Semi-Empirical Configuration Interaction Studies on the π-Electron Spectra of Nonbenzenoid Molecules

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A modification of the method of Yamaguchi *et al.* has been used to predict the π-electronic spectra of a number of nonbenzenoid molecules containing five- and seven-membered rings. Good correlation of the theoretical and experimental transition energies is found. The calculated intensities are also reasonably consistent with experiment, to the extent of raising questions as to the source of intensity in the bands of some molecules.

Semi-empirical self-consistent-field calculations have been applied to many molecules with π-electrons with considerable success in reproducing the electronic spectra and ground state properties such as heat of atomization and sites of reactivity.[1,2] The choice of parameters in the semi-empirical context is critical in some of these predictions. In particular, the value of β, the two-centre resonance integral, has a different range of values according to whether it is electronic spectra or heats of atomization that are to be predicted by the calculation.[1]

In the case of electronic spectra, there persist discrepancies between observed and calculated frequencies and oscillator strengths, even with an apparently adequate choice of β. In this paper we therefore report attempts to improve upon the predictions of spectra for some molecules for which we have recently given the results of self-consistent-fields calculations,[3,36,38] now using configuration interaction.

In such work, three primary variations in method can occur: the choice of formula for the two-centre resonance integral, the choice of formula for the two-centre two-electron repulsion integrals and the configurations to be included in the interaction study.

A computer programme was developed which was capable of generating all configurations arising from all possible one- and two-electron excitations involving all of the occupied and unoccupied orbitals obtained in a prior molecular orbital calculation. It was found that an adequate fit of the experimental spectra could be obtained using only those configurations arising from one-electron excitations, provided the orbitals were the self-consistent-field set, and that such a choice frequently gave a better fit than did the use of the full one- and two-electron excitation set. Therefore all of this work is on the basis of configurations arising from one-electron excitations involving orbitals obtained in a prior self-consistent-field calculation. In the case of the larger molecules studied in this work, even this restricted basis is unnecessarily large since many of the configurations which, within the orbital approximation, represent excitation beyond the ionization limit, contribute very little to the functions of interest: those with energies lying within about eight electron volts of the ground state. For such molecules a restricted number of the highest occupied orbitals and the lowest unoccupied orbitals were involved in excitations to form the configurations used as basis.

In the recent literature, two methods of calculating two-centre, two-electron repulsion integrals, γ_{ij}, have been much used: the formulae of Ohno[4] and of Nishimoto and Mataga.[5] The former has been used very successfully in the context of self-consistent-field studied toward obtaining heats of atomization and resonance energies.[1,2,6] We have also found it to be good for use for similar studies directed toward obtaining electronic spectra predictions.[3,36,38] In the present work, on the other hand, we have found that the Nishimoto-Mataga formula,

$$\gamma_{ij} = 14.397/(1.293+r_{ij}). \quad \text{(eV)} \qquad (1)$$

with r_{ij} the internuclear separation (Å), yields superior fitting between the observed spectra and those calculated using the configuration interaction method. In this formula the parameter value, 1.293, is chosen so that the one-centre two-electron repulsion integral, γ_{ij}, has the value 11.134 eV, equal to the difference between the sp^2 valenece state ionization energy (11.16 eV) and electron affinity (0.026 eV) for carbon.[7] In the self-consistent-field calculation, the γ_{ij} between neighbouring atoms were varied at each interaction on the basis of the internuclear separation, r_{ij}, calculated from the bond order (p_{ij})—bond length relation[8]

$$r_{ij} = 1.520 - 0.186p_{ij}. \quad \text{(Å)} \qquad (2)$$

The γ_{ji} integrals between non-neighbouring atoms were based upon a particular choice of molecular geometry and were not varied throughout the calculation. For the benzenoid systems the choice was with all bond lengths equal to 1.40 Å, all bond angles equal to 120°. For azulene,[9] aceheptylene,[10a] pentaleno[*def*]heptalene[10b] and acepleiadylene,[11] the structures reported in the literature were used. For the other molecuels, whose experimental structures were not available reasonable geometries[3,6,36,38] were selected.

