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SCF—MO Semi-empirical Methods in 1-2 Benzanthracene and 1-2-5-6 Dibenzanthracene

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With 1 Figure and 9 Tables (Received 4th August 1972)

Abstract

Pople's SCF method has been employed to analyse the electronic spectrum and different indices of reactivity for the 1-2-benzanthracene and 1-2-5-6-dibenzanthracene molecules.

The different semi-empirical approximations given by FLURRY, MATAGA, and PARISER–PARR for calculating the β^c_{pq} and the (pp/qq)integrals are compared. The agreement among the different methods and the carcinogenic activity of both molecules is discussed. The calculated spectral lines are compared with the experimental results given by CLAR.

1. Introduction

We attempt to give an interpretation of the experimental electronic spectra of 1-2 benzanthracene and 1-2-5-6-dibenzanthracene [1]. The theoretic spectra have been calculated according to (SCF–MO–CI) for the system of π electrons with POPLE's method [2]. The integrals were calculated employing the MATAGA–NISHIMOTO [3] and PARISER–PARR [4] semi-empirical approximations separately. Besides, we are studying the effect of considering the resonance integrals even for non-neighbour elements according to the formula suggested by FLURRY–BELL [5].

The electronic spectra calculated with the already mentioned methods are compared. Due to the known carcinogenic activity of these molecules or of some of their derivatives, we have obtained a series of indices of static, dynamic and dislocalization reactivities with each of the above mentioned approximations, to determine whether the results are essentially in agreement or if some important difference may be found.

2. Electronic Spectrum: Method Employed

A. Pople's Method

In the method (SCF), the Hamiltonian of an electron for the fundamental electronic closed shell configuration is

$$\mathbf{h}^{\mathrm{scF}} = \mathbf{h}^{\mathrm{c}} + \sum_{f} (2\mathbf{J}_f - \mathbf{K}_f) \equiv \mathbf{F} \tag{1}$$

where $\mathbf{J}_f$, $\mathbf{h}^{\mathrm{c}}$ and $\mathbf{K}_f$ are well-known operators [6]. The matrix elements between the molecular orbitals are

$$F_{[kr]} = h^{\mathrm{c}}_{[kr]} + \sum_{f}^{\mathrm{occ}} \{2[kr|ff] - [kf|rf]\} \tag{2}$$

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where the sum extends only up to the occupied molecular orbitals corresponding to the fundamental electronic configuration. The expressions $(kr|ff)$ and $(kf|rf)$ are the matrix elements of the $\mathbf{J}_f$ and $\mathbf{K}_f$ operators respectively:

$$[ce|fd] = \int \psi_c^*(i)\,\psi_e(i)\,(e/r_{ij})\,\psi_f(j)\,\psi_d(j)\,\mathrm{d}\tau \tag{3}$$

If the molecular orbitals are considered as a linear combination of atomic φ_p orbitals, the matrix elements of the F operator are obtained between the φ_p, φ_q atomic orbitals, given by the Pople expressions [6]:

$$F_{(pq)} = \beta^c_{pq} - \frac{1}{2} P_{pq}(pp|qq) \tag{4}$$

$$F_{(pp)} = -I_p + \frac{1}{2} P_{pp}(pp|pp) + \sum_{q \neq p} (P_{qq} - Z_q)\,(pp|qq) \tag{5}$$

β^c_{pq} and I_p being the resonance integral and the ionization potential in its corresponding state of valence, respectively. The Ppp and Ppq are the distributions of charge and bond order elements. The terms $(pp|qq)$ and $(pq|pp)$ are the one and two center coulombian integrals for the φ_p and φ_q atomic orbitals.

The eigen-values of the $\mathbf{F}(pq)$ matrix are the ε_i orbital energies corresponding to the ψ_i molecular orbitals.

The configuration interaction matrix elements have been calculated by the expressions given by POPLE [7]. Besides the fundamental configuration, sixteen singlet and triplet simply excited configurations have been chosen. These configurations have been formed employing the four occupied higher levels together with the four unoccupied lower ones.

