Tetrahedron. Vol 33, pp. 169 to 181. Pergamon Press 1977. Pnnted in Great Bntain

THEORETICAL STUDIES OF SOME NONBENZENOID HYDROCARBONS—IV

PLEIADIENE AND RELATED COMPOUNDS

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(*Received in USA* 30 *September* 1975; *Received in UK for publication* 8 *June* 1976)

Abstract—Pleiadiene and other similar compounds have been studied by the semi-empirical SCFMO method of Pariser, Parr and Pople using the core resonance integral value developed by Lo and Whitehead, Dewar *et al.* and Yamaguchi *et al.* It has been found that $\pi^*\leftarrow\pi$ transitions predicted by the methods of Lo and Whitehead and Dewar *et al.* suitable for the prediction of ground state properties are also in good agreement with experimental results where available and comparable to those predicted by the method of Yamaguchi *et al.* developed for the prediction of spectral transitions. The resonance stabilization of the molecules 3, 4, 5, 7, 8 and 9 have also been studied. It is found that ethylinic linkage across the naphthalene moity in pleiadiene increases the resonance energy of the final compound, in contrast to our previous observation, i.e. ethylinic linkage across the naphthalene moiety reduces the resonance energy of the final compound.

INTRODUCTION

Pleiadiene and its derivatives (Fig. 1) play an interesting role to synthetic organic chemists and quantum chemists. As early as 1952 Pullman *et al.*[1] using the HMO theory predicted that some of them would be stable compounds. The prediction became true when Boekelheide and Vick[2] synthesized pleiadiene (**1**) and acepleiadylene. Both of them are stable aromatic compounds. However, pleiadiene is less aromatic than acepleiadylene[2] in agreement with the theoretical results obtained by DasGupta and DasGupta.[3] In 1963 Cava and Schlessinger[4] attempted to synthesize molecules 2 and 4 and observed that these two compounds are less stable than pleiadiene and acepleiadylene. They could not isolate the compound 2 which dimerises readily. But compound 4 was isolated in solution. It also dimerises within a short time. Although benzopleiadiene (**2**) was not synthesized, still Mullen *et al.*[5] have synthesized the molecule 3 in which the benzene ring has been fused angularly to pleiadiene moiety instead of linearly as in benzopleiadiene. It is a question why molecule 3 is more stable than the molecule 2. In this paper we would like to study the stability of the molecules 3, 4 and 5 theoretically using the methods of Lo and Whitehead,[6] and Dewar *et al.*[7] along with some heteroanalogoues of 3 (molecules 7, 8, 9). However, the stability of the molecules 1, 2 and 6 have already been studied theoretically by DasGupta and DasGupta.[3,8] Although these methods[6,7] have been developed for the study of ground state properties of conjugated systems, still we[9] have seen that the spectral transitions for many nonbenzenoid hydrocarbons can also be predicted with reasonably good accuracy using these methods. Hence we would also like to report the calculated spectral transitions, correlate them with experimental ones where available, and compare the results with those calculated by the method of Yamaguchi *et al.*[10] developed for the prediction of spectral transitions.

Method and parameter

The method used here is the self-consistent molecular orbitals obtained by a linear combination of atomic orbitals–molecular orbitals (LCAO—MO) similar to that developed by Pariser and Parr[11] and Pople[12] within the zero differential overlap approximation. The method is well-known and has been described elsewhere.[13] Hence we would like to describe the salient features of the method and the mode of evaluation of certain integrals.

The resonance integrals $\beta_{\mu\nu}$ were calculated by four methods:

(1) In the first method designated as SCF(a), $\beta_{\mu\nu}$ was estimated using the method of Lo and Whithehead.[6]

(2) In the second one, SCF(b) method, $\beta_{\mu\nu}$ has been given a value of -1.7901 eV propqsed by Chung and Dewar[7a] and modified by Birss and DasGupta.[9a] In the SCF(a) and SCF(b) methods the integrals $\beta_{\mu\nu}$ were not varied during the iteration.

(3) The third and fourth methods designated as SCF(d) and SCF(e) were those due to Yamaguchi *et al.*[10] and Dewar and Harget[7b,c,d] respectively. In these methods the resonance integrals, $\beta_{\mu\nu}$, the bond length $r_{\mu\nu}$ and the two-centre, two-electron repulsion integrals $\gamma_{\mu\nu}$ for bonded atoms were adjusted according to the relations given below.

The relations used in the Dewar and Harget method[7b,c,d] (SCF(c)) are:

$$r_{\mu\nu}(\text{Å}) = A - Bp_{\mu\nu}$$

and

$$\beta_{\mu\nu} = K_{\mu\nu}S_{\mu\nu}$$

where $p_{\mu\nu}$ is the π-bond order and $S_{\mu\nu}$ is the overlap integral between two π_{2p} orbitals. The values of A, B and K are shown in Table 1.