The formula used for evaluation of the two-centre resonance integral between neighbouring centres was that of Yamaguchi *et al.*,[8a]

$$\beta_{ij} = \beta_0 \exp[1.7(1.397-r_{ij})], \qquad (3)$$

with the internuclear distance, r_{ij}, calculated as described above and varied at each self-consistent-field interaction. The parameter β_0 was chosen to depend upon the number of rings[8b] in the molecule under investigation, on the basis of fitting the spectra of benzenoid systems. For benzene, $\beta_0 = -2.38$ eV, for naphthalene and azulene, $\beta_0 = -2.28$ eV, and for larger molecules, $\beta_0 = -2.15$ eV were used. Results for these

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TABLE 1. $\pi^* \leftarrow \pi$ TRANSITIONS AND OSCILLATOR STRENGTHS, f

Molecule	Sym-metry	Experimental		Present work		Other work							
		eV	log ε (or f)	eV	f[c]	eV	f	eV	f	eV	f	eV	f[a]
I		Ref. 18				Ref. 14		Ref. 39		Ref. 40			
(10)[b]	B_{2u}	4.8		4.89	0	4.880		5.28	0	4.71	0		
	B_{1u}	6.2	0.1	6.19	0	5.760		5.90	0	6.01	0		
	E_{1u}	6.7	0.9	7.01	1.203	6.972		7.30	2.50	6.83	1.167		
II		Ref. 19				Ref. 14		Ref. 8		Ref. 40			
(26)	B_{3u}	4.0	0.002	4.02	0.001	4.033	0	4.18	0	4.02	0		
	B_{2u}	4.5	0.18	4.55	0.183	4.419	0.200	4.68	0.20	4.52	0.204		
	A_g			5.54	0	5.461	0	5.76	0				
	B_{3u}	5.6	1.70	5.61	1.901	5.582	1.960	5.77	1.96	5.66	1.949		
	B_{1g}			5.79	0	5.648	0	5.97	0				
	B_{1g}			6.10	0	5.993	0	6.29	0				
	B_{2u}	6.5	0.20	6.11	0.628	6.073	0.579	6.30	0.65	6.15	0.615		
	A_g			6.92	0	6.861	0						
				7.08	0	6.987	0						
	B_{1g}			7.58	0	7.536	0						
				7.65	0	7.603	0						
	B_{2u}	7.4	0.6	7.71	0.926	7.626	0.953						
III		Ref. 19				Ref. 14		Ref. 40		Ref. 41			
(26)	B_{3u}			3.46	0.003					3.58	0		
	B_{2u}	3.3	0.10	3.54	0.242	3.484	0.317	3.58	0.274	3.59	0.313		
						3.604	0						
	B_{1g}			4.62	0	4.656	0			4.50	0		
				4.63	0	4.677	0			4.79	0		
	A_g			4.70	0	4.814	0			4.81	0		
	B_{3u}	4.8	2.28	4.79	2.616	4.831	2.522	4.97	2.745	4.84	2.523		
										5.19	0.044		
	B_{2u}			5.30	0	5.264	0			5.36	0		
	B_{2u}	5.6	0.28	5.62	0.231	5.850	0.221	5.903	0.087	5.87	0.604		
	B_{3u}			5.72	0								
	B_{2u}			5.74	0.169	5.916	0.560						
	A_g			5.98	0	6.059	0						
				6.17	0	6.206	0			6.21	0		
				6.51	0	6.574	0						
	B_{1g}			6.65	0								
	B_{2u}	6.7	0.65	6.75	1.065								
IV		Ref. 20				Ref. 14		Ref. 39		Ref. 40			
(26)	A_1	3.8	0.003	3.61	0	3.630	0	4.00	—	3.75	0		
	B_2	4.2	0.18	4.19	0.244	4.157	0.322	4.15	0.30	4.28	0.311		
				4.45	0.006	4.615	0						
		4.9	1.09	4.88	1.564	4.922	1.486	4.73	1.78	5.03	1.541		
	A_1			4.99	0.544	4.978	0.540	5.04	1.09	5.12	0.572		
				5.18	0.002	5.249	0	5.17	—				
				5.44	0.270	5.497	0.330						
	B_2			5.73	0	5.757	0	5.23	—				
	A_1			5.75	0.001	5.820	0						
	B_2	5.8	0.60	5.89	0.283	5.950	0.265	5.85	0.24	5.67	0.303		
				6.03	0.099	6.071	0.200						
	A_1			6.43	0.001	6.445	0						
	B_2			6.44	0.002	6.468	0						
	A_1	6.6	0.59	6.53	0.455	6.657	0.446	6.32	0.26	6.15	0.263		
	B_2			6.58	0.162	6.763	0.125	6.74	0.47				
V		Ref. 21				Ref. 14		Ref. 40		Ref. 41			
(26)	B_{2u}	3.3	2.41	3.35	0	3.470	0	3.36	0	3.49	0		
	B_{3u}	3.7	4.74	3.64	0.629	3.556	0.680	3.68	0.701	3.64	0.675		
	B_{1g}			4.30	0	4.271	0			4.10	0		
	B_{1g}			4.38	0	4.306	0			4.27	0		

