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SEMIEMPIRICAL SCF MO CI CALCULATIONS ON THE ELECTRONIC SPECTRA OF AZAPHENANTHRENES WITH A VARIABLE β APPROXIMATION

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Abstract—The semiempirical SCF ASMO CI method with a variable β approximation has been applied to azaphenanthrenes. The UV spectra and other electronic properties of these molecules have been determined. In addition, the bond lengths were computed.

INTRODUCTION

THE Pariser–Parr–Pople semiempirical SCF ASMO method[1,2] has been very successfully applied to the calculation of electronic transitions in conjugated molecules. In particular, there has been a number of studies of nitrogen heterocyclic compounds.[3–11] Nishimoto and Forster[12,13] made a variable β modification to this method, in which each β and bond length for neighbouring atoms was computed by means of a linear relationship from the corresponding bond order at each iteration. We have extended the original relations established by Nishimoto and Forster for benzene, naphthalene and anthracene derivatives to phenanthrene and its aza derivatives.

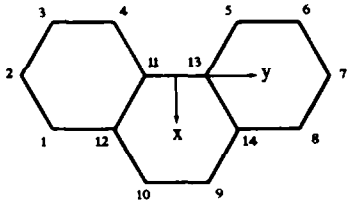

FIG. 1 Coordinate axes and numbering system.

METHOD AND PARAMETERS

The SCF formalism of the PPP method was used. It is known[12,13] that the variable β approximation is insensitive to the assumed geometry. All molecules were therefore assigned regular polygonal structures with equal bond lengths (1·4 Å) and all angles equal to 120°. The two-center repulsion integrals $\gamma_{\mu\nu}$ between non-neighbouring atoms were computed from this conventional geometry. The two-center core integrals $\beta_{\mu\nu}$, the bond lengths $r_{\mu\nu}$ and the two-center electronic repulsion integrals $\gamma_{\mu\nu}$ between neighbouring atoms were adjusted at each iteration according to the following equations which apply to phenanthrene and its aza derivatives:

$$\beta_{\mu\nu} = -0{\cdot}51\, p_{\mu\nu} - 1{\cdot}88$$
$$r_{\mu\nu} = -0{\cdot}18\, p_{\mu\nu} + 1{\cdot}517 \qquad \text{for all C—C bonds}$$

$$\beta_{\mu\nu} = -0{\cdot}53\, p_{\mu\nu} - 2{\cdot}06$$
$$r_{\mu\nu} = -0{\cdot}18\, p_{\mu\nu} + 1{\cdot}451 \qquad \text{for the C—N bonds}$$

and the classical Nishimoto–Mataga[14] approximation:

$$\gamma_{\mu\nu} = \frac{14{\cdot}397}{a_{\mu\nu} + r_{\mu\nu}}$$

The one-center repulsion integrals were estimated from the valence state ionization energies I_μ and electron affinities A_μ:

$$\gamma_{\mu\mu} = I_\mu - A_\mu$$

The values of these parameters given in Table 1 are the most usual ones.

TABLE 1. PARAMETER SUMMARY

Atoms	I_μ	γ_μ
C	11·16	11·13
N	14·12	12·34

The configuration interaction included the four highest occupied orbitals and the four lowest empty ones.

RESULTS

The calculated singlet transition energies and oscillator strengths are summarized in Table 2 together with the experimental data which were taken from a recent atlas of UV absorption spectra.[15] The experimental values of the oscillator strength f were estimated from the absorption curves by means of the relation[16]

$$f = 4{\cdot}32 \cdot 10^{-9} \cdot \varepsilon_{max} \cdot \Delta\bar{\nu}$$

where $\Delta\bar{\nu}$ is the band width (in cm^{-1}) at half-maximum extinction. The experimental polarization directions are taken from Ref. 18 for phenanthrene and from Ref. 9 for the azaphenanthrenes.

TABLE 2. TRANSITION ENERGIES (eV) AND INTENSITIES (f)

Molecule	Calc. ΔE	Calc. f	Expt. ΔE	Expt. f
Phenanthrene	3·730	0·0	3·76	0·005 (x)
	4·242	0·33 (y)	4·24	0·06 (y)
	4·696	0·0		
	4·973	1·55 (y)	4·95	0·87 (y)
	5·089	0·61 (x)	5·08	0·67
	5·367	0·0		
	5·569	0·35 (x)	5·63	0·15
	5·938	0·0		
	6·099	0·15 (y)		
	6·159	0·30 (y)		
	6·232	0·0		
1-Azaphenanthrene	3·735	0·06 (x, y)	3·77	0·05
	4·244	0·27 (y, x)	4·14 (s)	
	4·698	0·24 (y, x)	4·66	0·33
	5·024	0·92 (x, y)		