In the SCF(d) method the relations used are

$$r_{\mu\nu}(\text{Å}) = 1.520 - 0.186\, p_{\mu\nu}$$

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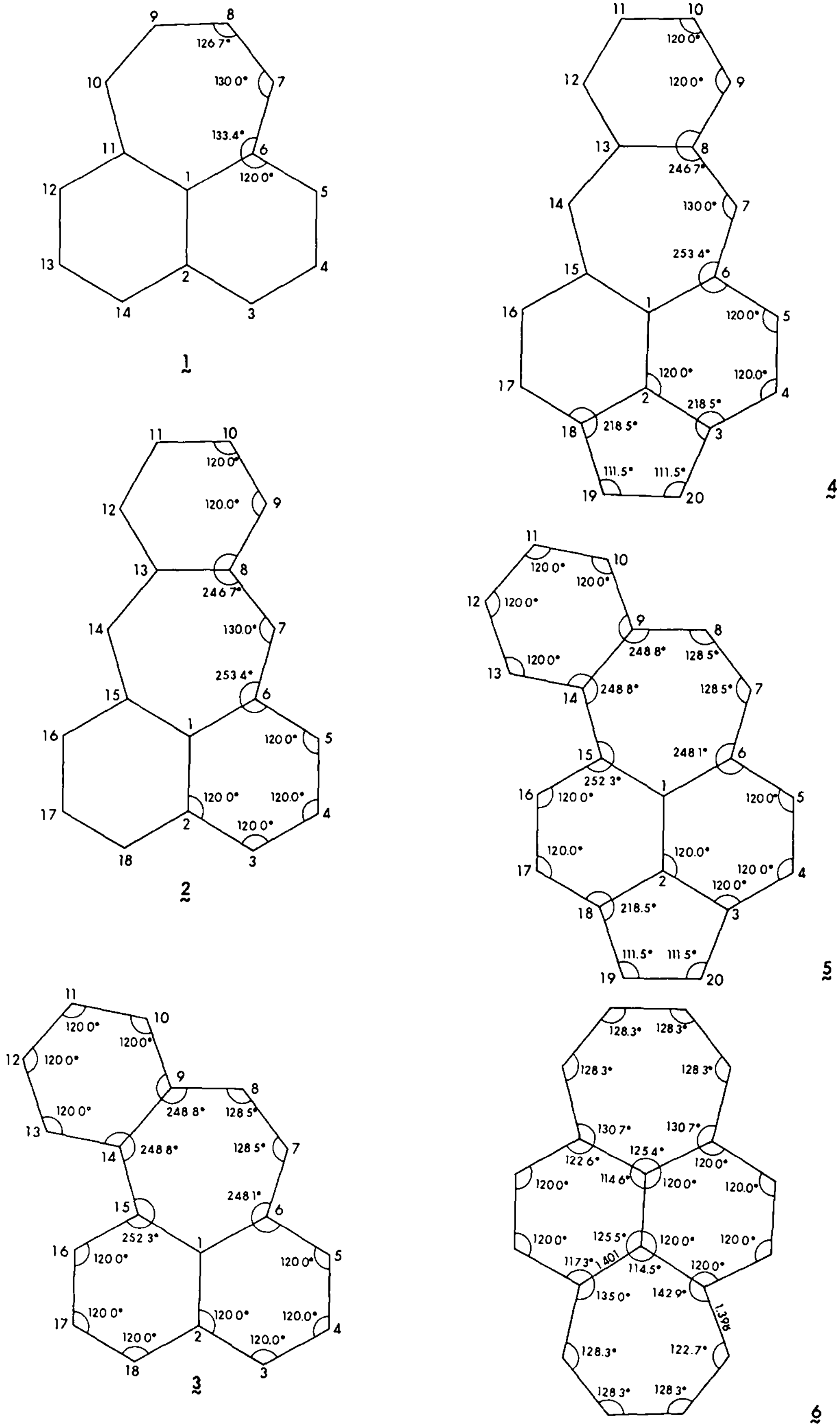
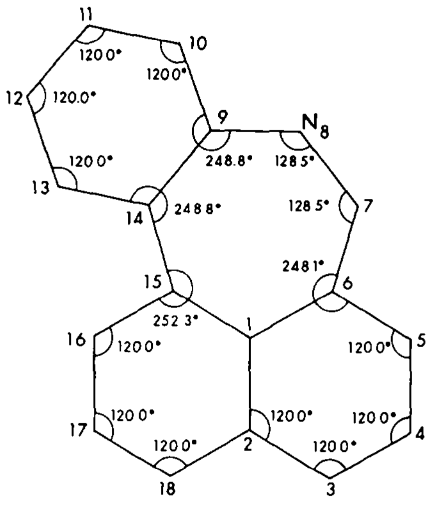

1
126.7°
130.0°
133.4°
120.0°
2
120.0°
246.7°
130.0°
253.4°
218.5°
111.5°
3
248.8°
128.5°
248.1°
252.3°
4
5
6
128.3°
130.7°
125.4°
122.6°
114.6°
125.5°
117.3°
1.401
114.5°
135.0°
142.9°
1.398
122.7°

Fig. 1.



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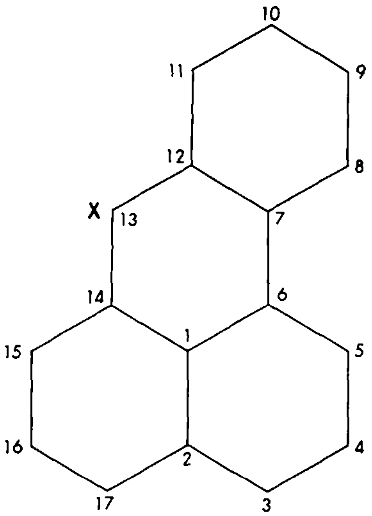

8 (X=O)
9 (X=S)

Fig. 1. Molecule 1: Pleiadiene; 2: Benzopleiadiene; 3: Benzo[4,5]cyclohepta[1,2,3-de]naphthalene; 4: Benzo[6,7]acepleiadylene; 5: Benzo[5,6]acepleiadylene; 6: dipleiadiene; 7: 8-Azabenzo[4,5]cyclohepta[1,2,3-de]-nathahalene; 8: Benzo[1,9]xanthene; 9: Benzo[1,9]thioxanthene.

Table 1.

Bond	K	A/Å	B/Å
C–C	-6.927	1.512	0.174
C–N	-6.9612	1.448	0.178
C–O	-9.2246	1.395	0.165
C–S	-10.7665*	1.802	0.229

* N.K. DasGupta and F.W. Birss (submitted for publication).

Table 2.

Atom or ion	I_μ (eV)	$\gamma_{\mu\mu}$ (eV)	Z_{eff}
C	11.16	11.134	3.18
N	14.12	12.341	3.55
O^+	33.901	18.600	5.43
S^+	23.74	12.095	6.957*

* N.K. DasGupta and F.W. Birss (submitted for publication)

and

$$\beta_{\mu\nu} = \beta_0 \exp\left[a(r_0 - r_{\mu\nu})\right]$$

where r_0 is equal to 1.397 (Å), $a = 1.7$ Å^{-1} and β_0 is the resonance integral for benzene. The value of β_0 decreases as the number of rings increases.[14] Using a value of −2.15 eV for β_0 we[9b,c,d] found that satisfactory prediction of $\pi^* \leftarrow \pi$ transitions for some nonbenzenoid hydrocarbons could be made.

For non-bonded atoms $\beta_{\mu\nu}$ was set equal to zero. The bond order-bond length relation for the calculation of bond length in the SCF(a) and SCF(b) method is due to Dewar and Gleicher.[15]

$$r_{\mu\nu} = 1.504 - 0.166\, p_{\mu\nu}$$

The one centre, two-electron repulsion integrals $\gamma_{\mu\nu}$ were determined from the corresponding valence state ionization potentials (I_μ) and electron affinities listed by Hinze and Jaffe.[16] Table 2 contains the values $\gamma_{\mu\mu}$ and I_μ together with the assumed values for the effective nuclear charge.

Except for the SCF(d) method the two-centre, two-electron repulsion integrals $\gamma_{\mu\nu}$ were evaluated using the method of Ohno[17] and for the SCF(d) method the formula of Mataga and Nishimoto[18] was used. In the SCF(a) and SCF(b) methods $\gamma_{\mu\nu}$ were not varied. In the SCF(c) and SCF(d) methods $\gamma_{\mu\nu}$ were also not varied for nonbonded atoms.

For the calculation of $\gamma_{\mu\nu}$ we assumed a planar geometry of the molecules with all bonds equal to 1.40 Å as shown in Fig. 1. The bond order and charge density (q_μ) are obtained from the eigenvector components $C_{\mu i}$ and $p_{\mu\nu}$ and q_μ are defined as:

$$p_{\mu\nu} = 2\sum_{i=1}^{n} C_{\mu i}C_{\nu i}$$

and

$$q_\nu = 2\sum_{i=1}^{n} C_{\mu i}^2.$$

For the first SCF iteration Hückel MO coefficients were used as the starting vectors. The iterative procedure continued until the self-consistency was achieved within the desired degree of accuracy.