If the $F_{[kr]}$ matrix elements are expressed in function of the atomic orbitals, we obtain

$$F_{[kr]} = \sum_{p,q} C_{kp}C_{rq}F_{(pq)}, \quad \text{with} \quad \psi_k = \sum_p C_{kp}\varphi_p \tag{6}$$

The singlet and triplet levels referred to the fundamental state are obtained by diagonalizing the total Hamiltonian matrix. Group theory has been applied in the 1-2-5-6-dibenzanthracene; for that reason the representations corresponding to the calculated levels are given (see Table 1).

The dipolar matrix elements necessary to calculate the line strenght have been employed through the ZDO approximation consistent with Pople's method, in the way given by HIGASI [8].

B. Approximations given for the integrals

As the approximations employed are widely known we only give a brief outline so as to show the semi-empirical parameters employed.

a) Mataga Nishimoto Method

The integrals are calculated through

$$(pp|pp) = I_p - A_p \quad \text{with} \quad I_p = 11{\cdot}16\,\text{ev}, \quad A_p = 0{\cdot}03\,\text{ev} \tag{7}$$

I_p is the ionization potential, A_p is the electronic affinity for the carbons in its corresponding state of valence.

$$(pp|qq) = \frac{e^2}{R_{pq} + a_p} \tag{8}$$

R_{pq} being the interatomic distance and $a = 1{\cdot}328$ Å.

The semi-empirical β^c_{pq} parameter are given in the following form,

$$\beta^c_{pq} \begin{cases} = 2{\cdot}388\text{ ev, if } p \text{ and } q \text{ are neighbour elements,} \\ = 0, \qquad \text{if } p \text{ and } q \text{ are not neighbour elements.} \end{cases} \tag{9}$$

b) Pariser–Parr Method

The integrals are given by the formulae,

$$(pp|qq) = (7{\cdot}1975/R_{pq})\,(1 + 2{\cdot}0007/R_{pq})^{-1/2}\,\text{ev}, \quad \text{if} \quad R_{pq} \geqq 2{\cdot}80\text{ Å} \tag{10}$$

$$(pp|qq) = (pp|pp) - 2{\cdot}625R_{pq} + 0{\cdot}1257R^2_{pq}\,\text{ev}, \quad \text{if} \quad R_{pq} < 2{\cdot}80\text{ Å} \tag{11}$$

For β^c_{pq} we have

$$\beta^c_{pq} = -2517{\cdot}5\exp(-5{\cdot}007R_{pq})\,\text{ev} \tag{12}$$

and $(pp|pp) = 10{\cdot}53$ ev.

c) Flurry–Bell Method

The integrals $(pp|qq)$ may be calculated by anyone of the preceding methods. The following expression is employed for β^c_{pq}:

$$\beta^c_{pq} = \frac{(2 - S_{pq})\,S_{pq}}{2 - S^2_{pq}}\,(I_pI_q)^{1/2} \tag{13}$$

where the S_{pq} overlapping integrals have been calculated as

$$S_{pq} = 3{\cdot}503(0{\cdot}5Z_{ef}R_{pq})^{1{\cdot}1526}\exp(-0{\cdot}7946Z_{ef}R_{pq}) \tag{14}$$

Z_{ef} being the effective charge for the carbon atom, $Z_{ef} = 3{\cdot}18$.

The integrals $(kr|ls)$ between molecular orbitals were obtained through the integrals between atomic orbitals here specified by means of the following formula:

$$[kr|ls] = \sum_p \sum_q C_{kp}C_{rp}C_{lq}C_{sq}(pp|qq) \tag{15}$$

The integrals $(pp|qq)$ are considered negligible for distances greater than 6 Å.

3. Indices of Calculated Reactivity

These indices are most frequently employed and were calculated for each one of the mentioned approximations.

a) Static Approximation

1. Charge distributions and bond orders:

$$q_r = \sum_j^{\text{occ}} 2C_{rj}^2, \quad P_{rs} = \sum_j^{\text{occ}} 2C_{rj}C_{sj}$$

2. Autopolarization:

$$\pi_{r,r} = 4\sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{C_{rj}^2 C_{rk}^2}{(\varepsilon_j - \varepsilon_k)} \qquad (16)$$

m number of occupied levels, n total number of elements.