TABLE 2—*continued*

Molecule	Calc. ΔE	Calc. f	Expt. ΔE	Expt. f
	5·070	0·74 (x, y)	4·97	0·27
	5·482	0·25 (x, y)	5·32	0·6
	5·630	0·32 (y, x)	5·74	0·27
	6·023	0·08 (x, y)	5·95	0·4
	6·122	0·21 (y, x)		
	6·257	0·19 (x, y)		
	6·342	0·06 (x, y)		
2-Azaphenanthrene	3·777	0·03 (x, y)	3·74	0·03
	4·236	0·36 (y, x)	4·25	0·17
	4·751	0·12 (y, x)		
	5·013	1·33 (y, x)	5·00	0·65
	5·165	0·49 (x, y)	5·12	0·54
	5·346	0·03 (x, y)		
	5·572	0·29 (x, y)		
	5·843	0·11 (x, y)		
	6·082	0·17 (y, x)	5·94	0·8
	6·220	0·04 (x, y)		
	6·333	0·26 (x, y)		
5-Azaphenanthrene	3·731	0·07 (y, x)	3·77	0·05
	4·238	0·26 (x, y)	4·20	0·05
	4·628	0·37 (x, y)	4·69	0·2
	5·039	0·53 (x, y)	5·03	0·32
	5·130	1·07 (y, x)	5·17	0·43
	5·456	0·37 (x, y)	5·33	0·8
	5·593	0·23 (y, x)	5·72	0·27
	5·986	0·04 (x, y)	5·99	0·56
	6·123	0·18 (y, x)		
	6·186	0·19 (x, y)		
	6·452	0·05 (x, y)		
6-Azaphenanthrene	3·765	0·03 (x, y)	3·78	0·02
	4·244	0·28 (y, x)	4·20	0·14
	4·753	0·13 (y, x)		
	4·973	1·35 (y, x)	4·96	0·56
	5·110	0·57 (x, y)	5·14	0·26
	5·430	0·08 (x, y)		
	5·621	0·28 (x, y)	5·66	0·27
	5·848	0·04 (x, y)		
	6·103	0·17 (y, x)		
	6·220	0·11 (x, y)		
	6·302	0·18 (y, x)		
9-Azaphenanthrene	3·823	0·0	3·76	0·02
	4·229	0·31 (y, x)	4·29	0·08
	4·592	0·64 (y, x)	4·60	0·13
	4·979	0·35 (x, y)	5·06	0·8
	5·386	1·14 (y, x)		
	5·550	0·6 (x, y)	5·69	0·18
	5·729	0·03 (x, y)	5·78	0·2
	6·028	0·0		

TABLE 2—*continued*

Molecule	Calc. ΔE	Calc. f	Expt. ΔE	Expt. f
	6·207	0·01 (x, y)		
	6·397	0·23 (x, y)		
	6·406	0·16 (x, y)		
1,5-Azaphenanthrene	3·812	0·01 (x, y)	3·86	0·01
	4·237	0·34 (y, x)		
	4·622	0·56 (y, x)	4·66	0·48
	4·987	0·39 (x, y)		
	5·302	1·02 (y, x)	5·34	0·74
	5·624	0·59 (x, y)		
	5·711	0·19 (x, y)		
	6·023	0·0		
	6·240	0·02 (y, x)		
	6·286	0·3 (y, x)		
	6·418	0·1 (y, x)		
1,6-Azaphenanthrene	3·760	0·18 (y, x)	3·81	0·2 (x, y)
	4·333	0·14 (x, y)		
	4·778	0·12 (x, y)	4·68	0·2 (x, y)
	5·057	1·39 (x, y)		
	5·139	0·47 (y, x)	5·21	0·6 (x, y)
	5·419	0·09 (x, y)		
	5·683	0·27 (x, y)		
	5·978	0·09 (y, x)	5·86	0·56
	6·139	0·06 (x, y)		
	6·189	0·42 (y, x)		
	6·409	0·02 (x, y)		
1,7-Azaphenanthrene	3·816	0·09 (x, y)	3·78	~0·08 (x, y)
	4·240	0·28 (y, x)	4·26	~0·1 (x, y)
	4·835	0·31 (y, x)	4·72	~0·2 (y, x)
	5·029	0·89 (y, x)		
	5·157	0·51 (x, y)		
	5·496	0·35 (x, y)	5·40	~0·3
	5·625	0·21 (y, x)	5·77	~0·1
	5·885	0·05 (x, y)		
	6·136	0·21 (y, x)		
	6·253	0·26 (x, y)		
	6·401	0·13 (y, x)		
1,8-Azaphenanthrene	3·784	0·04 (x)	3·78	0·01
	4·238	0·33 (y)		
	4·646	0·56 (y)	4·59	0·35
	5·010	0·42 (x)	4·98	0·08
	5·259	0·99 (y)	5·32	0·56
	5·640	0·0		
	5·727	0·63 (x)	5·79	0·24
	6·020	0·06 (y)	6·08	0·57
	6·295	0·07 (y)		
	6·355	0·0		
	6·468	0·31 (y)		
2,5-Azaphenanthrene	3·758	0·09 (y, x)	3·76	~0·08
	4·227	0·32 (x, y)	4·28	~0·1