TABLE 1. (Continued)

Molecule	Sym-metry	Experimental eV	Experimental log ε (or f)	Present work eV	Present work f[c]	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f[a]
	B_{2u}	4.6	4.73	4.73	0.099	4.703	0.948	4.84	0.956	4.77	0.954		
	A_g			4.86	0	4.832	0			4.90	0		
	B_{1g}			4.98	0	4.946	0			5.00	0		
	B_{3u}	5.2	4.94	5.14	1.612	5.207	1.468	5.38	1.616	5.25	1.485		
	A_g			5.21	0	5.199	0			5.08	0		
				5.27	0	5.266	0			5.33	0		
				5.95	0	5.939	0			5.98	0		
	B_{2u}	6.0	4.68	5.96	0.001	5.985	0						
	B_{1g}			6.02	0	5.997	0						
				6.04	0	6.040	0						
	B_{3u}	6.3	4.59	6.37	1.034	6.319	0.940			6.47	1.046		
VI		Refs. 20 and 22				Ref. 31		Ref. 32					
(82)	B_u	3.4	2.301	3.43	0.001	3.22	0.15	3.47	0.003				
	B_u	3.8	3.785	3.82	0.408	4.24	0.45	3.91	0.28				
	B_u	4.6	4.813	4.55	2.073	4.60	0.46	4.93	2.81				
	B_u			4.94	0.097								
	B_u			4.98	0.550								
	B_u			5.42	0.001								
	B_u	5.6	4.155	5.52	0.267	5.78	0.07	5.36	1.14				
	B_u			6.06	0.256								
	B_u	6.4	4.025	6.47	0.265	6.34	0.95						
	B_u	6.7	4.699	6.68	0.935								
VII		Ref. 23				Ref. 14		Ref. 8		Ref. 3b			
(26)	B_2	2.0	0.009	1.94	0.023	1.918	0.0221	2.05	0.025	2.28	0.13		
	A_1	3.4	0.08	3.42	0.005	3.370	0.005	3.53	0.005	3.63	0.85		
	B_2			4.26	0.132	4.221	0.117	4.41	0.13				
	A_1	4.5	1.10	4.65	1.827	4.616	1.818	4.78	1.88	4.10	0.47		
	B_2	5.2	0.38	5.50	0.392	5.499	0.443	5.68	0.41	5.05	0.28		
	A_1			5.83	0.010	5.806	0.022	6.03	0.010				
	B_2			6.19	0.188	6.147	0.118	6.41	0.19				
	A_1	6.4	0.65	6.51	0.387	6.439	0.402	6.72	0.39	6.17	0.22		
	B_2			6.80	0.744	6.791	0.782						
VIII		Ref. 16				Ref. 16		Ref. 15		Ref. 33			
(37)	B_2	2.7	1.4	3.05	0.014	2.75	0.04	2.614	0.041	2.796		2.74[49]	0.04
	B_2	3.7	3.7	3.63	0.124	3.75	0.31	3.699	0.243	3.744		3.72	0.30
	A_1	3.8	4.0	3.77	0.236	3.83	0.22	3.934	0.156	3.817		3.76	0.20
	A_1	4.5	3.5	4.59	0	4.75	0	4.551	0.044	4.824		4.74	0.002
	B_2	5.4	4.7	5.24	1.239	5.56	1.21	5.629	1.076	5.572		5.52	1.21
	A_1	≈6.14[49]		6.18	1.355								
IX		Ref. 24				Ref. 17		Ref. 13		Ref. 3b			
(37)	B_2	1.8		1.58	0.003	1.73	0.003	1.65	0	1.67	0.03		
	A_1	2.6	2.94	2.65	0.001	2.91	0.001						
	A_1	3.2	3.33					3.02	0	2.95	0.18		
	A_1	3.4	3.21	3.38	0.049	3.64	0.073			3.80	0.86		
	B_2	3.8	4.80	3.58	0.089	3.86	0.11	3.74	0.036	3.59	0.49		
	A_1							3.85	0.094				
	B_2	4.7	4.65	4.49	0.384	4.79	0.39	5.23	0.778	4.17	0.46		
	A_1			4.66	1.505								
X		Refs. 42 and 34				Ref. 36a		Ref. 31		Ref. 34			
(50)	B_{2u}	2.90		2.98	0.043			2.77	0.49				
		3.04											
		3.06								3.23	0.048		
		3.22				3.25	0.09	3.15	0.15				
	B_{3u}	3.64		3.52	0.276	3.51	0.65						
	B_{2u}	3.73		3.78	0.145	3.69	0.85	3.64	0.24	3.75	0.33		
		3.80								4.09	0.18		

