Theoretical Studies of Some Nonbenzenoid Hydrocarbons. V. Benzazulenes and Benzofluoranthenes

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The molecules benzazulenes and benzofluoranthenes have been studied by the semi-empirical method for π-molecular systems, similar to that of Pariser-Parr and Pople. Ground state properties and $\pi^* \leftarrow \pi$ spectra have been predicted and compared with experiment. Agreement between the theoretical values and observed ones is good; that between the experimental value of half-wave reduction potential and values calculated by SCF(d) method is very good.

Dewar and coworkers[1] and Lo and Whitehead[2] predicted the ground state properties of many conjugated systems using the self-consistent field molecular orbital (SCF MO) theory with core resonance integral values determined either by a hypothetical thermocycle[1a,2] or utilising a relation[1a] between overlap integral and resonance integral. By means of their methods not only the ground state properties of some nonbenzenoid hydrocarbons can be predicted but also the $\pi^* \leftarrow \pi$ spectral transitions can be obtained with reasonable accuracy.[3] In most cases this spectra thus predicted are better than those predicted by the 'β-variable' SCF method with core resonance integral proposed by Yamaguchi *et al.*[4a] and modified by Das Gupta and Birss.[4b]

In this paper we would like to report the results of our calculations on some benzazulenes and benzofluoranthenes using the semi-empirical SCF MO method with resonance integral proposed by Chung and Dewar,[1a] Lo and Whitehead,[2] and Dewar and Harget.[1c] The results are compared with those obtained by the 'β-variable' SCF method, the methods being designated as SCF(a), SCF(b), SCF(c), and SCF(d). The molecules (Fig. 1) have also been studied theoretically by others[5] using different sets of parameters. We have studied how the properties of azulene and fluoranthene change with the fusion of benzene nucleus to them.

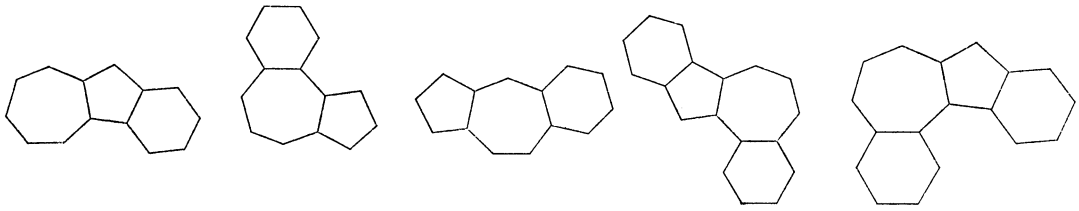
Method and Parameters

The method used here is the Pariser and Parr[6] and Pople[7] method within the zero-differential approximation.[8] The choice of parameters and mode of evaluation of certain integrals were reported.[3] For molecule **6** experimental structure[9] is available and core resonance integral and the two-center two electron repulsion integrals were evaluated by means of the structure. For other molecules whose experimental structure is not known we have used a planar and regular geometry with each bond length equal to 1.40 Å as far as possible for the evaluation of integrals.

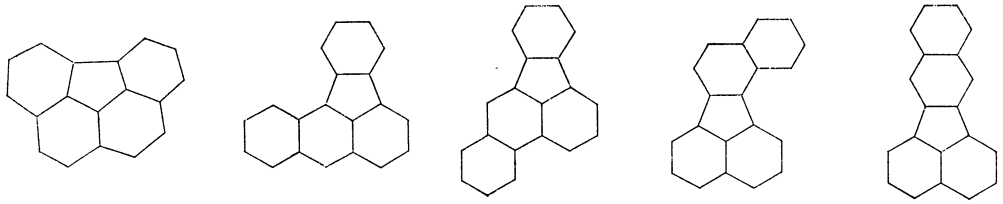
Results and Discussion

Bond Length. For monobenzazulenes the bond lengths calculated by the SCF(d) method is in good agreement with those of Dewar *et al.*[5f]

In the monobenzazulenes and dibenz[*a*,*e*]azulene the predicted bond lengths in the benzene ring have aromatic character, the bond length varying from 1.384



1 Benz[*a*]azulene **2** Benz[*e*]-azulene **3** Benz[*f*]-azulene **4** Dibenz[*a*,*e*]-azulene **5** Dibenz[*a*,*h*]azulene



6 Benzo[*ghi*]-fluoranthene **7** Benzo[*a*]-fluoranthene **8** Benzo[*b*]-fluoranthene **9** Benzo[*j*]-fluoranthene **10** Benzo[*k*]-fluoranthene

Fig. 1.

