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SCF Calculations of Aromatic Hydrocarbons The Variable β Approximation*

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The transition energies and intensities of naphthalene, anthracene, phenanthrene, pyrene, and azulene are calculated with a variable β modification of the Pariser-Parr-Pople method. In this procedure each β is determined from the bond order after every iteration. The dependence of β on bond order is given by $\beta = -0.51\,p + A_0$ eV where A_0 is -1.90 eV (naphthalene and azulene), -1.84 eV (anthracene and phenanthrene), and -1.82 eV (pyrene). Precise knowledge of the molecular geometry is not required and the results are in good agreement with experiment.

Nous avons calculé les énergies et intensités des transitions électroniques de naphthalène, anthracène, phénanthrène, pyrène et azulène par une méthode PPP modifiée, où les β sont déterminés des indices de liaison p après chaque itération: $\beta = -0{,}51\,p + A_0$ eV, où $A_0 = -1{,}90$ (pour naphthalène et azulène), $-1{,}84$ (anthracène et phénanthrène) et $-1{,}82$ (pyrène), respectivement. On n'a pas besoin des géometries exactes des molécules. Les résultats s'accordent bien à l'expérience.

Die elektronischen Anregungsenergien sowie die zugehörigen Intensitäten von Naphthalin, Anthrazen, Phenantren, Pyren und Azulen wurden mit der Modifikation „der variablen β" der Pariser-Parr-Pople Methode berechnet, bei welcher die β-Werte nach jedem Iterationsschritt als Funktion der Bindungsordnung neu berechnet werden. Ihre Abhängigkeit ist durch $\beta = -0{,}51\,p + A_0$ eV gegeben, wobei A_0 $-1{,}90$ (Naphthalin und Azulen), $-1{,}84$ (Anthrazen und Phenantren) bzw. $-1{,}82$ (Pyren) ist. Für das Verfahren ist die genaue Kenntnis der Geometrie des Moleküls nicht vonnöten und die Resultate befinden sich in guter Übereinstimmung mit dem Experiment.

Introduction

Any addition to the already voluminous literature describing the results of Pariser-Parr-Pople (P-P-P) treatments of aromatic molecules [*24*], requires justification. The purpose of the present study is the validation of a procedure within the general P-P-P framework, in which the precise molecular geometry need not be known and which is easily extended to molecules containing heteroatoms. A subsidiary goal is the evaluation of the semi-empirical parameters necessary for the computation of transition energies and intensities. Since we will extend this work to include derivatives of these aromatic systems, more careful attention is paid to the parameter estimation for the parent hydrocarbons than has been the usual practice [*27*].

In a detailed and comprehensive treatment of aromatic hydrocarbons, including overlap, HUMMEL and RUEDENBERG [*11*] concluded "the actual positions of the

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atoms are not negligible parameters". DEWAR and GLEICHER have recently computed aromatic hydrocarbon ground state properties by a modification of the P-P-P method [5]. After each iteration they readjusted β, the one-electron core integrals, and the two center repulsion integrals by computing the bond lengths from the bond orders. In the present work we apply a similar "variable β" method to the evaluation of excited state properties. In subsequent papers the same technique will be used with heteroatomic systems.

Method of calculation

The SCF formalism of the P-P-P method was employed. Penetration integrals were neglected. The one-center repulsion integrals $\gamma_{\mu\mu} = I_\mu - A_\mu$ were evaluated as 11.13 eV [10]. A number of prescriptions for determining the two-center repulsion integrals, $\gamma_{\mu\nu}$, have been suggested [6, 17, 20, 22, 24]. Two of these methods were used, the theoretical integrals with adjusted exponents [17, 26] (R integrals) and the NISHIMOTO and MATAGA procedure [20] (NM integrals). The nearest neighbor repulsion integral, γ_{12}, is too large when computed by the R method [8] and this quantity was determined by reference to the observed benzene spectrum as described in the next section.

