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The Electronic Structure of Angular Polyphenes

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SCF calculations of molecular orbitals and electronic transition energies for angular polyphenes of two through nine benzene rings have been made. The calculated sequences of the singlet and triplet energies of the α, β, β', and p bands (Clar's notation) are compared to the limited available experimental data.

PPP-Rechnungen mit begrenzter Konfigurationenwechselwirkung wurden für die Reihe der angular anellierten Polyphene durchgeführt. Die berechneten α-, β-, β'- und p-Banden werden mit den wenigen vorhandenen experimentellen Daten verglichen.

Calculs SCF des orbitales moléculaires et des énergies de transition électronique pour les polyphènes angulaires de deux à neuf cycles benzeniques. Les séries calculées pour les énergies singulet et triplet des bandes α, β, β' et p (notation de Clar) sont comparées aux quelques données expérimentales disponibles.

1. Introduction

Much attention has been given in recent years to the calculation of the electronic structures and spectra of alternate hydrocarbons, in particular the polyphene and polyacene series of hydrocarbon molecules. Pariser [1] calculated the spectra for the first five members of the polyacene series using Hückel molecular orbitals and extensive configuration interaction. Pople [2] used self-consistent field molecular orbitals and quite limited configuration interaction to calculate the spectra of the first three members of the polyacene series. Peacock and Wilkinson [3] employed self-consistent field orbitals and invoked slightly more configuration interaction than Pople to calculate the spectra of the first nine members of the polyacene series.

Little work, however, has been done along these lines on the "angular polyphene" series. The angular polyphenes consist of benzene rings arranged in a zig-zag pattern rather than the linear pattern of the polyacenes. Chrysene and picene are typical members of the angular polyphene series. This paper reports the results of the calculation of the spectra of eight members of the angular polyphene series commencing with naphthalene and terminating with a nine-ringed molecule using self-consistent field molecular orbitals and limited configuration interaction. The carbon atom skeleton of the series that is considered in this paper is illustrated in Fig. 1.

The electronic spectra of naphthalene, phenanthrene, chrysene and picene have been reported by Clar [4] and by Klevens and Platt [5]. The members of the series having more than five rings to our knowledge have not yet been prepared nor have their spectra been measured.

2. Procedure

The nine-ring molecule together with the coordinate system and the numbering of the carbon atoms is shown in Fig. 1. The numbering system has been chosen so that any member of the angular polyphene series can be generated by selecting carbon atoms numbered from 1 to $4n+2$ consecutively where n is the number of benzene rings in the molecule under consideration. Those members of this series that have trivial names are naphthalene, phenanthrene, chrysene and picene with 2, 3, 4 and 5 fused rings respectively.

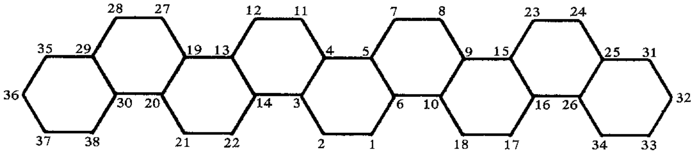

Fig. 1. Numbering system used for angular polyphenes

The calculations were performed on an IBM 7094 computer by means of a π SCF program (written by R. M. H.) [6] that uses a modified Mataga [7, 8] type algorithm for the two-electron integrals:

$$\gamma_{ij} = e^2/(a \cdot \exp(-bR^2) + R),$$

where e is the electronic charge, R is the distance between centers i and j, a and b are constants so chosen as to achieve the best fit to Pariser's [1] $\gamma_{11}, \gamma_{12}, \gamma_{13}$, and γ_{14}; an exponential extrapolation procedure is used to accelerate convergence.

The electronic spectra were calculated using four electronic configurations involving the two highest occupied orbitals and the lowest unoccupied orbitals.

The computer output consisted of SCF MO coefficients, orbital energies, the charge density-bond order matrix, and the singlet and triplet absorption band energies.

The orbitals are classified group theoretically. All even-ringed molecules of the angular polyphene series, except naphthalene, are classified according to the C_{2h} point group. Benzene is not considered in this paper and naphthalene, for the purposes of maintaining consistency of comparison, is considered in terms of C_{2h} symmetry rather than its full symmetry of D_{2h}. It is noted however that the MO coefficients for naphthalene are the same in either case.

3. Results

Since the ground state transforms according to the totally symmetric representation of the point group, only those transitions to excited states having the same representation as one of the dipole operators for a given point group are allowed. The electric dipole operators transform according to either A_u or B_u representations in the C_{2h} point group or A_1, B_1, or B_2 representations in the C_{2v} point group; hence only excited states having these symmetries will give rise to allowed dipole transitions. The molecular orbitals, the orbital energies, and the orbital symmetries are listed in Tables 1 and 2.