For the calculation of these molecules we used a program developed in the laboratory of Dr. F. W. Birss and modified by us according to our need. Computer time is almost negligible.

RESULTS AND DISCUSSION

Reactivity. Figures 2 and 3 show respectively the variation of charge density with different centres and bond order with different bonds. All the methods agree in predicting the centre of lowest charge density for the hydrocarbons and they also agree in predicting the centre of highest charge density for the molecules **1**, **2** and **5**. Though the center C_1 has been predicted as the centre of lowest charge density for the molecules **1**, **2**, **3** and **6**, still it it is not suitable for nucleophilic attack because of shielding effects. Similarly the centres C_6, C_2 and C_3 being the centres of highest charge density for the molecules **2**, **3** and **6** respectively are also not suitable for the electrophilic attack. Table 3 contains the centre of highest

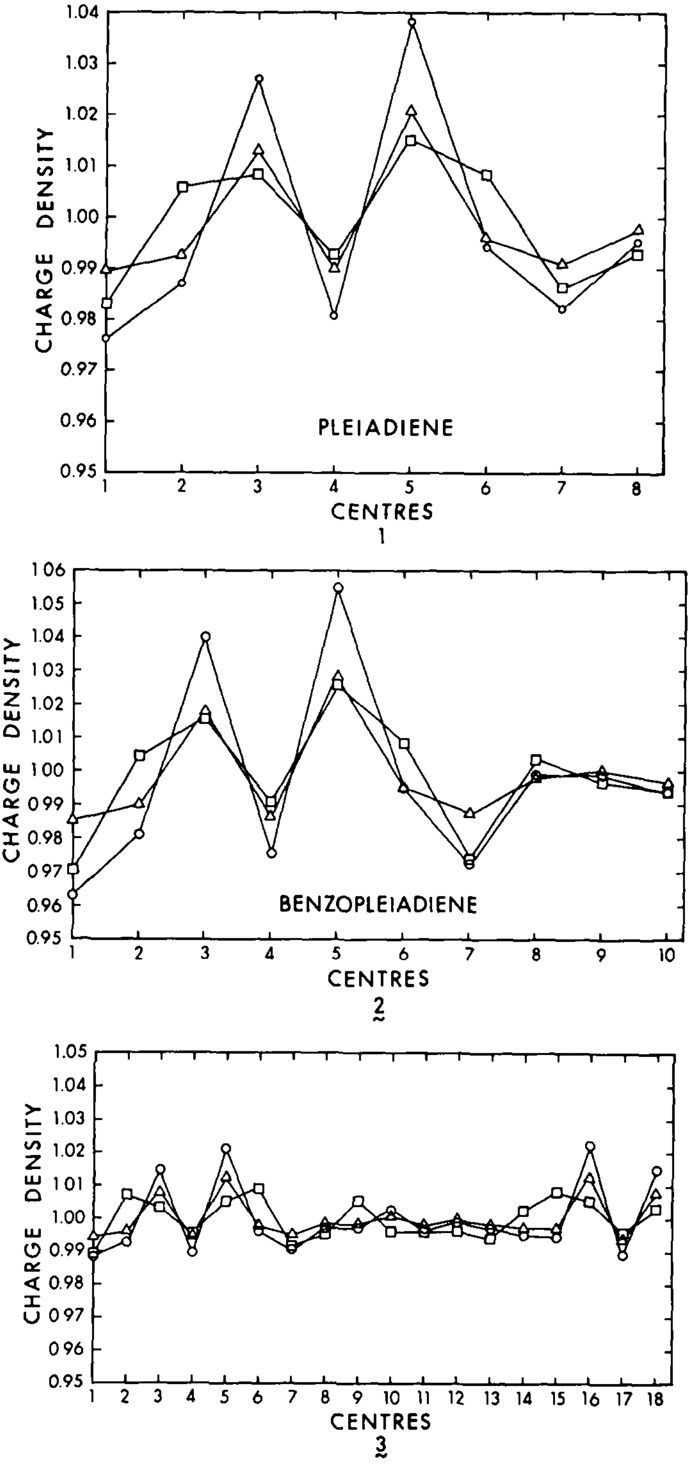

Fig. 2.

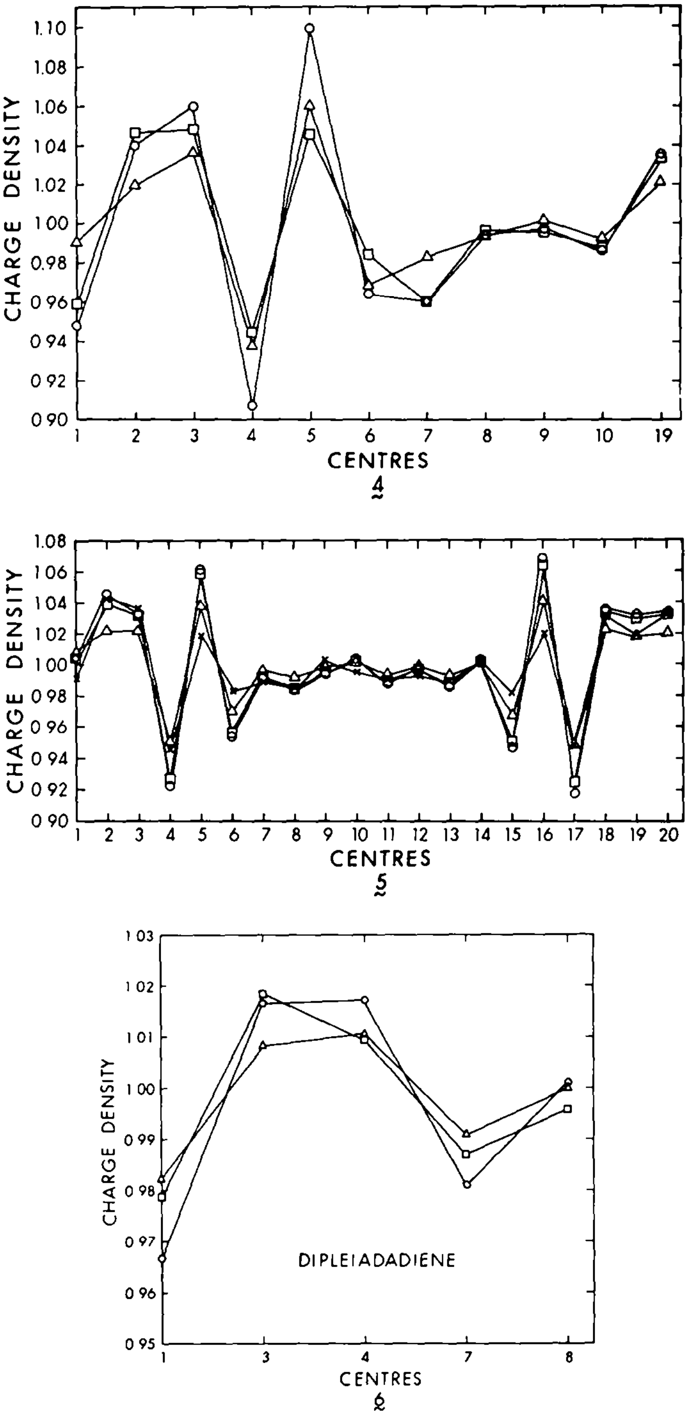

Fig. 2. Variation of charge density with different centres for the hydrocarbons: (SCF(a)—○, SCF(b)—□ for molecule **5** only, SCF(c)—△, SCF(d)—□ except molecule **5** and × for molecule **5**).†

and lowest charge density, most probable centre of electrophilic, nucleophilic and dienophilic attack.