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to 1.413 Å. In dibenz[*a*,*h*]azulene, however, the bond lengths of one of the benzene ring maintain the aromatic character whereas the bonds of the other benzene nucleus have marked deviation from aromatic character. In the first case they vary from 1.38 to 1.425 Å and in the second case from 1.36 to 1.45 Å. Thus the two benzene nuclei of the two dibenzazulenes are quite different; in one (Molecule **4**) both the six-membered rings have aromatic nature whereas in the other (Molecule **5**) only the benzene ring attached to the seven-membered ring maintains the character. This is also exhibited in the prediction of resonance energy. Molecule **4** has a higher value of resonance energy.

The peripheral bonds in azulene[3b] lie between 1.394 and 1.408 Å and are predicted to have aromatic character, but the fusion of benzene nucleus to azulene destroys the aromatic nature of the peripheral bonds in the five and seven-membered rings of the benzazulenes, except molecule **5** where the bond lengths predicted by the SCF(a), SCF(b), and SCF(d) methods have aromatic nature. The SCF(c) method gives the results which disagree. In all the molecules the common bond between the five and seven-membered rings has single bond character similar to that of azulene, the value lying between 1.45 and 1.47 Å calculated by these methods compared to 1.46 to 1.47 Å of azulene.[3b]

In the molecules **7**—**10** the fusion of a benzene ring in a fluoranthene moiety alters the predicted bond lengths of the six-membered ring to a considerable extent where the fusion takes place, the other bond lengths remaining almost the same as those of fluoranthene.[3e]

Resonance Stabilization

The heats of atomization (ΔH_a) and π-bond energy ($E_{\pi b}$) for the molecules calculated by the SCF(a), SCF(b), and SCF(c) methods are given in Table 1. The resonance energy (E_R) calculated by the methods of Lo and Whitehead[2], Dewar *et al.*[1] and Hess and Schaad[10] is given in Table 2, together with the resonance energy per C–C bond (E_R/C–C) since it is more useful for predicting the stability or aromaticity of a molecule. In benzazulenes the fusion of a benzene nucleus in azulene increases the E_R/C–C over that of azulene, whereas in benzofluoranthenes E_R/C–C is almost the same as that of fluoranthene. This suggests that all the benzazulenes should be more stable than azulene. It is also clear from the values of resonance energy and E_R/C–C bond that molecule **4**

Table 1. Heat of atomization (eV) and π-bond energy (eV)

Molecule	Heat of atomization				π-Bond energy			
	SCF(a)	SCF(b)	SCF(c)	Other work[a]	SCF(a)	SCF(b)	SCF(c)	Other work
1	122.910	123.041	123.211	123.68[b]	19.920	19.600	19.596	18.24[b]
2	122.955	123.086	123.253	123.70[b]	19.964	19.644	19.628	18.25[b]
3	122.909	123.040	123.218	123.69[b]	19.919	19.598	19.604	18.25[b]
4	156.624	156.798	157.054		26.441	26.023	25.858	
5	156.147	156.321	156.432		25.962	25.546	25.205	
6	153.227	152.002	153.259		27.930	27.525	26.912	
7	171.650	171.850	172.003		30.471	30.001	29.426	
8	171.987	172.185	172.316		30.809	30.336	29.729	
9	171.818	172.016	172.164		30.639	30.168	29.600	
10	171.768	171.967	172.129		30.590	30.119	29.576	

a) Heat of formation. b) Ref. 5f.

Table 2. Resonance energy and resonance energy per C–C bond

Molecule	Resonance energy						Resonance energy per C–C bond				
	(a) (eV)	(b) (eV)	Other work[5f] (eV)	(c) (eV)	(d) (eV)	(e) (β)	(a) (eV)	(b) (eV)	(c) (eV)	(d) (eV)	(e) (β)
1	3.908	4.055	2.32	0.621	1.108	0.411	0.244	0.253	0.039	0.069	0.026
2	3.953	4.099	2.37	0.666	1.151	0.425	0.247	0.256	0.042	0.072	0.027
3	3.907	4.054	2.37	0.620	1.112	0.428	0.244	0.253	0.039	0.069	0.027
4	6.006	5.967		1.335	1.958	0.648	0.286	0.284	0.064	0.093	0.031
5	5.528	5.490		0.858	1.367	0.562	0.263	0.261	0.041	0.065	0.027
6	7.592	7.306		2.465	2.683	0.865	0.345	0.333	0.112	0.122	0.039
7	7.605	7.610		2.123	2.701	0.886	0.317	0.317	0.088	0.113	0.037
8	7.943	7.945		2.461	3.014	0.984	0.331	0.331	0.103	0.126	0.041
9	7.773	7.777		2.291	2.862	0.934	0.324	0.324	0.095	0.119	0.039
10	7.724	7.728		2.242	2.717	0.931	0.322	0.322	0.093	0.113	0.039

a, b, c, d, and e represent SCF(a), SCF(b), SCF(c), Dewar and de Lano[1b] and Hess and Schaad[10] methods, respectively.