Table 1. (Continued)

Molecule	Sym-metry	Experimental		Present work		Other work							
		eV	log ε (or f)	eV	f[c]	eV	f	eV	f	eV	f	eV	f[a]
	B_{2u}	5.23		5.07	0.00	5.28	0.44	5.04	0.37	5.41	0.008		
	B_{3u}	5.69		5.56	0.26	5.54	0.60	5.67	0.37	5.99	2.18		
	B_{2u}			5.62	2.002								
XI		Ref. 25				Ref. 36a		Ref. 15		Ref. 31			
(50)	B_2	2.22	2.05			2.52	0.20	2.173	0.065	2.774	0.08	2.33[49]	0.06
		2.92	2.58	2.81	0.036								
		3.23	3.20										
		3.35	3.68										
	A_1	3.49	3.85	3.49	0.352	3.51	0.70	3.359	0.334	3.454	0.67	3.34	0.41
	B_2	3.64	3.90	3.55	0.058					3.539	0.01	3.68	0.10
		4.20	3.95			3.94	0.48	3.910	0.051				
	A_1	4.35	3.95	4.49	0.001							4.46	0.003
	B_2	4.59	3.87			4.60	0.68	4.286	0.015				
	B_2	4.98	4.49	4.95	0.602	5.10	0.67			4.900	0.44	5.10	0.85
	A_1	5.06		5.11	0.161	5.21	0.25	5.089	0.022	5.168	0.07	5.14	0.52
	B_2	5.39	4.42	5.25	0.390	5.23	0.44			5.368	0.05	5.53	0.07
				5.34	0.019								
	A_1	≈5.77[49]		5.65	0.901							5.82	0.85
	B_2	5.93	4.60	5.83	0.534	6.08	0.29						
	A_1			5.91	0.544								
XII		Ref. 24				Ref. 17		Ref. 13		Ref. 3b			
(50)	B_2	1.6	2.108	1.45	0.012	1.52	0.014	1.56	0.01	1.68	0.07		
	A_1	2.9	2.81	2.66	0.005	2.89	0.009	3.09	0.038	3.29	0.17		
	B_2	3.3	4.09	3.26	0.279	3.47	0.30	3.46	0.16	3.28	0.70		
	A_1	4.0	4.0	4.26	0.531	3.82	0.14	4.06	0.087	4.13	0.53		
	B_2			4.16	0.013	4.48	0.019			4.25	0.35		
	A_1	4.8		5.10	0.321	4.57	0.53						
	B_2	4.9		4.64	1.438	4.95	1.44	4.94	0	5.20	0.07		
XIII		Ref. 51				Ref. 16		Ref. 15		Ref. 36a		Ref. 51	
(65)	B_2	3.07	0.012	3.40	0.002	3.32	0.01	3.331	0.023	3.44	0.24	3.57	0.005
	A_1	3.41	0.17	3.51	0.372	3.51	0.52	3.583	0.640	3.57	0.81	3.69	0.43
	B_2	3.84	0.05	3.68	0.051	3.93	0.08	4.094	0.068	4.03	0.52	3.91	0.06
	A_1	4.30	0.55	4.26	0.214	4.48	0.22	4.697	0.199			4.50	0.22
	A_1	4.70	(0.14)[d]	4.75	0.020	5.08	0.01			4.83	0.53	5.03	0.02
	B_2	4.73	(0.08)	4.98	0.069	5.13	0.05	5.196	0.028	4.96	0	5.19	0.06
	A_1			5.06	0.517	5.26	0.60			5.18	0.20		
	B_2	5.23	0.44	5.12	1.078	5.39	1.28	5.252	0.003	5.57	0.01	5.34	1.16
	A_1	5.39	(0.13)	5.53	0.829							5.31	0.58
	A_1	5.73	0.26	5.90	0.012							5.80	0.81
	B_2	6.08	(?)	6.07	0.241							6.17	0.01
XIV		Refs. 12 and 25				Ref. 3a		Ref. 15		Ref. 34			
(65)	A_1	2.5	3.6	2.82	0.259			2.504	0.002	2.98	0.28		
								2.553	0.056				
	B_2	3.0		2.95	0.013	2.9	0.26	2.986	0.115	3.15	0.026		
				3.09	0.059	3.1	0.31						
						3.3	0.98			3.32	0.066		
	B_2	3.8	4.6	3.54	0.017	3.9	0.43	3.998	1.715	3.87	0.025		
	A_1			4.25	0.642	4.2	0.39	4.187	0.207	4.50	0.96		
				4.35	0.365	4.4	0.51			4.67	0.16		
						4.6	0.0						
	B_2	4.8	4.3	4.79	0.798	4.7	0.01			5.09	0.87		
						5.0	0.0						
	A_1			4.90	0.032					5.13	0.010		
	A_1			5.27	0.027	5.34[g]	0.44			5.26	0.021		
	B_2			5.29	0.375	5.35[g]	0.23						
	B_2					5.4	0.01						