Bond length. Figure 4 compares the bond lengths calculated by these methods for the molecules **1**–**6**. It is clear from the figure that the empirical relationship between bond order and bond length, whether it enters in the SCF procedure or not, works best for bond lengths intermediate between single and double bonds.

An interesting feature is observed if we consider the peripheral bonds of the hydrocarbon. The peripheral bonds in the naphthalene moity are delocalized. The bonds in the benzene ring of **3** and **5** are also delocalized whereas those in the benzene ring of the molecules **2** and **4** are localized. The peripheral bonds in the 5-membered ring of **4** and **5** and 7-membered rings of **1**, **3**, **5** and **6** are also localized and have single bond and double bond

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†In other cases the SCF(a) and SCF(b) methods are almost the same.

character. Whereas the peripheral bonds of 7-membered rings of 4 are less localized than those of the molecule 2. Thus in all these hydrocarbons the peripheral bonds are of two types—one is aromatic and the other is polyolefinic. Hence we should not apply any definition of aromaticity on these hydrocarbons based on the global π-electron character.

Spectra. Tables 4 and 4a contain the calculated $\pi^* \leftarrow \pi$ singlet-singlet transitions along with the experimental values and other theoretical results where available for the hydrocarbons and heteromolecules respectively. Since the molecules are not simple it is difficult to have point-to-point correlation between the theoretical results and observed spectra, although we have tried to do so.

In some cases we could not have point-to-point correlation with the observed and theoretical transitions and there we made a general correlation over quite a wide spectral region. The oscillator strengths f, were obtained from the following relation[19]

$$f = 1.085 \times 10^{-5}\, \bar{\nu}\mu^2$$

with μ as the dipole length for the corresponding

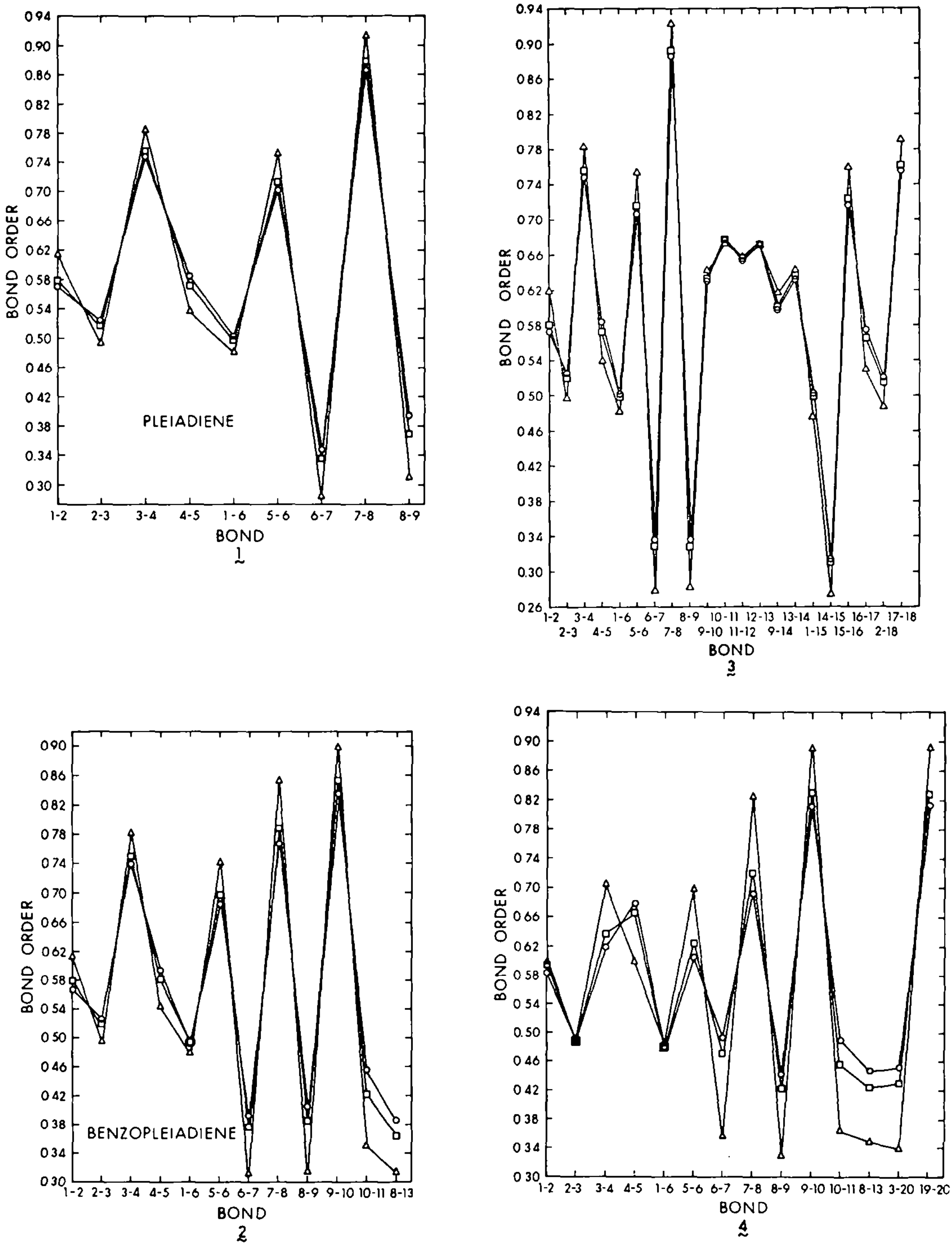


Fig. 3.