3. Free Radical Valence:

$$F_r = \sqrt{3} - \sum_s P_{rs} \qquad (17)$$

4. Free Ionic Valence:

$$F_r^{\pm} = F_r \pm \sum_s C_{rm}C_{sm} \qquad (18)$$

In the formulae (17) and (18) the sum extends to the s elements adjacent to the considered one.

b) Dynamic Approximation

This approximation consists in assuming that the reaction is produced through an activated complex where two, one, or none electron is localized in the reacting carbon, according as the reaction is electrofilic, free radical, or nucleofilic, respectively. The localized energy of n electrons ($n = 0, 1, 2$) in the r^{th} carbon is

$$L_r = 2\sum_{j=1}^{m} (\eta_{rj} - \varepsilon_j) + (2 - \nu)(\alpha_r - \eta_{rm}) \qquad (19)$$

m number of occupied levels, n total number of elements ($\eta_{r1} < \eta_{r2} < \cdots < \eta_{r,n-1}$), corresponding to the reduced Fock matrices where the line and column j have been omitted. The value $\nu = 0, 1, 2$ corresponds to the electrofilic, free radical, and nucleofilic cases respectively. The α_r are the coulombian integrals of the r^{th} atom already considered. The position corresponding to the least localized energy has the greatest probability to produce the reaction.

c) Dislocalized Approximation

This approximation has been given by FUKUI [8] who has defined two indices, f_r (frontier electrons) and S_r (superdislocalization).

The f_r index is given by

$$f_r = (2 - \nu)\, C_{m,r}^2 + \gamma / C_{m+1,r}^2 \qquad (20)$$

where $\nu = 0, 1, 2$ for the electrofilic, free radical, and nucleofilic reactions respectively. The S_r index, called superdislocalization, is given by

$$S_r = (2 - \nu)\sum_{j=1}^{m} \frac{C_{rj}^2(-\beta)}{(\alpha_r - \varepsilon_j)} + \nu \sum \frac{C_{rj}^2(-\beta)}{(\varepsilon_j - \alpha_r)} \tag{21}$$

where $(-\beta)$ is the resonance integral of the bencene corresponding to the employed approximation.

Another index we have calculated is that of the Nakajima stabilized energies. These are given by the formulae

$$E_r = 2\sum_j C_{rj}^2 \varepsilon_j/(-\beta) \tag{22}$$

$$E_r^+ = E_r + C_{rm}^2 \varepsilon_m/(-\beta) \tag{23}$$

$$E_r^- = E_r - C_{rm}^2 \varepsilon_m/(-\beta) \tag{24}$$

The element with greater probability to be attacked is given by the greatest value for f_r and S_r, while the smallest value corresponds to E_r.

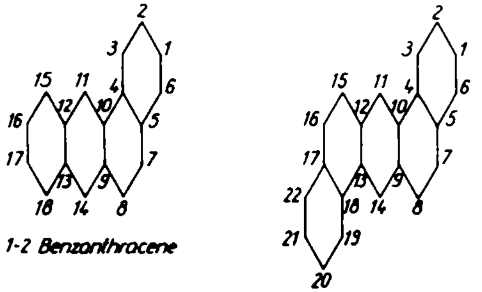
4. Numerical Results and Discussion

The electronic spectrum of both molecules has been studied in the already mentioned approximations. The orbital energies of the 4 higher occupied levels and the 4 unoccupied lower ones for each of the employed methods are shown in Table 1.

Table 1. Orbital energies

1 ··· 2 Benz-anthracene	Beta Pariser	Coulom. Integrals Mataga	Beta Flurry	Coulom. Integrals Mataga	Beta Pariser	Coulom. Integrals Pariser	Beta Flurry	Coulom. Integrals Pariser
$m-3$	−10·357		−10·324		−11·617		−11·460	
$m-2$	−9·890		−9·653		−11·096		−10·770	
$m-1$	−9·133		−8.627		−10·283		−9·724	
m	−8·411		−7·830		−9·499		−8·942	
$m+1$	−2·779		−2·054		−2·411		−1·825	
$m+2$	−2·057		−1·342		−1·628		−1·051	
$m+3$	−1·300		−0·621		−0·815		−0·312	
$m+4$	−0·834		−0·209		−0·293		−0·150	
1-2-5-6 Dibenz-anthracene								
Au $m-3$	−10·085		−9·906		−11·309		−11·026	
Au $m-2$	−9·428		−9·081		−10·622		−10·220	
Bg $m-1$	−8·985		−8·374		−10·110		−9·460	
Bg m	−8·436		−7·851		−9·524		−8·955	
Au $m-1$	−2·754		−1·994		−2·386		−1·761	
Au $m-2$	−2·205		−1·486		−1·801		−1·214	
Bg $m-3$	−1·762		−1·042		−1·289		−0·726	
Bg $m-4$	−1·106		−0·416		−0·602		−0·088	