TABLE 1. (Continued)

Molecule	Sym-metry	Experimental eV	Experimental log ε (or f)	Present work eV	Present work f[c]	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f[a]
	B_2			5.67	0.111								
	A_1									5.64	0.021		
	B_2	5.8		5.84	0.665	5.84[g]	0.31			5.68	0.40		
	A_1			5.91	1.043								
XV		Refs. 12 and 26				Ref. 3a		Ref. 15		Ref. 12			
(65)		2.2	2.8	2.36	0.080	2.6	0.46	1.803		2.10	0.08		
		3.0	3.4	3.04	0.068	2.9	0.24	2.792		2.89	0.3		
				3.47	0.054			3.496					
		3.6	3.9	3.65	0.182	3.7	0.73	3.722		3.61	0.6		
						3.8	0.35						
		4.0		4.04	0.051	4.1	0.49	4.153		3.90	0.1		
						4.2	0.18						
										4.31	0.2		
				4.66	0.223								
		4.6	4.5	4.70	0.623	4.7	0.42			4.51	1.3		
XVI		Refs. 12 and 27				Ref. 3a		Ref. 15		Ref. 12			
(65)		2.4	2.9	2.44	0.107			1.949		2.23	0.1		
						2.8	0.24						
		2.9	3.8	3.08	0.095	2.9	0.77	2.746		2.90	0.5		
		3.4		3.41	0.092	3.5	0.21	3.674					
				3.75	0.160					3.78	0.3		
				4.12	0.071	3.9	0.56	3.910		3.83	0.07		
		4.3	4.5	4.52	0.234	4.3	0.49	4.118		4.18	1.2		
						4.4	0.16			4.37	0.8		
				4.57	0.494	4.6	0.32						
		4.9	4.8	4.73	0.913	5.0	0.11			4.61	0.4		
						5.2	0.37						
XVII						Ref. 3b		Ref. 12					
(26)	B_2			0.54	0.029	0.77	0.09	0.22	0.01				
	A_1			2.29	0.092	2.37	0.27	1.98	0.2				
	A_1			2.36	0.135	2.49	0.19	2.22	0.03				
	B_2			2.98	0.006			3.39	0.004				
	B_2			3.29	0.019	3.37	0.48	3.45	0.02				
	B_2			4.05	0.353	3.77	0.85	3.90	1.6				
	A_1			4.08	0.158	4.26	0.47						
	B_2			4.16	0.009	4.21	0.09						
						4.23	0.00						
	A_1			4.36	0.125	4.48	0.09						
	B_2			4.80	2.321								
	A_1			5.09	0.766								
	A_1			5.48	0.076								
XVIII		Refs. 12 and 28				Ref. 3a		Ref. 12					
(65)		1.8	2.1	1.65	0.006			1.81	0.004				
		2.2	3.1	2.18	0.009	2.2	0.016	2.38	0.05				
		2.8	3.8	2.96	0.056	2.9	0.21	3.11	0.3				
				3.11	0.076	3.0	0.55	3.20	0.09				
		3.4		3.58	0.101	3.4	0.53	3.66	1.1				
				3.95	0.074	3.8	0.37	4.07	0.9				
				4.17	0.522	4.1	0.31	4.30	0.2				
		4.3		4.43	1.665	4.3	0.22	4.43	1.1				
		4.9		4.84	0.277	5.0	0.20						
XIX		Ref. 29				Ref. 3b		Ref. 12		Ref. 35			
(26)	B_{1g}	(1.61)	(1—1.65)	1.67	0	1.83	0	1.82	0	1.81	Forb.		
	B_{2u}	2.6	4.11	2.41	0.139			2.54	0.2	2.62	0.163		
	A_g			2.98	0			3.05	0	3.19	Forb.		
	B_{3u}	3.0	2.92	3.21	0.010	3.27	0.74	3.20	0.1	3.46	0.015		