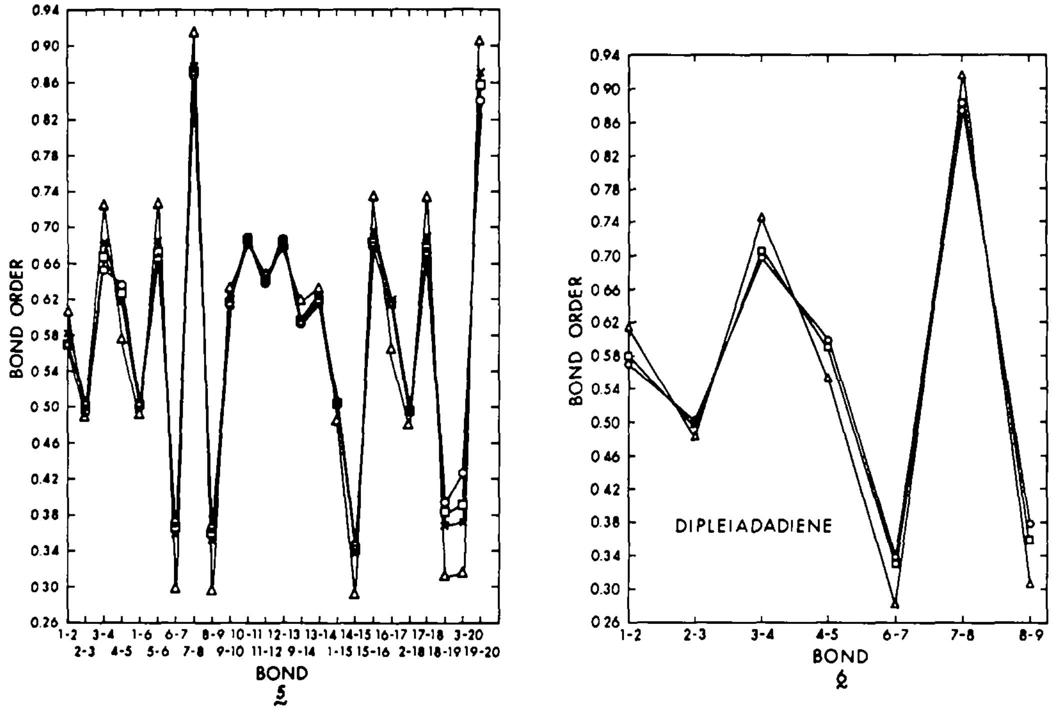


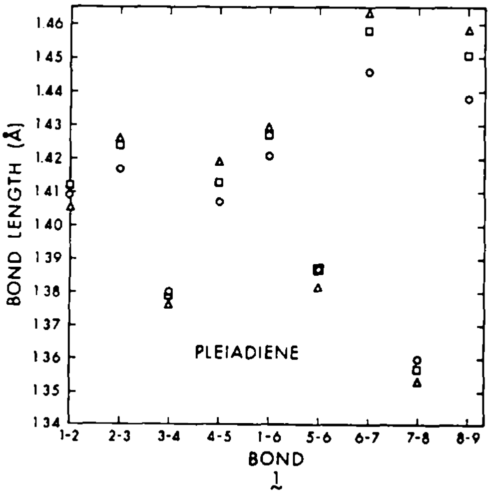
Fig. 3. Variation of bond order with different bonds for the hydrocarbons: (SCF(a)—○, SCF(b)—□ for molecule 5 only, SCF(c)—△, SCF(d)—□ except molecule 5 and × for molecule 5).†

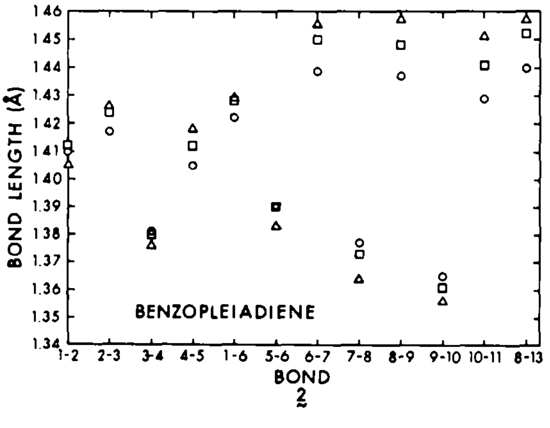
transition in Å and $\bar{\nu}$ as the transition energy in cm^{-1}. Oscillator strengths are also included in those Tables.

At lower transitions pleiadiene has a large number of peak maxima from 2.22 to 2.92 eV and there is only one theoretical transition in this region. Apart from this the agreement between the present results and observed spectra is good and comparable to those of Kontecky *et al.*[20] and Fuvini *et al.*[21] However, for the SCF(c) method there is no transition corresponding to the experimental spectra of lower transitions. There is no experimental results for the molecules 2, 5 and 6. The results calculated by these methods for these molecules are in good agreement with each other and for molecule 6 the agreement between our results and those of Fuvini *et al.*[21] and Yamaguchi *et al.*[22] is also good. For molecule 3 the agreement between the present result and observed spectra is very good. With the SCF(d) method, the agreement is excellent.

The overall agreement between our results and the observed spectra of 4 is good especially with SCF(a) and SCF(b) methods. For the SCF(c) method, there is no theoretical counterpart corresponding to the observed spectra at lower transitions from 1.84 to 2.01 eV.

The spectra of the heteromolecules 7, 8 and 9 have some resemblance with those of molecule 3, the parent hydrocarbon. As in the hydrocarbon 3, the SCF(c) method





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† In other cases the SCF(a) and SCF(b) methods are almost the same.