The values corresponding to a group of singlet levels determined by simply excited configuration interactions are shown in Tables 2 and 3. The 16 chosen configurations are the possible combinations that can be chosen with the 4 higher occupied levels and the 4 unoccupied lower ones.



1-2 Benzanthracene

1-2-5-6 Dibenzanthracene

Fig. 1.

The concordance among the different methods is not very satisfactory (specially for the strength f). Besides, none of the employed methods seems to be chosen as the best approximation of the experimental results obtained, and though the concordance seems to be some what better for the 1-2-5-6-dibenzanthracene, we consider this as accidental.

The reasons why it is difficult to get an accurate approximation of the intensities have been discussed by several authors (9).

Table 2

P–M	*I*	F–M	*I*	P–P	*I*	F–P	*I*	Exp	*I*
3·337	4·945	3·515	5·303	2·723	4·357	3·393	4·609	3·23	2·88
3·475	3·952	3·614	4·243	3·478	5·298	3·654	5·344	3·79	3·77
4·191	4·961	4·430	5·865	3·848	6·064	4·378	6·041		
4·271	6·416	4·535	6·549	4·544	6·127	4·692	6·570	4·31	4·87
4·764	4·819	4·956	6·264	4·745	6·447	5·043	5·285		
4·810	5·836	5·026	4·643	5·167	6·498	5·225	5·999		
5.131	5·401	5·554	4·910	5·583	5·431	5·940	5·049		
5·656	6·610	5·795	6·723	5·876	5·705	6·180	5·240	5·41	4·33
5·789	6·518	6·052	6·120	6·728	6·225	6·361	6·812		
5·799	6·342	6·392	5·045	6·779	4·502	7·007	5·828		
6·226	5·878	6·599	5·862	7·274	6·155	7·218	4·831	6·13	4·25
6·527	4·547	6·918	4·107	7·802	5·367	7·536	5·984		
6·582	5·056	6·999	6·117	8·733	6·269	7·567	5·201		
6·782	4·724	7·309	6·238	8·886	5·981	8·148	4·587	6·76	4·25
7·177	5·000	7·717	4·802	9·648	5·820	8·308	4·075		
7·772	4·822	8·329	4·710	9·715	5·892	8·932	5·374		

I = Intensity, i.e. P–M (Beta Pariser, Integrals Mataga–Nishimoto), the same order than in Table 1. The fundamental configuration is taken as zero Reference. The energies are given in ev. 1-2 Benzanthracene

$I = \log E = \log f + 5$

Table 3

P-M	*I*	F-M	*I*	P-P	*I*	F-P	*I*	Exp	*I*
3·283		3·447		3·348	4·146	3·395	3·958	3·14	3·19
3·462	4·599	3·646	4·437	3·614		3·628	3·357		
4·044		4·312		4·480		4·529	5·491		
4·182	5·401	4·365	5·442	4·489	5·478	4·576		4·13	5·10
4·468		4·691	3·453	4·604		4·684		4·27	4·95
4·774	5·120	4·930	5·139	5·362		5·363	5·187		
5·015		5·297		5·367	5·193	5·456			
5·372		5·666		6·411		6·478		5·39	4·50
5·659		5·875		6·466		6·583			
5·959		6·369		7·131		7·256			
6·251	4·808	6·569		7·279		7·365			
6·306		6·600	4·840	7·325	4·878	7·458	4·884		
6·491		6·843	3·766	7·606		7·715	3·698		
6·668		7·027		7·871	4·704	8·014			
6·923	4·893	7·394	4·901	7·937		8·073	4·688		
7·434	3·827	7·905	4·053	8·489	4·159	8·679	4·336		