The estimation of β, the central problem in this investigation and discussed in detail below, has been subject to some uncertainty [7, 13, 18]. An essential feature of the variable β method is the insensitivity of the results to the assumed geometry. All molecules were assigned regular polygonal structures with equal carbon-carbon bond lengths (1.395 Å).

Transition energies were calculated by including configuration interaction between all singly-excited configurations within D eV of lowest excited (singlet or triplet) states. The value of D (3 — 4 eV) used in each CI calculation is specified in Tab. 3 — 7.

Estimation of γ_{12} (R integrals)

In previous work [8] it was not possible to calculate the correct order of the naphthalene transitions using the R integrals unless the nearest neighbor γ_{12} were reduced considerably. The arbitrary value, 7.00 eV, (ca. 0.8 eV below the calculated quantity) was chosen for this parameter. A direct procedure for estimating this quantity involves determining the magnitude that produces the best fit of the benzene spectrum. In the P-P-P method the benzene ${}^1B_{2u}$ energy is $-2\beta + \frac{1}{6}\gamma_{12} - \frac{1}{2}\gamma_{13} + \frac{1}{3}\gamma_{14}$ [19]. If the experimental energy, 4.88 eV, is combined with the computed γ_{13} and γ_{14}, then β is a function only of γ_{12}. The effect of varying γ_{12} upon the benzene transition energies is indicated in Tab. 1. The calculated energies are not very sensitive to γ_{12} and we choose 6.6 eV as the best value to be used in subsequent calculations.

Estimation of β: The variable β method

The total energy can be expressed in terms of E_σ, the compression energy for the neutral molecule, E_π, and the core repulsion energy, E_C.

$$E = E_\sigma + E_\pi + E_C \, .$$

If we designate the actual bond distances and the single bond distances (corresponding to appropriate hybridization) by $r_{\mu\nu}$ and $r_{\mu\nu}(s)$

$$E_\sigma = \sum_{\mu>\nu} \tfrac{1}{2} k_{\mu\nu}(\sigma)\,[r_{\mu\nu} - r_{\mu\nu}(s)]^2$$

$k_{\mu\nu}(\sigma)$ referring to the single bond force constant. Only the portion of the π-energy dependent upon bond distance is required and this may be expressed as [*27*]

$$E_\pi(r) = \sum_{\mu>\nu} [q_\mu (q_\nu - 2)\,\gamma_{\mu\nu} + 2\,\beta_{\mu\nu}\,p_{\mu\nu} - \tfrac{1}{2}\,p_{\mu\nu}^2\,\gamma_{\mu\nu}]$$

where q_μ is the π-charge density on the μth atom. When each atom in the π-framework donates one electron

$$E_C = \sum_{\mu>\nu} r_{\mu\nu}^{-1} \cong \sum_{\mu>\nu} \gamma_{\mu\nu}\,.$$

For alternant hydrocarbons

$$E(r) = \sum_{\mu>\nu} \{\tfrac{1}{2} k_{\mu\nu}(\sigma)\,[r_{\mu\nu} - r_{\mu\nu}(s)]^2 + 2\,\beta_{\mu\nu}\,p_{\mu\nu} - \tfrac{1}{2}\,p_{\mu\nu}^2\gamma_{\mu\nu}\}\,.$$

At equilibrium

$$\frac{\partial E(r)}{\partial r_{\mu\nu}} = 0\,.$$

The mobile bond orders, $p_{\mu\nu}$, are dependent on the entire molecule rather than on a specific bond length and are not regarded as r-dependent. If we focus attention only on nearest neighbor $r_{\mu\nu}$ and drop the subscripts we obtain

$$\frac{\partial E}{\partial r} = k(\sigma)\,[r - r(s)] + 2\,p\frac{\partial\beta}{\partial r} - \tfrac{1}{2}\,p^2\frac{\partial\gamma}{\partial r} = 0$$

for each bond in the π-framework. When $p = 0$, $r = r(s)$ and $\frac{\partial\gamma}{\partial r} = 0$. Thus, in this approximation, the nearest neighbor two-center repulsion integrals are independent of bond length and