TABLE 2—*continued*

Molecule	Calc. ΔE	Calc. f	Expt. ΔE	Expt. f
	4·756	0·41 (y, x)	4·75	~0·3
	5·095	0·53 (y, x)		
	5·198	0·75 (x, y)	5·38	
	5·495	0·53 (x, y)		
	5·594	0·2 (x, y)	5·77	
	5·836	0·05 (x, y)		
	6·179	0·21 (y, x)		
	6·296	0·09 (y, x)		
2,6-Azaphenanthrene	3·832	0·04 (x, y)	3·84	~0·03
	4·227	0·31 (y, x)	4·21	~0·1
	4·779	0·36 (x, y)	4·78	~0·2
	4·986	1·06 (y, x)	5·13	~0·4
	5·204	0·38 (y, x)		
	5·424	0·16 (x, y)		
	5·648	0·31 (x, y)		
	5·951	0·08 (x, y)		
	6·036	0·08 (y, x)		
	6·215	0·07 (y, x)		
	6·320	0·35 (x, y)		
2,7-Azaphenanthrene	3·789	0·12 (x)	3·69	0·03 (x)
	4·233	0·43 (y)	4·28	0·9 (y)
	4·803	0·07 (y)	4·78	0·09 (y)
	5·179	1·24 (y)	5·16	0·43 (y)
	5·243	0·33 (x)	5·28	0·6 (y)
	5·318	0·0		
	5·604	0·33 (x)		
	5·670	0·13 (y)	5·77	0·42
	6·119	0·22 (x)		
	6·169	0·18 (y)		
3,5-Azaphenanthrene	3·765	0·19 (y, x)	3·81	~0·2
	4·301	0·15 (x, y)	4·40	~0·1
	4·759	0·18 (x, y)	4·84	~0·2
	5·101	0·73 (x, y)		
	5·132	1·16 (y, x)	5·21	~0·5
	5·410	0·16 (x, y)		
	5·668	0·22 (y, x)	5·83	~0·5
	5·987	0·12 (y, x)		
	6·124	0·09 (x, y)		
	6·266	0·23 (y, x)		
3,6-Azaphenanthrene	3·789	0·03 (x)	3·79	~0·02 (x)
	4·299	0·26 (y)	4·26	~0·1 (y)
	4·762	0·36 (y)		
	5·006	1·22 (y)	5·08	~0·6 (y)
	5·137	0·56 (x)		
	5·478	0·0	5·58	~0·1
	5·701	0·04 (y)		
	5·704	0·23 (x)	5·85	~0·5
	6·177	0·02 (x)		
	6·270	0·23 (y)		

TABLE 3. ATOMIC π CHARGE DENSITIES

Molecule	Atoms													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1-Azaph.	1·233	0·879	1·018	0·952	1·003	0·998	1·000	0·997	0·998	0·999	1·013	0·918	0·999	1·003
2-Azaph.	0·879	1·227	0·909	1·018	0·995	0·999	0·995	1·000	1·002	0·995	0·966	1·016	1·005	0·994
5-Azaph.	1·003	0·996	1·001	0·986	1·233	0·880	1·017	0·952	1·001	1·002	1·004	0·996	0·916	1·013
6-Azaph.	0·997	0·999	0·995	1·001	0·880	1·228	0·909	1·019	1·004	0·986	0·996	1·003	1·016	0·966
9-Azaph.	0·988	1·002	0·986	1·001	1·001	1·005	0·995	1·000	1·229	0·849	0·971	1·017	1·011	0·946
1,5-Azaph.	1·236	0·875	1·019	0·938	1·235	0·878	1·018	0·950	0·989	1·001	1·017	0·914	0·915	1·016
1,6-Azaph.	1·231	0·878	1·013	0·954	0·883	1·226	0·909	1·016	0·992	0·985	1·009	0·921	1·015	0·968
1,7-Azaph.	1·234	0·874	1·017	0·948	1·021	0·906	1·228	0·876	0·983	1·001	1·017	0·912	0·965	1·018
1,8-Azaph.	1·231	0·879	1·015	0·955	0·955	1·105	0·879	1·231	0·987	0·987	1·012	0·921	1·012	0·921
2,5-Azaph.	0·882	1·224	0·910	1·004	1·229	0·879	1·012	0·952	1·003	0·997	0·970	1·011	0·921	1·007
2,6-Azaph.	0·876	1·227	0·904	1·019	0·875	1·228	0·904	1·019	1·006	0·981	0·962	1·019	1·021	0·960
2,7-Azaph	0·879	1·223	0·908	1·014	1·014	0·908	1·223	0·879	0·997	0·997	0·970	1·010	0·970	1·010
3,5-Azaph.	1·021	0·905	1·230	0·866	1·235	0·875	1·017	0·950	0·987	1·006	1·021	0·961	0·913	1·016
3,6-Azaph.	1·016	0·908	1·224	0·881	0·881	1·224	0·908	1·016	0·990	0·990	1·012	0·969	1·012	0·969