Table 3. $\pi^*\leftarrow\pi$ Transitions and oscillator strength†††

Molecule	Experimental††		Sym.	SCF (a)		SCF (b)		SCF (d)		Sym.	CI		Other works					
	eV	log ε		eV	f	eV	f	eV	f		eV	f	eV	f	eV	f	eV	f
1	1.98	2.54		2.12	0.18	2.11	0.19	2.39	0.26		2.17	0.075	1.503[a]	0.029	2.39[b]		1.581[d]	0.030
	3.25	3.64		3.37	0.92	3.36	0.92	3.60	0.92		3.19	0.077	2.905	0.177	3.19		3.020	0.126
	4.25	4.78		4.26	0.44	4.24	0.44	4.44	0.44		4.30	1.05	3.977	1.339	3.99		4.114	1.344
													4.259	0.230	4.38		4.426	0.248
													4.301	0.566			4.457	0.454
	5.21	4.03		5.30	0.22	5.27	0.22	5.40	0.19		5.45	0.121						
2	2.15	2.5		2.10	0.15	2.09	0.15	2.37	0.19		2.18	0.060	1.444[a]	0.028	2.49[b]		1.550[d]	0.022
	3.12	3.51		3.32	0.67	3.30	0.66	3.52	0.65		3.13	0.068	2.82	0.057	3.24		3.016	0.104
				3.75	0.58	3.73	0.58	{3.98	0.59		3.89	0.036						
	4.09	4.46		4.24	0.65	4.22	0.65	{4.36	0.68		4.00	0.495	3.816	1.168	4.09		4.120	1.009
				4.42	0.11	4.40	0.11	4.45	0.16		4.40	0.758	4.197	0.196			4.375	0.080
													4.204	0.085			4.457	0.401
	4.90	4.32		4.67	0.38	4.64	0.38	4.77	0.34		4.86	0.537			4.40			
	5.44	4.23		5.30	0.10	5.27	0.10	5.36	0.08		5.41	0.215						
3	2.05			2.38	0.25	2.37	0.25	2.52	0.23		2.23	0.051	1.706[a]	0.040	2.44[b]			
				3.34	0.67	3.33	0.67				3.18	0.017	2.931	0.048				
	3.57	3.56		3.59	1.01	3.57	1.00	3.65	0.76		3.77	0.070	3.948	0.738	3.21			
	4.30	4.75		4.31	0.35	4.29	0.35	4.42	0.34		4.14	1.585	4.177	0.847	4.04			
	5.08	4.20		5.03	0.27	5.01	0.27	5.20	0.29		4.97	0.103	4.508	0.363	4.463			
4	1.83	2.47											1.747[a]					
				2.45	0.50	2.44	0.49	2.68	0.55		2.46	0.198						
	3.28	3.89		3.38	0.37	3.37	0.36	3.55	0.39		3.24	0.012	2.997					
	3.85	4.89		3.59	0.57	3.58	0.57	3.75	0.58		3.71	0.471	3.763					
											3.99	0.285	4.108					
				4.38	0.77	4.36	0.77	4.41	0.79		4.26	0.81	4.120					
	4.63	4.12		4.57	0.05	4.55	0.05	4.53	0.06		4.69	0.157						
				5.08	0.39	5.06	0.38	5.14	0.35		5.12	0.514						
5				1.69	0.13	1.68	0.13	1.65	0.13		1.36	0.031	0.940[a]	0.030				
	2.11										2.55	0.039	2.593	0.035				
	3.11			{3.09	0.77	{3.07	0.77	{3.05	0.84		3.46	1.338	3.451	1.308				
				{3.21	0.84	{3.20	0.83	{3.21	0.89									
	3.91			{3.99	0.03	{3.97	0.03	{3.82	0.02		3.98	0.140	3.607	0.166				
				{4.13	0.63	{4.11	0.63	{4.16	0.64				3.781	0.321				
	4.86			{4.55	0.41	{4.53	0.41	{4.58	0.40		4.82	0.571						
				{5.15	0.10	{5.12	0.10	{5.06	0.11									

TABLE 3. (Continued)