$$k(\sigma)\,[r - r(s)] + 2\,p\frac{\partial\beta}{\partial r} = 0\,. \tag{1}$$

If $\beta(r)$ is expanded in a power series and only the first two terms retained, $\frac{\partial\beta}{\partial r}$ is constant. This is reasonable for the small bond length changes (0.18 Å) encountered here. When $p = 1$, $r = r(d)$, the pure double bond length, and (1) becomes

$$k(\sigma)\,[r(d) - r(s)] + 2\frac{\partial\beta}{\partial r} = 0\,. \tag{2}$$

Combining (1) and (2)

$$r = r(s) - [r(s) - r(d)]\,p\,. \tag{3}$$

The same expression has been suggested on different grounds by LONGUET-HIGGINS and SALEM [*14*].

Integration of (2) yields

$$\beta = -\tfrac{1}{2}\,k(\sigma)\,[r(d) - r(s)]\,r + c\,. \tag{4}$$

Substitution of (3) into (4) gives

$$\beta = A_1 p + A_0 \tag{5}$$

with

$$A_1 = -\tfrac{1}{2}\,k(\sigma)\,[r(d) - r(s)]^2\,. \tag{6}$$

Table 1. *The Dependence of Benzene State Energies on* γ_{12} *(*R *integrals)*
Energy (eV)

State	γ_{12} =						Expt.
	7.0	6.9	6.8	6.7	6.6	6.5	
$^1B_{2u}$	4.880	4.880	4.880	4.880	4.880	4.880	4.88[a, b]
$^1B_{1u}$	5.760	5.860	5.960	6.060	6.160	6.260	6.05[b]
^1E_u	6.972	6.922	6.872	6.822	6.772	6.722	6.70[b]
$^3B_{1u}$	3.705	3.672	3.639	3.605	3.572	3.539	3.65[c]
β	-2.405	-2.413	-2.421	-2.428	-2.435	-2.444	

[a] Assumed. [b] Ref. [*19*]. [c] Ref. [*16*].

Table 2. *Relation between* A_0 *and* A_1 *in* $\beta = A_1 p + A_0$ *Established by Using Benzene* β *(Tab. 1)*
Naphthalene State Energies (eV)

$-A_1$ (eV)	$^1B_{3u}$ (α)[a]	$^1B_{2u}$ (p)	$^1B_{3u}$ (β)	$^1B_{2u}$ (β')
R integrals				
0	4.360	4.594	6.007	6.510
0.2	4.362	4.633	6.003	6.469
0.4	4.366	4.677	5.999	6.427
0.8	4.385	4.783	5.994	6.342
1.0	4.403	4.849	5.994	6.301
NM integrals				
0	4.245	4.516	5.818	6.508
0.2	4.246	4.552	5.814	6.469
0.4	4.249	4.591	5.810	6.428
0.8	4.270	4.690	5.810	6.351
1.0	4.288	4.735	5.812	6.252
Expt.	3.99[b]	4.51[b]	5.62[b]	7.44[c]

[a] Clar notation. [b] Ref. [*19*]. [c] Ref. [*15*].

After each iteration in the SCF calculation new β values are computed and the process continued until self-consistency is achieved. The values of A_0 and A_1 are chosen semi-empirically subject only to the requirement of physical reasonableness. To reduce the number of parameters it is desirable to relate A_0 and A_1. One way to do this involves the use of the benzene $\beta = -2.435$ eV (R integrals) or $\beta = -2.378$ eV (NM integrals), corresponding to $p = \frac{2}{3}$. The transition energies of naphthalene calculated in this manner are summarized in Tab. 2. It is evident that the correspondence between theory and experiment is not satisfactory.

It has been suggested [*21*] that β, corresponding to a given bond length, decreases in absolute magnitude as the number of rings is increased. Consequently, the use of the benzene β to relate A_0 and A_1 may not be valid for naphthalene. By independent adjustment of A_0 and A_1 it is possible to obtain an excellent fit of the naphthalene spectrum (Tab. 3). The final expressions are

$$\beta = -0.40\,p - 1.97\ \text{eV (R integrals)}, \qquad (7)$$
$$\beta = -0.51\,p - 1.90\ \text{eV (NM integrals)}.$$

These correspond to $\beta = -2.24$ eV for $p = \frac{2}{3}$ and the calculated ^1L_a energy is improved over that calculated with constant β [*8*].