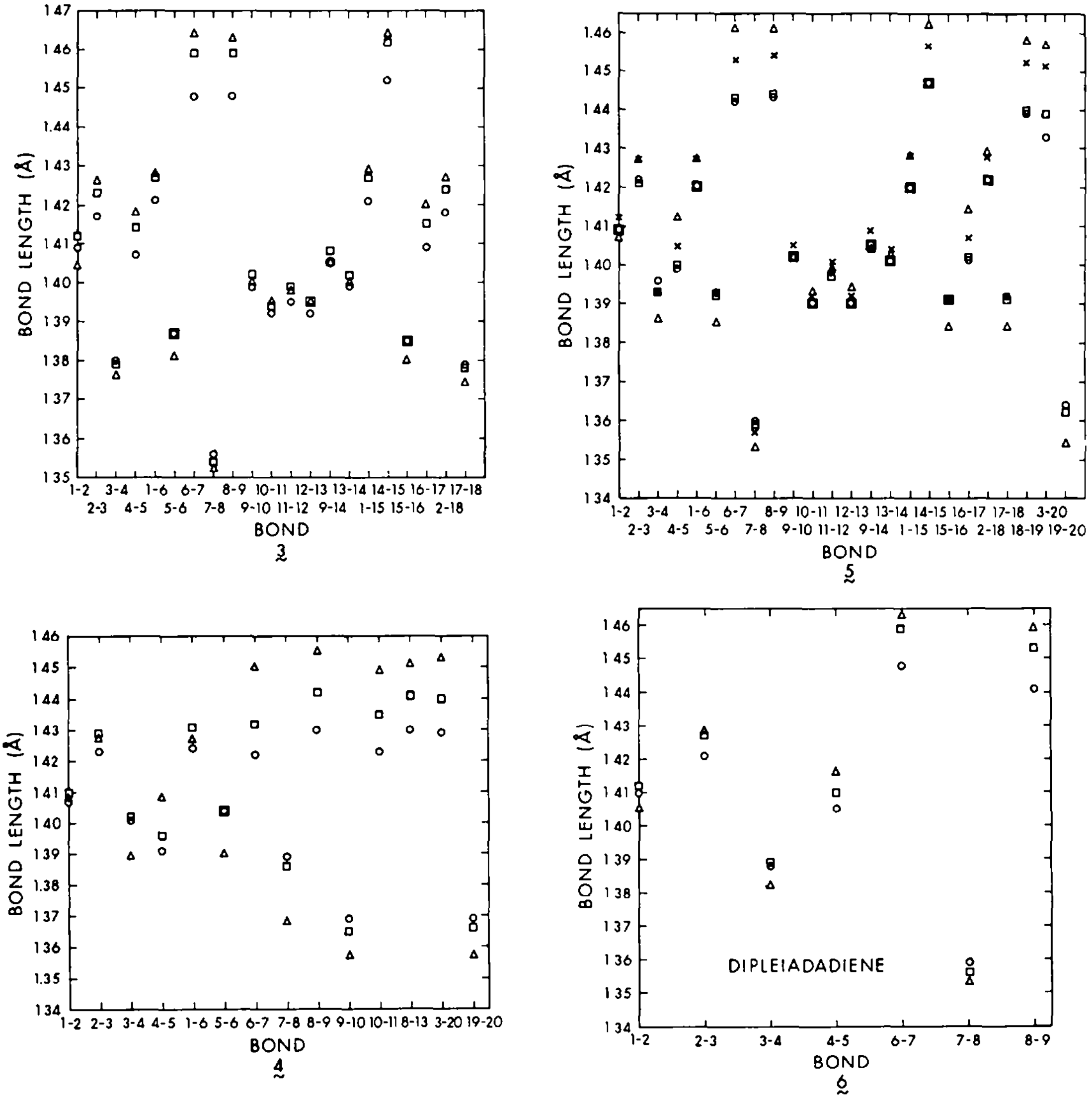

Fig. 4. Comparison of bond lengths for the hydrocarbons: (SCF(a)—○, SCF(b)—□ for molecule 5 only, SCF(c)—△, SCF(d)—□ except molecule 5 and × for molecule 5).†

has no transitions corresponding to the observed lower transitions of the molecules **8** and **9**. Apart from this the agreement between the theoretical results and experimental ones for the heteromolecules is good. It is surprising that as in the case of nonbenzenoid hydrocarbons, the β integral designed for the prediction of ground state properties of heteromolecules predicts the spectra of heteromolecules also with reasonably good accuracy.

Ionization potential, electron affinity and dipole moment: According to Koopmans' theorem,[23] ionization potential of a molecule is equal to the highest occupied molecular orbital energy. But is seen that the ionization potential obtained in this way is 1 or 2 eV[24] higher than the true value. There are several relations in the literature for obtaining correct ionization potential (IP). We are using the relation of Bloor[25] and Kunii and Kuroda[26] in the constant β integral method and β variable method respectively for predicting correct ionization potential. Bloor's relation is given below.

$$\text{I.P.} = -(\epsilon_h + 1.33)\,\text{eV}$$

where ϵ_h is the highest occupied orbital energy. The electron affinity (E.A.) is also obtained from the relation of Kunii *et al.*[26] The relations of Kunii *et al.* are as follows

$$\text{I.P.} = -(\epsilon_h + 1.06)\,\text{eV}$$

and

$$\text{E.A.} = -\epsilon_l - 1.90\,\text{eV}$$

where ϵ_l is the lowest unoccupied orbital energy and ϵ_h defined earlier. Table 5 contains the uncorrected and corrected ionization potential and electron affinity of these molecules along with their predicted π-dipole moment.

Resonance stabilization. Resonance stabilization for

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†In other cases the SCF(a) and SCF(b) methods are almost the same.

Table 3.

Molecule	Method*	Charge Density		Centre or Position of Attack		
		Centre of Highest	Centre of Lowest	Electrophilic	Nucleophilic	Dienophilic
1	a, b	5	1	5	4	C_7–C_8
	c	5	1	5	4	C_7–C_8
	d	5	1	5	7	C_7–C_8
2	a, b	5	1	5	4,7	C_9–C_{10}
	c	5	1	5	4	C_9–C_{10}
	d	5	1	5	7	C_9–C_{10}
3	a, b	16	1, 4, 17	16	17, 4	C_7–C_8
	c	16	1, 4, 17	16	17, 4	C_7–C_8
	d	6	1	16	7	C_7–C_8
4	a, b	5	4	5	4	C_{19}–C_{20}
	c	5	4	5	4	C_{19}–C_{20}
	d	3	4	5	4	C_9–C_{10}
5	a, b	5	17	5	17	C_7–C_8
	c	5	17	5	17	C_7–C_8
	d	3	4	20	4	C_7–C_8
6	a, b	4	1	4	7	C_7–C_8
	c	4	1	4	7	C_7–C_8
	d	3	1	4	7	C_7–C_8

*a, b, c and d respectively refer to SCF(a), SCF(b), SCF(c) and SCF(d) methods.

Table 4.

Molecule	Symmetry	$\pi^* \leftarrow \pi$ Transitions and Oscillator Strengths													
		Experiment*		SCF(a)		SCF(b)		SCF(c)		SCF(d)		Other Work			
		eV	log ε	eV	f	eV	f	eV	f	eV	f	eV	f	eV	f
1		2.22	2.05									2.173 (a)	0.065	(b)	
		2.41	2.40												
	B_2	2.58	2.60	2.52	0.20	2.52	0.20							2.774	0.08
		2.76	2.62												
	B_2	2.92	2.58							3.00	0.21				
	B_2	3.23	3.20					3.20	0.21						
		3.35	3.68												
	A_1	3.49	3.85	3.53	0.80	3.51	0.70					3.359	0.334	3.454	0.67
	A_1	3.64	3.90					3.87	0.70	3.71	0.80			3.539	0.01
	B_2	4.20	3.95	3.96	0.48	3.94	0.48	4.13	0.45	4.03	0.52	3.910	0.051		
		4.35	3.95												
	B_2	4.59	3.87	4.63	0.69	4.60	0.68	4.59	0.67	4.74	0.70	4.286	0.015		
	A_1	4.98	4.49	5.13	0.68	5.10	0.67	5.08	0.43					4.900	0.44
	B_2	5.17	4.42	5.24	0.26	5.21	0.25			5.37	0.70	5.089	0.022	5.168	0.07
	A_1	5.39	4.42	5.26	0.45	5.23	0.44	5.45	0.62	5.52	0.30			5.368	0.05
								5.52	0.25						
	B_2	5.93	4.60	6.12	0.29	6.08	0.29								

Table 4 (cont'd)