TABLE 4. π DIPOLE MOMENTS

Molecule	π Dipole moment (Debyes)
1-Azaphenanthrene	1·08
2-Azaphenanthrene	1·23
5-Azaphenanthrene	0·89
6-Azaphenanthrene	1·27
9-Azaphenanthrene	1·41
1,5-Azaphenanthrene	1·05
1,6-Azaphenanthrene	0·39
1,7-Azaphenanthrene	0·93
1,8-Azaphenanthrene	1·81
2,5-Azaphenanthrene	1·95
2,6-Azaphenanthrene	1·08
2,7-Azaphenanthrene	0·45
3,5-Azaphenanthrene	2·13
3,6-Azaphenanthrene	1·65

TABLE 5. BOND LENGTHS

Bond	Phenanthrene	Azaphenanthrenes													
		1-	2-	5-	6-	9-	1,5-	1,6-	1,7-	1,8-	2,5-	2,6-	2,7-	3,5-	3,6-
1–2	1·386	1·324	1·324	1·386	1·386	1·386	1·324	1·324	1·324	1·324	1·324	1·324	1·324	1·388	1·388
2–3	1·409	1·409	1·344	1·409	1·409	1·409	1·409	1·409	1·409	1·409	1·344	1·344	1·344	1·344	1·344
3–4	1·387	1·387	1·388	1·387	1·387	1·386	1·387	1·387	1·387	1·387	1·389	1·388	1·388	1·324	1·324
5–6		1·387	1·387	1·324	1·324	1·386	1·324	1·324	1·388		1·324	1·324		1·324	
6–7		1·409	1·409	1·409	1·344	1·409	1·409	1·344	1·344		1·409	1·344		1·409	
7–8		1·386	1·386	1·386	1·388	1·386	1·386	1·388	1·324		1·386	1·388		1·386	
9–10	1·368	1·367	1·368	1·367	1·367	1·306	1·367	1·367	1·367	1·367	1·367	1·367	1·368	1·367	1·367
1–12	1·415	1·350	1·415	1·414	1·415	1·415	1·350	1·350	1·350	1·350	1·415	1·415	1·414	1·414	1·414
10–12	1·438	1·439	1·438	1·438	1·438	1·437	1·439	1·439	1·439	1·439	1·438	1·438	1·438	1·438	1·438
4–11	1·413	1·412	1·412	1·413	1·413	1·414	1·413	1·413	1·413	1·413	1·412	1·412	1·412	1·413	1·413
11–12	1·410	1·411	1·411	1·410	1·410	1·411	1·411	1·411	1·411	1·411	1·410	1·411	1·410	1·410	1·410
5–13		1·413	1·413	1·348	1·413	1·414	1·348	1·413	1·412		1·348	1·413		1·349	
11–13	1·443	1·443	1·443	1·444	1·443	1·442	1·444	1·443	1·443	1·443	1·445	1·443	1·444	1·443	1·443
13–14		1·410	1·410	1·411	1·410	1·411	1·411	1·410	1·411		1·411	1·411		1·411	
8–14		1·414	1·415	1·414	1·414	1·416	1·414	1·414	1·415		1·414	1·414		1·414	
9–14		1·438	1·438	1·438	1·438	1·371	1·438	1·438	1·438		1·438	1·438		1·438	

The atomic π charge densities are given in Table 3 and the π dipole moments in Table 4.

The computed bond lengths are listed in Table 5. Accurate experimental values are lacking for the molecules studied. Any bond order may of course be deduced from the corresponding bond length by means of the relations given above.

It may be concluded that the general features of the spectra of phenanthrene and its aza derivatives are well interpreted by the variable β modification of the PPP method.

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