It can be seen (Fig. 1) that the observed bond length sequence in naphthalene [*4*] will be reproduced only when the magnitude of A_1 is less than 0.6 eV. A value in the neighborhood of —0.5 eV is quite reasonable on this basis.

Although it would be consonant with the spirit of semi-empirical methods to accept these values of A_0 and A_1 without further ado, additional justification for the use of these quantities may be obtained by direct estimation of A_1 from (6). Carbon-carbon single bond force constants fall in the range 4.5 — 5.6 md/Å [*31*] which corresponds to

$$-A_1 = 0.46 - 0.57\ \text{eV}$$

(average is 0.51 eV). These force constants refer to sp^3 hybridization and it is expected that the sp^2 hybrids have larger k (σ). However, the C — C stretching force constant in oxalyl chloride is only 4.84 md/Å [*34*]. The close agreement between the theoretical and semiempirical A_1 establishes the validity of this method.

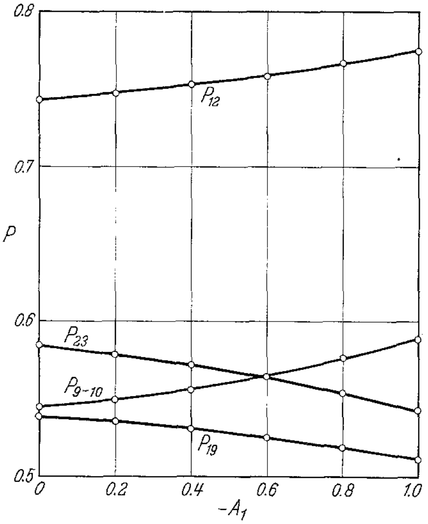

Fig. 1. Bond order vs. A_1 for naphthalene. NM integrals, $\beta = A_1 p + A_0$; $A_0 = -2.24 - 2/3\,A_1$. The results for R integrals are almost identical

Results-Transition energies

The results are presented in Tab. 3 — 7. It is interesting to note that the β (p) expressions obtained for naphthalene are applicable to azulene and analogously anthracene and phenanthrene can be treated with the same β (p) relations. The number of carbon atoms in the π-framework is apparently the controlling factor. When $p = \frac{2}{3}$ is substituted in the β (p) expressions for naphthalene and anthracene, almost the same values are obtained as in previous calculations [*21*]. Therefore, A_0 for pyrene is estimated as —1.83 eV (R integrals) and —1.82 eV (NM integrals).

It should be noted that while Dewar and Gleicher [*5*] adjusted β and $\gamma_{\mu\nu}$ after each iteration, we determined the repulsion integrals for 1.395 Å bond lengths and only changed β at each iteration.

A comparison of experimental and theoretical transition energies is often rendered difficult by the character of the experimental spectra. The transition energies were estimated from the positions of the most intense vibronic bands or the band maxima. In many cases an uncertainty of 0.2 — 0.3 eV in these experimental quantities is to be expected. Except for transition energies in excess of 6.2 eV, these quantities were obtained from solution spectra.

Table 3. *Naphthalene* (D[a] = *3.5 eV*) *Transition Energies* (*eV*) *and Intensities*