Molecule	Symmetry	Experiment*		SCF(a)		SCF(b)		SCF(c)		SCF(d)		Other Work			
		eV	log ε	eV	f	eV	f	eV	f	eV	f	eV	f	eV	f
<u>2</u>	B_2			1.98	0.28	1.98	0.28			2.22	0.29				
	A_1			3.23	1.03	3.21	1.03	3.62	0.87	3.31	1.03				
	B_2			3.84	0.38	3.83	0.37			3.81	0.39				
				3.89	0.15	3.88	0.15	4.12	0.35	3.98	0.14				
	A_1			4.35	0.95	4.33	0.95	4.77	0.86	4.50	1.00				
	B_2			4.77	0.65	4.74	0.65	4.60	0.04	4.81	0.65				
	A_1							4.87	0.48						
	A_1			5.08	0.07	5.06	0.07	5.17	0.21	5.07	0.11				
<u>3</u>		3.40	3.96	3.26	0.27	3.25	0.27			3.45	0.25				
		3.54	3.99	3.27	0.79	3.26	0.78	3.64	0.22	3.51	0.83				
		4.13	3.58	4.20	0.53	4.18	0.52	4.34	0.48	4.22	0.54				
		4.59	3.96	4.57	0.71	4.55	0.71	4.70	0.71	4.64	0.71				
		5.20	4.54	5.30	0.44	5.27	0.43	5.15	0.41	5.29	0.18				
		5.39	4.58	5.39	0.26	5.36	0.26	5.44	0.30	5.45	0.28				
<u>4</u>		1.84	3.20												
	B_2	1.91	3.17	2.26	0.34	2.26	0.34			2.35	0.33				
		2.01	3.14												
	B_2							2.71	0.31						
	A_1			2.94	1.23	2.93	1.22			2.81	1.23				
	B_2	3.29	4.69	3.24	0.30	3.22	0.30	3.49	0.33	3.35	0.28				
	A_1	3.43	4.51	3.53	0.71	3.52	0.70	3.25	1.00	3.42	0.68				
	B_2	4.23	4.25	4.07	0.39	4.04	0.39	4.27	0.31	4.13	0.46				
	B_2	4.38	4.23	4.31	0.05	4.29	0.05	4.33	0.12	4.31	0.04				
	A_1	5.17	4.23	5.00	0.02	4.98	0.02	5.21	0.56	4.87	0.53				
	A_1	5.46	4.32	5.56	0.45	5.52	0.45	5.24	0.42	5.49	0.03				
<u>5</u>				2.97	0.35	3.03	0.31								
				3.13	0.97	3.17	1.00	3.51	0.87	3.18	1.00				
				3.43	0.31	3.36	0.28	3.50	0.34	3.55	0.28				
				3.79	0.38	3.82	0.39	3.73	0.26						
								3.97	0.40	3.94	0.49				
				4.41	0.55	4.47	0.35			4.39	0.61				
				4.49	0.32	4.50	0.57	4.51	0.46	4.58	0.25				
								5.04	0.55						
				4.84	0.40	4.84	0.39	5.07	0.38	4.94	0.38				
				5.41	0.41	5.36	0.41	5.28	0.40	5.57	0.22				
												(b)		(c)	
<u>6</u>	B_{1g}			1.70	0	1.70	0	2.63	0	2.17	0			2.15	0
	B_{3u}											2.628	0.59		
	B_{2u}			3.17	1.07	3.16	1.00	3.54	0.92	3.27	1.07	3.096	0.01	3.13	0.014
	B_{3u}			3.26	0.33	3.25	0.33								
	B_{3u}			3.50	0.39	3.48	0.38	3.60	0.17	3.41	0.27	3.449	0.15	3.30	0.60
										3.65	0.47				
	A_g			4.42	0	4.41	0	4.74	0	4.43	0			4.51	0
	B_{3u}			4.46	0.58	4.45	0.58	4.62	0.63	4.54	0.57	4.51	0.03		
	B_{3u}			4.71	0.63	4.68	0.62	4.96	0.53	4.75	0.64				
	A_g			4.81	0	4.79	0	5.06	0	4.74	0			4.91	0
	B_{2u}			4.97	1.01	4.95	1.00	5.28	0.92	5.05	1.04	5.11	1.08	4.70	0.091
	B_{2u}			5.28	0.44	5.25	0.44	5.19	0.36	5.35	0				

*Molecule <u>1</u> Ref. 2 (a) Ref. 20
<u>3</u> Ref. 5 and Ref. 29 (b) Ref. 21
<u>4</u> Ref. 4 (c) Ref. 22

Table 4A.

*π ← π Transitions of the Heteroanalogues

Molecule	Experiment*		SCF(c)		Molecule	Experiment*		SCF(c)		Molecule	Experiment*		SCF(c)	
	eV	log ε	eV	f		eV	log ε	eV	f		eV	log ε	eV	f
7					8	3.27	4.00			9	3.32	4.00		
	3.60	3.86	3.51	0.54		3.44	4.11							
											3.84	3.86	3.91	0.68
	4.05	4.12	3.78	0.36		4.11	3.63	3.99	0.71		4.00	3.86		
						4.47	3.78	4.59	0.67					
											4.74	4.27	4.73	0.66
											4.96	4.33	5.14	0.45
	5.25	4.96	5.28	0.14		5.17	4.35	5.09	0.43		5.29	4.60	5.24	0.04
													5.50	0.28
	5.51	4.90	5.59	0.23		5.64	4.53	5.55	0.30					
											5.64	4.53	5.59	0.51
	5.69	4.75	5.61	0.11		5.79	4.58	5.78	0.45					
			5.79	0.09				5.89	0.37					

* Molecule 7 Ref. 29 and 30
8 and 9 Ref. 5

Table 5. Ionization potential (I.P.), electron affinity (E.A.), and π-dipole moment

Molecule	Method*	I.P. (EV) Uncorrected	I.P. (eV) Corrected	E.A. (eV) Uncorrected	E.A. (eV) Corrected	π-dipole Moment (D)
1	a	-8.69	7.36	-1.86		0.73
	b	-8.68	7.35	-1.86		0.72
	c	-9.06	-	-1.46		0.36
	d	-8.30	7.24	-2.09	0.19	0.55
2	a	-8.21	6.88	-2.71		1.30
	b	-8.21	6.88	-2.71		1.29
	c	-8.66	-	-2.20		0.60
	d	-7.86	6.80	-3.07	1.17	0.97
3	a	-8.82	7.49	-1.90		0.45
	b	-8.82	7.49	-1.91		0.44
	c	-9.13	-	-1.65		0.23
	d	-8.42	7.36	-2.34	0.44	0.36
4	a	-8.43	7.10	-2.95		3.38
	b	-8.43	7.10	-2.95		3.36
	c	-8.74	-	-2.37		1.80
	d	-8.02	6.96	-3.29	1.39	3.46
5	a	-9.04	7.71	-2.56		2.10
	b	-9.03	7.70	-2.52		1.95
	c	-9.24	-	-2.24		1.11
	d	-8.63	7.57	-3.02	1.12	2.01
6	a	-8.09	6.76	-2.17		0.01
	b	-8.10	6.77	-2.17		0.01
	c	-8.60	-	-1.74		0.01
	d	-7.80	6.74	-2.61	0.71	0.01
7	c	-9.27		-2.11		2.43
8	c	-9.47		-1.59		0.19
9	c	-9.31		-1.55		0.43