Molecule	Experimental†† eV	Experimental†† log ε	Sym.	SCF (a) eV	SCF (a) f	SCF (b) eV	SCF (b) f	SCF (d) eV	SCF (d) f	Sym.	CI eV	CI f	Other works eV	Other works f	Other works eV	Other works f	Other works eV	Other works f
6	2.93	2.47								B_2	3.23	0.043	3.283[a]	0.002				
	3.10	2.90	B_2			3.33	0	3.49	0	B_2	3.50	0.132	3.537	0.375				
	3.68	4.23	B_2			3.78	0.96	3.76	1.00	A_1	3.66	0.029	3.763	0.053				
										A_1	3.95	0.014	4.192	0.012				
	4.38	4.58	B_2	4.29	0.85	4.35	0.70	4.35	0.71	B_2	4.29	0.843	4.501	0.906				
7													2.730[a]	0.181				
	2.90	3.92		3.06	0.73	3.05	0.73	3.13	0.73		2.77	0.360	3.070	0.174				
	3.47	3.70		3.25	0.22	3.24	0.22	3.39	0.21		3.35	0.060	3.736	0.086				
	4.15	3.91		4.31	0.74	4.29	0.73	4.25	0.80		4.26	0.074	4.102	0.368				
	4.97	4.86		5.15	0.67	5.12	0.66	5.16	0.69		4.95	0.781	4.409	0.128				
8	3.36	3.86									3.32	0.233	3.346[a]	0.324				
	3.55	4.00		3.59	1.07	3.58	1.06	3.72	1.12		3.42	0.383	3.578	1.129				
													3.612	0.096				
	4.24	4.58		4.57	0.35	4.55	0.35	4.48	0.34		4.13	0.168	4.419	0.175				
	4.97	4.57		4.97	0.58	4.94	0.58	5.01	0.61		4.91	0.707	4.689	0.126				
				5.15	0.65	5.12	0.65	5.13	0.65									
9													2.764[a]	0.097				
	3.27	4.09		3.27	0.43	3.26	0.43	3.34	0.41		3.26	0.370	3.389	0.584				
	3.88	4.14		3.51	0.74	3.49	0.74	3.62	0.78		3.84	0.458	3.959	0.132				
				4.12	0.15	4.11	0.15											
	4.07	4.50		4.40	0.45	4.38	0.45	4.26	0.60		4.25	0.162	4.124	0.446				
	5.41	4.70		5.48	0.23	5.45	0.23	5.41	0.19		5.16	0.950	4.389	0.226				
											5.37	0.211						
10	3.16	4.09	A_1	3.49	0.96	3.48	0.96	3.51	1.01		3.13	0.499	3.237[a]	0.678	3.163[c]	0.134	3.22[e]	>0.5
			B_2								3.48	0.000	3.503	0.002			3.53	<0.1
	3.66		B_2	3.83	0.20	3.82	0.20	3.97	0.20		3.67	0.001	3.927	0.063	3.906	0.057	3.87	<0.1
	4.02	4.76	A_1	4.36	0.95	4.34	0.94	4.43	0.98		3.89	0.713	4.054	0.142	4.235		4.07	>0.5
			B_2	4.07	0.25	4.05	0.25	4.16	0.23		3.93	0.167			3.982		4.03	0.1—0.5
			A_1	4.81	0.03	4.79	0.03	4.69	0.02		4.51	0.227	4.131	0.85			4.65	0.1—0.5
			B_2	5.07	0.16	5.05	0.16	4.75	0.39		4.79	0.006					4.96	<0.1
			A_1	5.24	0.24	5.22	0.24	5.48	0.01		4.95	0.203					5.21	0.1—0.5
	4.93		B_2	4.97	0.39	4.94	0.39	5.07	0.16		5.04	1.062					5.24	>0.5
	5.27	4.79	A_1	5.26	0.45	5.22	0.44	5.07	0.22		5.20	0.423					5.08	>0.5

†† Molecule **1** Refs. 11, 12; **2** Refs. 12, 5a; **3** Refs. 11, 12, 13; **4** Ref. 5b; **5**—**9** Ref. 11; **10** Refs. 11, 22, 23.
††† Calculated using the relation in Ref. 20. a) Ref. 5b, b) Ref. 5a; c) Ref. 5c; d) Ref. 21; e) Ref. 22.

should be more stable than molecule **5**. All the methods agree that the monobenzazulenes should be equally stable as shown by Dewar and Gleicher.[5f]

Molecules **7**, **8** and **9** or **10** can be treated as either anthracene and benzene, phenanthrene and benzene, and two naphthalene molecules joined by single bonds respectively. The resonance energy for these molecules corresponds almost to the sum of the resonance energies of anthracene and benzene, phenanthrene and benzene, and two naphthalene molecules. The best result is obtained by the method of Dewar and Harget.[1c]