	R integrals $\beta = -0.40\ p - 1.97$ eV		NM integrals $\beta = -0.51\ p - 1.90$ eV		Expt.
	Energy (eV)	f	Energy	f	
Singlets	4.001	0	4.033	0	3.97 ($f = 0.002$)[b] (x)
	4.420	0.223 ($y$pol.)	4.419	0.200 (y)	4.51 (0.18)[b] (y)
	5.364	0	5.461	0	
	5.404	0	5.582	1.960 (x)	
	5.626	1.875 (x)	5.648	0	5.63 (1.70)[b] (x)
	5.840	0	5.993	0	
	6.003	0.666 (y)	6.073	0.579 (y)	6.51 (0.21)[b]
	6.869	0	6.861	0	
	7.156	0	6.987	0	
	7.176	0	7.536	0	
	7.178	0	7.603	0	
	7.697	0.824 (y)	7.626	0.953 (y)	7.44 (~ 0.8)[c]
	7.787	0			
Triplets	2.726		2.473		2.64[d]
	3.393		3.107		
	3.688		3.531		
	4.048		3.896		
	4.125		4.033		
	4.179				

[a] Configurations with energies within D eV of lowest configuration included.

[b] Ref. [*19*]. [c] Ref. [*15*]. [d] Ref. [*16*].

Table. 4. *Anthracene Transition Energies* (*eV*) *and Intensities*
$D = 3.5$ eV

	R integrals $\beta = -0.40\ p - 1.85$ eV		NM integrals $\beta = -0.51\ p - 1.84$ eV		Expt.[a]
	Energy	f	Energy	f	
Singlets	3.549	0.338 ($y$pol.)	3.484	0.317 (y)	3.34 ($f = 0.10$)
	3.593	0	3.604	0	
	4.375	0	4.656	0	
	4.703	0	4.677	0	
	4.939	0	4.814	0	
	5.006	2.487 (x)	4.831	2.522 (x)	4.83 (2.28)
	5.280	0	5.264	0	
	5.421	0.001 (y)	5.850	0.221 (y)	5.61 (0.28)
	5.877	0.779 (y)	5.916	0.560 (y)	
	6.248	0	6.059	0	
	6.338	0	6.206	0	
	6.436	0	6.574	0	
Triplets	1.674		1.581		1.85[b]
	2.851		2.772		
	3.369		3.282		
	3.622		3.604		

[a] Ref. [*19*]. [b] Ref. [*16*].

Table 5. *Phenanthrene Transition Energies* (*eV*) *and Intensities*
$D = 3.0$ eV

	ℜ integrals $\beta = -0.40\,p - 1.85$ eV		𝔑𝔐 integrals $\beta = -0.51\,p - 1.84$ eV		Expt.[a]
	Energy	f	Energy	f	
Singlets	3.546	0	3.630	0	3.75 (0.003) (y)
	4.206	0.317 (x)	4.157	0.322 (x)	4.23 (0.18) (x)
	4.490	0	4.615	0	
	4.953	1.019 (x)	4.922	1.486 (x)	4.91 (1.09) (x)
	4.990	0.398 (y)	4.978	0.540 (y)	
	5.295	0.431 (y)	5.249	0	
	5.355	0.805 (x)	5.497	0.330 (y)	
	5.432	0	5.757	0	
	5.834	0	5.820	0	
	5.886	0	5.950	0.265 (x)	5.83 (0.60)
	6.196	0.132 (x)	6.071	0.200 (x)	
	6.394	0.039 (x)	6.445	0	
	6.426	0.472 (y)	6.468	0	
	6.732	0	6.657	0.446 (y)	6.62 (0.59)
	6.787	0.651 (y)	6.763	0.125 (x)	
Triplets	2.474		2.320		2.67[b]
	3.186		3.064		
	3.236		3.105		
	3.573		3.455		
	3.765		3.690		
	3.768		3.756		

[a] Ref. [*12*]. [b] Ref. [*16*].

Table 6. *Pyrene Transition Energies* (*eV*) *and Intensities*
$D = 3.0$ eV

	ℜ integrals $\beta = -0.40\,p - 1.83$ eV		𝔑𝔐 integrals $\beta = -0.051\,p - 1.82$ eV		Expt.[a]
	Energy	f	Energy	f	
Singlets	3.500	0	3.470	0	3.34 (y)
	3.637	0.577 ($x$pol.)	3.556	0.680 (x)	3.70 (x)
	4.044	0	4.271	0	
	4.193	0	4.306	0	
	4.823	0.925 (y)	4.703	0.948 (y)	4.55 (y)
	4.935	0	4.832	0	
	5.008	0	4.946	0	
	5.009	0	5.199	0	
	5.280	1.133 (x)	5.207	1.468 (x)	5.15 (x)
	5.385	0	5.266	0	
	5.878	0	5.939	0	
	5.956	0	5.985	0	5.99
	6.053	0	5.997	0	
	6.281	0	6.040	0	
	6.326	1.448 (x)	6.319	0.940 (x)	6.32
Triplets	1.957		1.825		
	3.061		3.019		
	3.218		3.117		
	3.241		3.144		

[a] Ref. [*1*].