* a, b, c and d indicate SCF(a), SCF(b), SCF(c) and SCF(d) methods, respectively.

the molecules **1**, **2** and **6** has been discussed by DasGupta and DasGupta[3,8] using the method of Lo and Whitehead[6] and Dewar *et al.*[7,27] Table 6 contains the heats of automization, π-bond energy and σ-bond energy for the molecules **3**, **4**, **5**, **7**, **8** and **9** calculated by the SCF(a), SCF(b) and SCF(c) (for both hydrocarbons and heterosystems) methods. Table 7 contains the resonance energy (E_R), and resonance energy per carbon–carbon bond calculated by the methods of Lo and Whitehead,[6] Chung and Dewar,[7a] Dewar and de Llano[27] and Dewar and Harget,[7b] for the hydrocarbons along with E_R and E_R/C–C values for the heterosystems calculated by the method of Dewar and Harget.[7b,c,d] The compound **2** is very unstable and it dimerises immediately. Whereas the molecule **3** is a stable compound. Structurally, the only difference between these two compounds is that in molecule **3** the benzene ring is angularly fused to the 7-membered ring of pleiadiene moiety whereas in molecule **2** it is linearly fused. It seems that the angularly fused benzene ring in pleiadiene has stabilized the molecule **3**.

The greater stability of molecule **3** compared to **2** can be explained qualitatively. The benzene ring in **2** has little delocalization whereas the benzene ring in **3** is completely delocalized as evidenced in the calculated bond length. Moreover, we can draw more Kekule structures with alternate single bond and double bond for the molecule **3** than the molecule **2**. The same conclusion can also be drawn from the resonance energy and resonance energy per carbon–carbon bond (E_R/C–C) calculated by the methods of Lo and Whitehead[6] and Dewar *et al.*[7,27] These values are greater for **3** than for **2**. Since resonance energy per C–C bond is a measure of aromaticity the molecule **3** is aromatic because its resonance energy per C–C bond (0.086) calculated by the method of Dewar and de Llano[27] is comparable to that of similar aromatic semibenzenoid hydrocarbons[3] such as acenaphthylene (0.077), pleiadiene (0.070), acepleiadylene (0.080), fluroanthene (0.101), naphth[cde]azulene (0.052), and cyclohept[bc]acenaphthylene (0.060). The instability of molecule **4** is also in agreement with its E_R/C–C value

Table 6. Heats of atomization (ΔHa) and bond energies

Molecule	ΔHa (eV) SCF(a)	ΔHa (eV) SCF(b)	ΔHa (eV) SCF(c)	π-bond Energy ($E_{\pi b}$) (eV) SCF(a)	π-bond Energy ($E_{\pi b}$) (eV) SCF(b)	π-bond Energy ($E_{\pi b}$) (eV) SCF(c)	σ-bond Energy ($E_{\sigma b}$) (eV) SCF(a)	σ-bond Energy ($E_{\sigma b}$) (eV) SCF(b)	σ-bond Energy ($E_{\sigma b}$) (eV) SCF(c)
3	157.100	157.273	157.429	26.920	26.497	26.233	76.930	77.526	77.946
4	170.530	170.731	170.987	29.345	28.884	28.495	87.935	88.597	89.242
5	171.144	171.509	171.718	30.255	29.630	29.204	87.640	88.630	89.264
7			152.154			26.390			76.952
8			142.593			23.536			74.681
9			141.284			23.683			73.226

Table 7. Resonance energy and resonance energy per bond

Molecule	Resonance Energy (eV) a	Resonance Energy (eV) b	Resonance Energy (eV) c	Resonance Energy (eV) d	Resonance Energy per Bond a	Resonance Energy per Bond b	Resonance Energy per Bond c	Resonance Energy per Bond d
2	5.524	5.543	0.853	1.566	0.263	0.264	0.041	0.075
3	6.4819	6.4408	1.8111	2.3634	0.3087	0.3067	0.0862	0.1125
4	6.4852	6.4936	1.0033	1.6848	0.2702	0.2706	0.0418	0.0702
5	7.0998	7.2382	1.6178	2.4164	0.2958	0.3016	0.0674	0.1007
7				2.3959				0.1142
8				2.3412				0.1171
9				2.3583				0.1179

* Ref. 3 and 8.

(a) Method of Lo and Whitehead (Ref. 6)

(b) Method of Chung and Dewar (Ref. 7a)

(c) Method of Dewar and de Llano (Refs. 3 and 27)

(d) Method of Dewar and Harget (Ref. 7b,c,d)

(0.042) which is less than that of aromatic semibenzenoid compounds mentioned above, and it is comparable to that of pyracylene (0.045), benzopleiadiene (0.041), and dipleiadadiene (0.030) which are not aromatic compounds. Again, the molecule **2** is less stable than **4** which can be isolated in solution stable for 80 min, and whose UV spectra in solution has been reported.[4] This is also in agreement with their E_R/C–C value calculated by all the methods[6,7a,27] except Dewar and Harget method[7b] according to which the E_R/C–C value of **2** is greater than that of **4**. But we[8] have seen that the method of Dewar and Harget is less effective than the method of Dewar and de Llano in correlating the theoretical results with experimental results. Although the synthesis of the molecule **5** is not found in the literature still it is expected from its resonance energy and resonance energy per C–C bond that it would be a stable aromatic compound. The heteroanalogues (**7**, **8** and **9**) of **3** have resonance energy and resonance energy per bond similar to **3** and it is expected that they will also be aromatic compounds.

If there is ethylinic linkage in napthalene moity, it is found that the resonance energy of the final compound[28] is less than that of naphthalene. Thus the resonance energy of acenaphthylene is less than that of naphthalene and E_R of pyracylene is also less than that of acenaphthylene. Similarly we[28] have also seen that E_R of acefluoranthylene, aceanthrylene and acephenanthrylene is less than that of fluoranthene, anthracene and phenanthrene respectively. But when a seven membered ring is fused in the naphthalene moiety, the ethylinic linkage increases the resonance energy of the final compound. Thus the E_R of acepleiadylene[3,8] is greater than that of pleiadiene and similar situation is also found in other cases. As for example, the resonance energy of the molecules **4** and **5** is greater than that **2** and **3** respectively.

Summary

The fundamental object of the SCF(a), SCF(b) and SCF(c) methods is to predict reasonably accurate heats of atomization, but other ground state properties predicted by these methods are all consistent with one another in spite of the fact that in SCF(c) method the β integrals and certain γ integrals are varied at each iteration. Moreover spectral transitions predicted by the SCF(a) and SCF(b) methods are also in better agreement with experimental results than those of SCF(d) method which is parameterised for spectral transitions.

Acknowledgements—The authors express their sincerest gratitude to Professor F. W. Birss for valuable comments, helpful discussions and financial support. They are also thankful to Computing Services, University of Alberta for computational facilities.

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