3,30
Triplet [3]			[2, 7]			[2, 8]			[2, 8]			[2, 8]	
$^3B_{2u}^+$	( $^3E_{1u}^+$ )	4,40	4,15		4,23	4,22		4,32	3,56		4,22	3,19	
$^3B_{3u}^+$					4,39	3,64		3,50	3,50		3,22	3,45	
$^3B_{2u}^+$	( $^3B_{1u}^+$ )	2,96	3,59	3,59	2,69	2,18	2,64	1,94	1,66	1,85	1,33	1,10	1,27
$^3B_{3u}^-$	( $^3B_{2u}^-$ )	5,28	4,71		3,90	4,02		3,80	3,72		3,42	3,56	



**Fig. 6**



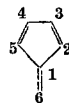
**Fig. 5**



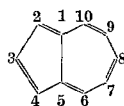
Finally, charge densities for the non-alternant systems fulvene [11] and azulene [4] in their lower electronic states are given in Tab. 3.

Table 3. Charge densities and bond orders  
a) Fulvene

	State	$\Psi_0$	$\Psi_1$	$\Psi_2$
	$\Delta E_i$	0	3,189	5,438
	$f$	-	0,03	1,08
$Q_\mu$	$\mu$			
	3	1,002	1,003	0,958
	2	1,041	0,827	1,153
	1	0,959	1,123	1,010
	6	0,956	1,219	0,769
$P_{\mu\nu}$	$\mu$ $\nu$			
	1 6	0,887	0,558	0,376
	1 2	0,325	0,516	0,541
	2 3	0,876	0,475	0,596
	3 4	0,369	0,726	0,429



b) Azulene



	State	$\Psi_0$	$\Psi_1$	$\Psi_2$	$\Psi_3$	$\Psi_4$
	$\Delta E_i$	0	1,916	3,380	4,042	4,409
	$f$	-	0,02	0,007	1,65	0,18
$Q_\mu$	$\mu$					
	3	0,971	1,124	0,936	0,969	0,775
	4	1,110	0,879	1,027	1,106	1,176
	5	1,011	1,031	0,994	1,008	0,959
	6	0,893	1,050	0,992	0,954	0,923
	7	1,027	0,914	1,052	1,012	1,152
	8	0,946	1,128	0,933	0,870	0,806
$P_{\mu\nu}$	$\mu$ $\nu$					
	3 4	0,643	0,636	0,582	0,580	0,524
	4 5	0,611	0,459	0,523	0,531	0,598
	5 6	0,622	0,483	0,555	0,476	0,550
	6 7	0,640	0,671	0,581	0,643	0,538
	7 8	0,645	0,581	0,589	0,567	0,578
	1 5	0,334	0,557	0,397	0,466	0,285

**Acknowledgement.** This work has been supported by the Schweizerische Nationalfonds (Projekt 2766) and by the CIBA Aktiengesellschaft in Basel.

### Appendix I

*Organisation of the calculations.* The procedure has been programmed for an IBM 1620 computer (storage 20000 digits, variable word length) in SPS language

(SPS = Symbolic Programming System). Due to the limitations in storage capacity the complete treatment has to be carried out in three steps:

Step 1. Calculation of Hückels MOs

Input: Incidence matrix **B** for the  $\pi$ -electron system.

Procedure: Diagonalization according to the Jacobi method.

Output: Eigenvectors  $\mathbf{C}_J = (c_{J\mu})$  (Hückel MOs).

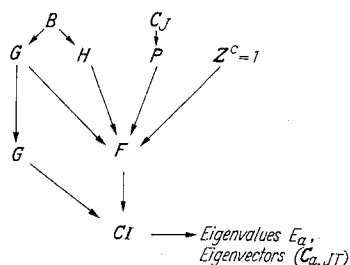
Step 2. CI-treatment: a) Calculation of CI-matrix

b) Diagonalisation of the CI-matrix

Input: Matrix **B** and Vectors  $\mathbf{C}_J$  of Step 1.

Parameters  $\beta'$  (through  $k_0, k_1, k_2$ ),  $\gamma'_{11}, \gamma'_{12}$

Procedure: Calculation of the CI-Matrix, its eigenvalues and eigenvectors according to the following diagram:



1. Provisions are included to change any matrix element in **G**, **H** and  $\mathbf{Z}^c$ . This allows the use of the complete set of  $\gamma_{\mu\nu}$  and the introduction of the parameters necessary for heteroatoms.

2. After the matrices **G** and **F** have been computed, the program may be switched to the calculation of either singlet or triplet states.

Output: CI-Matrix, Eigenvalues  $E_a$ , Excitation energies  $\Delta E_a = E_a - E_0$ , Eigenvectors  $(\mathbf{C}_a, JT)$ .

Step 3. Calculation of charge densities and transition moments

Input: Input and output of Step 2 Coordinates  $x_\mu, y_\mu, z_\mu$  of all centers.

Procedure: Calculation according to the formulae given above.

Output: Components of transition moments, oscillator strength, charge densities and dipole moments, if desired.

## Appendix II

*Calibration of the parameters.* If a CI treatment of benzene is carried out under the simplified assumptions proposed by LONGUET-HIGGINS and SALEM and used in this paper, the following energies for the first three excited states are obtained:

$$\begin{aligned} E(B_a) = E(B_b) &= -2\beta'_0 + \gamma'_{11}/6 + 2\gamma'_{12}/3 \\ E(L_a) &= -2\beta'_0 + \gamma'_{11}/3 - 5\gamma'_{12}/6 \\ E(L_b) &= -2\beta'_0 + \gamma'_{12}/6 \end{aligned}$$

$\beta'_0$  is the value which  $\beta'(P_{\mu\nu})$  takes for the bond order  $P_{12} = 0.667$  in benzene.

From the observed energies  $E(B_a) = E(B_b) = 6.76$  eV,  $E(L_a) = 6.12$  eV and  $E(L_b) = 4.90$  eV the following values for the parameters are calculated:

$$\begin{aligned}\beta'_0 &= -2.35 \text{ eV} \\ \gamma'_{11} &= 7.44 \text{ eV} \\ \gamma'_{12} &= 1.24 \text{ eV}\end{aligned}$$

With this set of parameters, that is, assuming a constant value of  $\beta'$  for all bonds, poor agreement with experiment is obtained, especially for those  $\pi$ -electron systems that show a pronounced alternation in their bond lengths. On the other hand it may be argued that benzene, in view of its high symmetry is an inappropriate standard to use for such a calibration procedure.

As mentioned above, better agreement is obtained if  $\beta'$  is assumed to be a function of the bond order  $P_{\mu\nu}$  of the particular bond. If  $\beta$  is allowed to vary with  $P_{\mu\nu}$  there exists no longer a unique set of parameters which fits the observed band positions of a test compound within the experimental limits of error. Using naphthalene as a basis for calibration and testing the sets of parameters so obtained by carrying out calculations for the compounds given in this paper, the following set was found to be quite satisfactory:

$$\begin{aligned}\beta'(P_{\mu\nu}) &= -1.35 P_{\mu\nu}^2 - 0.45 P_{\mu\nu} - 1.60 \text{ (eV)} \\ \gamma'_{11} &= 7.0 \text{ eV} \\ \gamma'_{12} &= 1.7 \text{ eV}.\end{aligned}$$

For  $P_{\mu\nu} = 0.667$  the value  $\beta'(0.667) = \beta'_0 = -2.5$  eV. This set of parameters has been used for all the results quoted in this paper and in the following two papers of this series. The same set has also been used for the calculation of the triplet states.

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