$\pi^*\leftarrow\pi$ Spectra, Ionization Energy and Electron Affinity. The $\pi^*\leftarrow\pi$ spectra calculated by the SCF methods (except the SCF(c)[3] method which is not as good as the other SCF methods in predicting the spectral transitions) with and without configuration interaction (CI) along with the experimental spectra[11-13] are given in Table 3. For the sake of comparison, the results of other workers[5] are given. In the CI procedure the final vectors and integrals obtained by the SCF(d) method were used, all the single excitations being included. For benzazulenes our results are in good agreement with the experimental value, in particular, the results predicted by the CI method which is better than those predicted by Koutecky *et al.*[5b] The same conclusion can be drawn for the benzofluoranthenes (**7**—**10**). However, for molecule **6** the agreement between our results and experimental values is not so good; the results predicted by the CI method are better than the results predicted by other workers.[5b]

Although SCF(a) and SCF(b) methods were parameterized to predict the ground state properties, the spectral transitions predicted by them are in better agreement with the experimental values than the SCF(d) method which was parameterized to predict the $\pi^*\leftarrow\pi$ spectra. The same has been observed.[3]

According to Koopmans' theorem[14] ionization potential (*IP*) is equal to the highest occupied orbital energy. But *IP* predicted in this way is 1 or 2 eV higher than the true ionization potential. Hence a correction should be introduced. The ionization potential can be given by the relation

$$IP = -(\varepsilon_i + c)\ \text{eV}$$

where ε_i is the highest occupied orbital energy and '*c*' is the correction term. Bloor[15a] used a value of 1.33 for the correction term '*c*' and we have used it in predicting the *IP* by the SCF(a) or SCF(b) method. For the SCF(d) method the value of the correction term is 1.06 as suggested by Kunii and Kuroda.[16] It has been found that a value of 1.88[15b] for '*c*' gives very good prediction of *IP* in SCF(c) method. The calculated values of ionization potential are given in Table 4. According to Bloor[15a] the half-wave reduction potential, measured in 95% aqueous dioxane, can be fitted by a relation. If the SCF(d) method is used, the half-wave reduction potential for molecules **7**—**10** are well reproduced by the relation

$$\varepsilon_{1/2} = -(\varepsilon_j + 4.60)\ \text{eV}$$

where ε_j is the lowest unoccupied orbital energy. The predicted values of half-wave reduction potential, $\varepsilon_{1/2}$, using the SCF(d) method along with the experimental values of $\varepsilon_{1/2}$ where available and calculated values of π-dipole moment are also given in Table 4. The experimental value $(1+0.2D)$[19] has been reported only for molecule **10**. For comparison we have included the values of Dewar *et al.*[5f] for monobenzazulenes.

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Table 4. Ionization potential (eV), electron affinity (eV) and π-dipole moment (*D*)

Molecule	Ionization potential			Electron affinity		π-Dipole moment			Other work	
	SCF(a) or SCF(b)[a]	SCF(c)	SCF(d)	$\varepsilon_{1/2}$, Bloor, SCF(d)	$-\varepsilon_{1/2}$, expt.	SCF(a) or SCF(b)[a]	SCF(c)	SCF(d)	Ref. 5f	Ref. 21
1	7.36	7.23	7.23	−1.95		2.4	1.39	2.32	1.86, 1.32	2.24
2	7.77 (7.76)	7.54	7.60	−1.69		2.5 (2.4)	1.46	2.34	1.96, 1.41	2.40
3	7.65	7.46	7.49	−1.78		2.3	1.52	2.52	2.01, 1.41	
4	7.50 (7.49)	7.32	7.39	−1.83		2.0	1.79	1.16		
5	7.01	6.88	6.86	−1.27		3.7	2.37	3.76		
6	8.46 (8.15)	7.73	7.92	−2.08		0	0	0.10		
7	7.64 (7.63)	7.30	7.51	−1.66	1.495[b]	0.9	0.57	0.80		
8	8.11 (8.10)	7.72	7.95	−2.02	1.895[b]	0.6	0.41	0.67		
9	7.92	7.61	7.78	−1.85	1.685[b]	0.9	0.57	0.87		
10	7.74	7.43	7.60	−2.09	1.91[b]	0.5	0.26	0.38		0.522[c]

a) Values in parentheses obtained by the SCF(b) method. b) Ref. 17. The half-wave reduction potential has been lowered by 0.52V (Ref. 18). c) Ref. 5c.

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