The allowed singlet and triplet transition energies are listed in Tables 3 and 4. It is evident that the configurations ${}^{1,3}X_{16\to18} \pm {}^{1,3}X_{17\to20}$ for the eight-ring molecule are of A_g symmetry. Hence the transitions corresponding to the α and β bands of the eight-ring molecule are forbidden. Experimental values measured by Clar [4] of the singlet α, p, and β bands of the first four members of the series considered in this paper are tabulated in Table 3, too.

Bond orders are closely related to bond lengths (the higher the bond order, the shorter is the bond length). It is of interest to examine the behavior of the bond orders of the terminal bonds as the number of rings in the molecule increases. Bond order data for these bonds are listed in Table 5. It is readily seen that the terminal bond orders, $P_{\mu\nu}$ and $P_{\nu\lambda}$, approach constant values of .6083 and .7240 respectively as the molecule becomes larger. The molecular orbital coefficients required to calculate these and all other bond orders may be obtained from the authors.

Table 1. *Even-ringed angular polyphene molecular orbitals and orbital energies classified according to C_{2h} point group*

MO	Naphthalene		Chrysene		Six-ring		Eight-ring	
	E(eV)	Sym	E(eV)	Sym	E(eV)	Sym	E(eV)	Sym
1	-14.727	A_u	-15.214	A_u	-15.360	A_u	-15.422	A_u
2	-12.892	B_g	-14.356	B_g	-14.899	B_g	-15.137	B_g
3	-11.932	B_g	-13.092	A_u	-14.166	A_u	-14.674	A_u
4	-10.809	A_u	-12.633	B_g	-13.216	B_g	-14.050	B_g
5	-9.782	A_u	-11.839	A_u	-12.722	B_g	-13.288	A_u
6	-1.117	B_g	11.528	B_g	-12.476	A_u	-12.733	B_g
7	-0.150	B_g	-10.613	B_g	-11.945	A_u	-12.577	A_u
8	0.973	A_u	-10.151	A_u	-11.779	B_g	-12.504	B_g
9	1.933	A_u	-9.348	A_u	-10.961	A_u	-12.076	B_g
10	3.768	B_g	-1.611	B_g	-10.864	B_g	-11.755	A_u
11			-0.808	B_g	-9.974	B_g	-11.353	A_u
12			-0.346	A_u	-9.880	A_u	-11.134	B_g
13			0.569	A_u	-9.143	A_u	-10.458	B_g
14			0.880	B_g	-1.816	B_g	-10.394	A_u
15			1.674	A_u	-1.079	B_g	-9.744	A_u
16			2.133	B_g	-0.985	A_u	-9.621	B_g
17			3.397	A_u	-0.095	A_u	-9.030	A_u
18			4.255	B_g	0.002	B_g	-1.929	B_g
19					0.820	A_u	-1.338	A_u
20					0.985	B_g	-1.215	B_g
21					1.517	B_g	-0.565	B_g
22					1.763	A_u	-0.501	A_u
23					2.257	A_u	0.175	A_u
24					3.207	B_g	0.394	B_g
25					3.940	A_u	0.796	B_g
26					4.401	B_g	1.117	A_u
27							1.545	A_u
28							1.618	B_g
29							1.814	A_u
30							2.329	B_g
31							3.091	A_u
32							3.715	B_g
33							4.178	A_u
34							4.462	B_g

Table 2. *Odd-ringed angular polyphene molecular orbitals and orbital energies classified according to C_{2v} point group*

MO	Phenantherene		Picene		Seven-ring		Nine-ring	
	E(eV)	Sym	*E*(eV)	Sym	*E*(eV)	Sym	*E*(eV)	Sym
1	−15.052	A_2	−15.305	A_2	−15.396	A_2	−15.440	A_2
2	−13.801	B_1	−14.688	B_1	−15.039	B_1	−15.208	B_1
3	−12.577	A_2	−13.734	B_1	−14.463	A_2	−14.829	A_2
4	−11.874	A_2	−12.687	A_2	−13.697	B_1	−14.312	B_1
5	−11.349	B_1	−12.615	B_1	−12.821	A_2	−12.942	B_1
6	−10.172	B_1	−12.052	B_1	−12.725	A_2	−12.942	B_1
7	− 9.663	A_2	−11.493	A_2	−12.523	B_1	−12.782	A_2
8	− 1.297	B_1	−10.977	A_2	−11.990	A_2	−12.618	B_1
9	− 0.787	A_2	−10.421	B_1	−11.720	B_1	−12.430	A_2
10	0.390	A_2	− 9.849	B_1	−11.336	B_1	−12.975	A_2
11	0.915	B_1	− 9.263	A_2	−10.842	A_2	−11.925	B_1
12	1.618	B_1	− 1.696	B_1	−10.433	A_2	−11.426	A_2
13	2.842	A_2	− 1.110	A_2	− 9.964	B_1	−11.211	B_1
14	4.091	A_2	− 0.538	A_2	− 9.652	B_1	−10.783	B_1
15			0.018	B_1	− 9.087	A_2	−10.438	A_2
16			0.534	B_1	− 1.872	B_1	−10.072	A_2
17			1.093	A_2	− 1.307	A_2	− 9.762	B_1
18			1.656	A_2	− 0.995	A_2	− 9.472	B_1
19			1.728	B_1	− 0.526	B_1	− 8.995	A_2
20			2.775	B_1	− 0.117	B_1	− 1.964	B_1
21			3.729	A_2	0.377	A_2	− 1.487	A_2
22			4.346	A_2	0.761	A_2	− 1.197	A_2
23					1.030	B_1	− 0.887	B_1
24					1.564	A_2	− 0.521	B_1
25					1.766	B_1	− 0.176	A_2
26					1.862	B_1	0.252	A_2
27					2.738	A_2	0.467	B_1
28					3.504	B_1	0.966	A_2
29					4.080	A_2	1.016	B_1
30					4.437	B_1	1.471	B_1
31							1.659	A_2
32							1.823	B_1
33							1.983	A_2
34							2.714	B_1
35							3.353	A_2
36							3.870	B_1
37							4.249	A_2
38							4.481	B_1