Table 7. *Azulene Transition Energies* (*eV*) *and Intensities*

$D = 4.0$ eV

	R integrals $\beta = -0.40\,p - 1.97$ eV		NM integrals $\beta = -0.51\,p - 1.90$ eV		Expt.
	Energy	f	Energy	f	
Singlets	1.921	0.025 ($y$pol.)	1.918	0.0221 (y)	2.13[a] (0.045) (y)
	3.246	0.003 (x)	3.370	0.005 (x)	3.50[b] (0.08) (x)
	4.134	0.094 (y)	4.221	0.117 (y)	? (y)[c]
	4.794	1.706 (x)	4.616	1.818 (x)	4.52[b] (1.10) (x)
	5.326	0.372 (y)	5.499	0.443 (y)	5.24[b] (0.38) (y)
	5.773	0.049 (x)	5.806	0.022 (x)	
	6.322	0.083 (y)	6.147	0.118 (y)	
	6.400	0.456 (x)	6.439	0.402 (x)	6.42[b] (0.65)
	6.650	0.039 (x)	7.059	0.007 (x)	
	6.691	0.785 (y)	6.791	0.782 (y)	
Triplets	1.539		1.455		
	2.002		1.763		
	2.339		2.166		
	3.430		3.245		

[a] Ref. [*9*]. [b] Ref. [*23*]. [c] Ref. [*32*].

Table 8. *Ionization Potentials*

I.P. (eV)

Molecule	R integrals	NM integrals	Expt.
benzene	—	—	9.245[a]
naphthalene	8.098	8.228	8.12[a]
anthracene	7.524	7.645	7.55[b]
phenanthrene	8.051	8.167	8.03[b]
pyrene	7.512	7.668	7.72[b]
azulene	7.450	7.483	7.72[b]

[a] Ref. [*30*]. [b] Ref. [*29*].

With few exceptions (e.g. the 6.51 eV naphthalene transition) the agreement between the theory and experiment is quite good. As expected for MO calculations, the calculated intensities are often too large. Of particular interest is the good fit obtained for the azulene spectrum, a molecule for which the HUMMEL and RUEDENBERG calculations were inadequate [*11*]. The predicted polarizations of the pyrene transitions are in accord with the results of BECKER, SINGH, and JACKSON [*1*]. The calculated polarization of the 4.91 eV phenanthrene band is in agreement with the results of fluorescence polarization measurements [*33*].

The ionization potentials calculated from the expression

$$I = -\varepsilon_1 - [\varepsilon_1\,(\text{benzene}) + 9.245] + [A_0 - A_0\,(\text{benzene})]\ \text{eV} \tag{8}$$

where ε_1 refers to the energy of the highest occupied orbital, are given in Tab. 8. The last term in (8) corrects for the differences in the core correlation energy between benzene and the molecule in question.

Results, bond lengths

The bond lengths computed from $r = 1.517 - 0.180\,p$ are compared with the experimental values in Tab. 9. The numbering systems are shown in Fig. 2. The difficulties in the X-ray determination of bond lengths are discussed by Cruickshank and Sparks [4] and errors of 0.01 Å are minimal in all but the most favorable circumstances. We would hope that the correct bond length ordering is obtainable from the theory, a situation that has not always obtained [27]. Little dependence of bond length on the class of integrals (R or NM) is observed. The calculated bond lengths obtained here are very close to those computed by Dewar and Gleicher [5]. Several striking discrepancies are found in both studies. The 10 — 11 and 1 — 11 bonds in phenanthrene and the pyrene 4 — 5 bond are in substantial disagreement with experiment.