1-2-5-6 dibenzanthracene $I = \log E = \log f + 5$

Symmetry forbidden or very weak lines intensities are not given. The values are given in the same way than in Table 2

Table 4. Bond orders

Bond	1-2-Benzanthracene				1-2-5-6-Dibenzanthracene			
	P-M	F-M	P-P	F-P	P-M	F-M	P-P	F-P
1-2	0·623	0·620	0·621	0·619	0·619	0·616	0·617	0·614
2-3	0·704	0·704	0·707	0·707	0·708	0·708	0·712	0·712
3-4	0·592	0·596	0·591	0·594	0·588	0·591	0·585	0·588
4-5	0·578	0·574	0·592	0·589	0·576	0·579	0·590	0·587
5-6	0·583	0·584	0·584	0·584	0·578	0·579	0·578	0·579
6-1	0·708	0·707	0·710	0·710	0·711	0·711	0·714	0·715
4-10	0·406	0·408	0·388	0·388	0·415	0·417	0·399	0·399
10-9	0·518	0·513	0·525	0·521	0·539	0·533	0·551	0·546
9-8	0·440	0·446	0·418	0·423	0·451	0·457	0·431	0·435
8-7	0·825	0·819	0·841	0·837	0·818	0·812	0·834	0·829
7-5	0·445	0·450	0·424	0·427	0·453	0·459	0·434	0·438
10-11	0·658	0·659	0·665	0·666	0·656	0·657	0·667	0·668
11-12	0·579	0·584	0·575	0·579				
12-13	0·522	0·513	0·535	0·529				
13-14	0·582	0·586	0·578	0·581				
14-9	0·649	0·647	0·658	0·656	0·648	0·647	0·659	0·657
12-15	0·517	0·522	0·506	0·509				
15-16	0·757	0·754	0·767	0·765				
16-17	0·567	0·566	0·557	0·556				
17-18	0·757	0·754	0·767	0·765				
18-19	0·517	0·521	0·505	0·509				

In general, it is interesting to know the energies associated to the electronic transitions, since there is a correlation between certain parameters: the 1/2 potential wave and the cm^{-1} frequency of these transitions [10]. Slifkim [11] has given correlations between the ionizing potentials and the electronic affinities. That is to say, these parameters can be calculated through an approximation of the same order as those obtained for the corresponding electronic transitions.

The indices of calculated reactivity show a satisfactory agreement in both molecules for all the employed approximations. For both molecules we give only the corresponding values of the most reactive elements, except the free valencies, and the 1-2-benzanthracene auto-polarizability where all the values have been tabulated. On the other hand, there is a complete agreement among the free valencies and the localized energies, and among the free (*R*) valency and the auto-polarizability.

All the bond orders of both molecules are reported (the ones omitted in the 1-2-5-6-dibenzanthracene come immediately out by symmetry).

Besides, the comparéd elements (1 to 11) in both molecules give only small differences such as we might have expected beforehand.