Table 3. *Calculated (and experimental) singlet electronic spectra of the angular polyphenes*

Molecule	Absorption band (eV)			
	α	p	β	β'
Naphthalene	4.296 (3.94)	4.611 (4.30)	5.980 (5.60)	6.242
Phenantherene	4.223 (3.59)	4.602 (4.21)	5.458 (4.86)	5.278
Chrysene	4.107 (3.45)	4.225 (3.88)	5.395 (4.65)	5.473
Picene	4.339 (3.29)	4.130 (3.78)	5.134 (4.33)	5.224
Six-ring	4.172	4.057	5.300	5.296
Seven-ring	4.842	4.015	4.856	5.445
Eight-ring	5.511[a]	4.025	4.528[a]	5.630
Nine-ring	5.357	4.034	4.547	5.489

[a] Symmetry forbidden transitions.

Table 4. *Calculated triplet electronic spectra of the angular polyphenes*

Molecules	Absorption band (eV)			
	α	p	β	β'
Naphthalene	4.296	2.825	3.952	4.611
Phenantherene	4.223	3.141	3.801	4.079
Chrysene	4.107	3.009	3.881	4.526
Picene	4.339	3.166	3.641	4.382
Six-ring	4.172	3.227	3.966	4.611
Seven-ring	4.842	3.331	3.594	4.718
Eight-ring	5.511[a]	3.427	3.416[a]	5.004
Nine-ring	5.357	3.521	3.534	4.867

[a] Symmetry forbidden transitions.

Table 5. *Terminal bond orders for molecules of n rings*

n	$P_{\mu\nu}$	Value	$P_{\nu\lambda}$	Value
2	P_{23}	.5856	P_{12}	.7443
3	$P_{12,13}$	.6154	$P_{13,14}$	.7173
4	$P_{12,13}$	.6058	$P_{13,14}$	.7263
5	$P_{20,21}$	.6092	$P_{21,22}$	.7232
6	$P_{20,21}$	.6080	$P_{21,22}$	.7243
7	$P_{28,29}$	.6084	$P_{29,30}$	.7239
8	$P_{28,29}$	.6083	$P_{29,30}$	.7240
9	$P_{36,37}$	.6083	$P_{37,38}$	.7240

4. Discussion

In the spectra of the angular polyphenes observed to date, the bands occur in the order of α, p, β, and β', the order of increasing energy. The intensity of the α band is quite low compared to the intensity of the p band. The p band is quite intense and is characterized by a sharp boundary between it and the α band. Since it is easier to measure accurately the maximum energy of a comparatively intense band, it is expected that the experimental p and β band values of the corresponding transition energies are more accurate than the α band values measured. Hence a comparison of calculated vs. experimental results for the α band may be less meaningful.

From Table 3 good qualitative agreement between the calculated and experimental values for the p band and β band is evident. The calculated and experimental p band values differ by an almost constant amount of .35 eV, the calculated values being too high in each case. The β band calculated values are also too high but they do vary in about the same way as the experimental values. The α band values are still too high compared to the experimental values but, in picene, the calculated energy rises rather than continuing to drop as experiment indicates. The error in both the α and β band cases increases as the molecule becomes larger.

The semi-empirical parameters of the mathematical model have been adjusted to produce the optimum agreement with the experimental benzene spectrum. The spectrum predicted for naphthalene then is in excellent agreement with experiment with about the same magnitude of error for all bands. The agreement with experiment deteriorates as the molecule becomes larger in the sense that the α and β band discrepancy tends to increase resulting in the calculated α band energy becoming greater than the p band energy for picene in defiance of experiment. Also a degeneracy between the α and β bands is predicted for the seven-ring molecule and the α band energy is greater than the β band energy for the nine-ring molecule. Neither prediction is expected on the basis of the behavior of the experimental spectra for the smaller sized members of the series.

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