Table 9. *Bond Lengths* (Å)

Molecule	Bond	R integrals	NM integrals	Expt.
naphthalene	1 – 2	1.381	1.381	1.364[a]
	2 – 3	1.414	1.415	1.415
	1 – 9	1.422	1.422	1.421
	9 – 10	1.415	1.416	1.418
anthracene	1 – 2	1.376	1.376	1.368[a]
	2 – 3	1.421	1.421	1.419
	1 – 17	1.430	1.430	1.436
	9 – 11	1.406	1.406	1.399
	11 – 12	1.424	1.425	1.428
phenanthrene	1 – 2	1.387	1.387	1.381[b]
	2 – 3	1.408	1.408	1.398
	3 – 4	1.387	1.387	1.383
	4 – 12	1.413	1.413	1.405
	11 – 12	1.410	1.411	1.404
	1 – 11	1.414	1.414	1.457
	9 – 10	1.368	1.368	1.372
	12 – 14	1.444	1.443	1.448
	10 – 11	1.438	1.438	1.390
azulene	1 – 2	1.398	1.399	1.391[c]
	1 – 9	1.407	1.406	1.413
	9 – 10	1.465	1.466	1.483
	8 – 9	1.408	1.407	1.383
	7 – 8	1.399	1.399	1.401
	6 – 7	1.401	1.401	1.385
pyrene	1 – 2	1.396	1.396	1.380[d]
	3 – 12	1.406	1.406	1.420
	4 – 12	1.440	1.439	1.442
	4 – 5	1.365	1.367	1.320
	15 – 16	1.431	1.429	1.417
	12 – 16	1.418	1.418	1.417

[a] Ref. [4]. [b] Ref. [28]. [c] Ref. [25]. [d] Ref. [3].

The calculated dipole moment of azulene is 2.8 D, rather larger than previously calculated [2, 23].

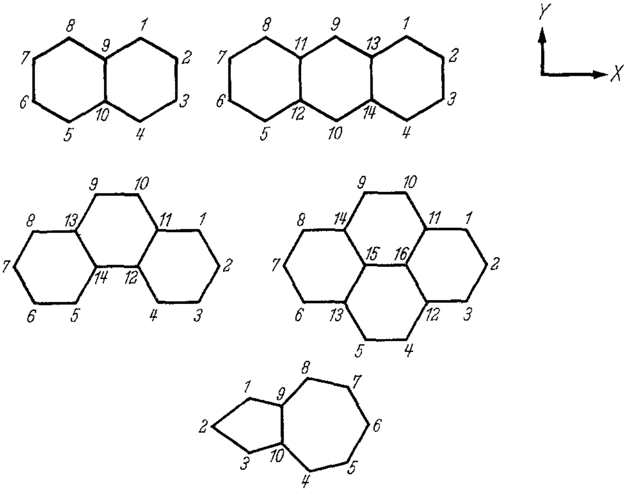

Fig. 2. Topology and numbering system

Conclusions

The expressions for the computation of β from bond order (p) depend upon the two-center repulsion integrals used. These relations are:

R integrals	NM integrals
$\beta = -0.40\,p - 2.17$ eV	$-0.51\,p - 2.04$ benzene
$\beta = -0.40\,p - 1.97$ eV	$-0.51\,p - 1.90$ naphthalene and azulene
$\beta = -0.40\,p - 1.85$ eV	$-0.51\,p - 1.84$ anthracene and phenanthrene
$\beta = -0.40\,p - 1.83$ eV	$-0.51\,p - 1.82$ pyrene.

When β is computed in this manner, neither set of integrals is demonstrably superior to the other (nearest neighbor $\gamma_{\mu\nu}$ integrals are reduced by 1.2 eV in the R procedure).

The parameters evaluated in this work lead to results in good agreement with the experimental bond lengths and transition energies and should provide a sound basis for the extension to heteroatomic systems.

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