Table 5

		1	2	3	6	7	8	11	14	15	16	17	18
F	P–M	0·400	0·404	0·434	0·440	0·461	0·466	0·493	0·500	0·457	0·407	0·407	0·458
	F–M	0·403	0·406	0·431	0·440	0·462	0·465	0·488	0·498	0·455	0·411	0·411	0·455
	P–P	0·401	0·404	0·434	0·438	0·467	0·473	0·490	0·494	0·459	0·408	0·408	0·460
	F–P	0·402	0·405	0·429	0·436	0·466	0·471	0·486	0·494	0·457	0·410	0·410	0·457
E	P–M	0·406	0·430	0·434	0·455	0·494	0·503	0·563	0·590	0·493	0·433	0·422	0·502
	F–M	0·412	0·430	0·431	0·451	0·489	0·501	0·562	0·586	0·492	0·435	0·426	0·499
	P–P	0·406	0·430	0·433	0·452	0·491	0·507	0·562	0·587	0·494	0·433	0·422	0·502
	F–P	0·411	0·431	0·429	0·449	0·492	0·506	0·559	0·582	0·492	0·435	0·424	0·499
N	P–M	0·406	0·430	0·434	0·455	0·494	0·503	0·563	0·590	0·493	0·433	0·422	0·502
	F–M	0·411	0·431	0·431	0·450	0·495	0·504	0·559	0·586	0·496	0·437	0·427	0·503
	P–P	0·405	0·430	0·433	0·452	0·491	0·507	0·562	0·587	0·494	0·433	0·422	0·502
	F–P	0·410	0·430	0·429	0·447	0·498	0·507	0·561	0·585	0·496	0·436	0·426	0·503
F	P–M	0·400	0·404	0·436	0·441	0·459	0·462	0·484					
	F–M	0·403	0·406	0·431	0·441	0·460	0·462	0·481					
	P–P	0·400	0·403	0·434	0·439	0·463	0·466	0·479					
	F–P	0·402	0·405	0·430	0·438	0·464	0·466	0·476					
E	P–M	0·402	0·430	0·438	0·461	0·503	0·494	0·548					
	F–M	0·406	0·431	0·432	0·457	0·500	0·495	0·545					
	P–P	0·401	0·429	0·436	0·459	0·505	0·496	0·545					
	F–P	0·404	0·431	0·432	0·456	0·502	0·496	0·540					
N	P–M	0·402	0·430	0·438	0·461	0·503	0·494	0·548					
	F–M	0·406	0·432	0·432	0·455	0·504	0·498	0·549					
	P–P	0·401	0·429	0·436	0·459	0·505	0·496	0·545					
	F–P	0·405	0·431	0·431	0·453	0·505	0·500	0·548					

Free valence indices *E* Electrophilic N Nucleophilic F Free radical

Table 6. Autopolarization × Beta

	1	2	3	6	7	8	11	14	15	16	17	18
P–M	0·2334	0·2347	0·2400	0·2425	0·2453	0·2457	0·2615	0·2615	0·2451	0·2351	0·2348	0·2454
F–M	0·2159	0·2169	0·2227	0·2242	0·2275	0·2278	0·2408	0·2434	0·2272	0·2175	0·2172	0·2275
P–P	0·1963	0·1972	0·2010	0·2028	0·2049	0·2054	0·2145	0·2170	0·2048	0·1975	0·1973	0·2050
F–P	0·1884	0·1891	0·1933	0·1944	0·1970	0·1973	0·2070	0·2088	0·1967	0·1896	0·1894	0·1969
P–M	0·2334	0·2346	0·2402	0·2427	0·2455	0·2450	0·2560					
F–M	0·2159	0·2168	0·2230	0·2244	0·2276	0·2271	0·2390					
P–P	0·1963	0·1971	0·2013	0·2030	0·2050	0·2048	0·2129					
F–P	0·1884	0·1891	0·1935	0·1945	0·1970	0·1968	0·2054					

Table 7. Localization energies (in $-\beta$ units)

		1-2-5-6-Dibenzanthracene					1-2-Benzanthracene				
		11	8	7	6	3	14	11	8	7	18
	E	2·08	2·15	2·14	2·17	2·19	2·06	2·08	2·15	2·14	2·14
P–M	R	3·00	3·06	3·06	3·08	3·10	2·97	2·99	3·05	3·06	3·06
	N	3·95	3·99	3·99	4·01	4·03	3·91	3·93	3·99	3·99	3·99
	E	2·09	2·19	2·18	2·23	2·24	2·06	2·08	2·19	2·18	2·19
F–M	R	3·12	3·22	3·21	3·24	3·25	3·10	3·11	3·21	3·21	3·21
	N	4·15	4·24	4·24	4·26	4·27	4·12	4·14	4·24	4·24	4·24
	E	2·67	2·76	2·76	2·78	2·79	2·64	2·66	2·75	2·75	2·75
P–P	R	3·62	3·70	3·71	3·73	3·75	3·58	3·60	3·68	3·69	3·68
	N	4·50	4·57	4·57	4·59	4·60	4·47	4·49	4·55	4·55	4·55
	E	2·68	2·77	2·77	2·79	2·80	2·65	2·67	2·76	2·76	2·76
F–P	R	3·67	3·76	3·76	3·80	3·81	3·64	3·66	3·76	3·76	3·76
	P	4·58	4·68	4·68	4·69	4·70	4·57	4·58	4·67	4·67	4·67

The steric effects motivated by the hydrogens in certain positions must be considered, because the 11 ··· 14 positions which are very reactive according to the obtained results only got a low activity for the mentioned reasons [12].

These molecules are carcinogenic since they have the following properties:

a) They can form addition compounds, or equivalently, there is a region of high bond order (region K), in the 7 ··· 8 positions of both molecules (the symmetric bond in 1-2-5-6 dibenzanthracene must obviously be considered) [13].

b) A high probability for substitution reactions, or equivalently, high electrophilic free valency [12, 14].

Table 8

		1-2-5-6-Dibenzanthracene				1-2-5-6-Dibenzanthracene			
		f_r				S_r			
		11	7	8	2	11	7	8	3
	E	0·2617	0·1907	0·1746	0·0906	0·5473	0·5197	0·5176	0·4996
P–M	R	0·2617	0·1907	0·1746	0·0906	0·5473	0·5197	0·5175	0·4996
	N	0·2617	0·1907	0·1746	0·0906	0·5473	0·5197	0·5175	0·4996
	E	0·2699	0·1826	0·1726	0·0896	0·5902	0·5367	0·5325	0·5051
F–M	R	0·2689	0·1874	0·1759	0·0885	0·5289	0·4955	0·4927	0·4731
	N	0·2679	0·1922	0·1792	0·0875	0·4677	0·4543	0·4529	0·4412
	E	0·2608	0·1875	0·1744	0·0890	0·4500	0·4298	0·4286	0·4159
P–P	R	0·2608	0·1875	0·1744	0·0890	0·4500	0·4298	0·4286	0·4159
	N	0·2608	0·1875	0·1744	0·0890	0·4500	0·4298	0·4286	0·4159
	E	0·2618	0·1827	0·1732	0·0891	0·4810	0·4443	0·4421	0·4263
F–P	R	0·2667	0·1851	0·1761	0·0871	0·4432	0·4200	0·4186	0·4053
	N	0·2717	0·1876	0·1790	0·0850	0·4053	0·3957	0·3950	0·3844

The four methods predict the same region K in both molecules. These results agree with those previously obtained by other authors employing different approximations [12, 15]. The f_r and S_r indices are completely in agreement with the previous ones, as we can see in the following Tables.

Table 9

		1-2 Benzanthracene					1-2 Benzanthracene				
		f_r					S_r				
		14	11	8	18	7	14	11	8	18	7
	E	0·3792	0·3054	0·1939	0·1936	0·1623	0·5649	0·5537	0·5204	0·5190	0·5190
P–M	R	0·3792	0·3054	0·1939	0·1936	0·1623	0·5649	0·5537	0·5204	0·5190	0·5190
	N	0·3792	0·3054	0·1939	0·1936	0·1623	0·5649	0·5537	0·5204	0·5190	0·5190
	E	0·3747	0·3166	0·1849	0·1906	0·1480	0·6159	0·6027	0·5353	0·5343	0·5346
F–M	R	0·3696	0·3088	0·1869	0·1954	0·1558	0·5465	0·5370	0·4957	0·4941	0·4945
	N	0·3645	0·3009	0·1890	0·2002	0·1636	0·4772	0·4712	0·4561	0·4540	0·4544
	E	0·3766	0·3070	0·1948	0·1890	0·1609	0·4715	0·4602	0·4314	0·4308	0·4312
P–P	R	0·3766	0·3070	0·1948	0·1890	0·1609	0·4715	0·4602	0·4314	0·4308	0·4311
	N	0·3766	0·3070	0·1948	0·1890	0·1609	0·4715	0·4602	0·4314	0·4308	0·4312
	E	0·3703	0·3148	0·1898	0·1859	0·1493	0·4956	0·4882	0·4419	0·4427	0·4428
F–P	R	0·3703	0·3104	0·1891	0·1903	0·1553	0·4548	0·4488	0·4204	0·4186	0·4194
	N	0·3703	0·3061	0·1884	0·1948	0·1612	0·4140	0·4094	0·3989	0·3946	0·3960

On the other hand, the indices of atomic stabilization show a less satisfactory agreement, this is the reason for not reporting them here.

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