Table 1. (Continued)

Molecule	Sym-metry	Experimental		Present work		Other work							
		eV	log ε (or f)	eV	f[c]	eV	f	eV	f	eV	f	eV	f[a]
	B_{2u}	3.6	4.13	3.86	0.048	3.51	0.73	3.91	0.0004				
	B_{3u}	4.2	4.32	3.98	0.678	4.07	0.23	3.72	1.7				
	B_{2u}	4.6	5.03	4.70	0.987	4.59	0.59	4.18	2.1	4.19	0.51		
XX		Ref. 43				Ref. 12		Ref. 3b		Ref. 35		Ref. 43	
(65)	B_{1g}	1.74	0.002	1.61	0	1.84	0	1.72	0	1.85	0	1.88	0
	B_{2u}	2.47	0.04	2.40	0.205	2.64	0.5			2.68	0.254	2.54	0.24
	A_g	2.93	0.002	2.95	0	2.93	0	3.08	0	3.21	0	2.85	0
	B_{3u}	3.19	0.09	3.19	0.025	3.20	0.2	3.25	1.27	3.47	0.058	3.21	0.16
		3.22											
	B_{2u}	3.60	0.09	3.64	0.004	3.47	0.4	3.57	0.63	3.93	0.007	3.66	0.09
	B_{1g}			3.87	0			3.84	0				
	B_{3u}	3.87	0.26	4.08	0.619			3.87	0.61			4.41	0.45
	B_{2u}	4.33	1.2	4.49	2.810	4.01	2.5	4.00	0.97			4.74	3.25
	B_{3u}	4.65		5.18	0.486							5.38	0.43
	B_{1g}	5.02		5.22	0							5.51	0
	A_g	5.27		5.25	0							5.56	0
	A_g	5.52		5.53	0								
XXI		Ref. 30				Ref. 3b		Ref. 35					
(82)	B_2	1.2	1.74	1.03	0.012	1.41	0.01	1.19	0.017				
	A_1	2.1	2.44	2.08	0.006	2.57	0.04	2.29	0.005				
	B_2			2.93	0.049			3.18	0.191				
	A_1	3.1	3.67	3.07	0.114	3.21	0.01	3.36	0.117				
	A_1			3.26	0.146			3.54	0.208				
	B_2	3.7	3.88	3.64	0.236	3.76	0.14						
	B_2			3.83	0.054								
	B_2	4.2	4.88	4.10	1.221	4.26	0.78						
	A_1			4.78	1.205								
	B_2			5.20	0.726								
	A_1	5.32	4.40	5.34	0.468	5.17	0.01						
XXII						Ref. 34		Ref. 31		Ref. 36a			
(82)	B_{1g}			2.07	0	2.15	0			1.70	0		
	B_{3u}			2.93	0.006			2.628	0.59	3.25	0.33		
	B_{2u}			3.07	0.527	3.13	0.014	3.096	0.01	3.16	1.00		
	B_{3u}			3.42	0.113	3.30	0.60	3.449	0.15	3.48	0.38		
	B_{2u}					3.69	0.15						
	A_g			4.16	0	4.51	0			4.41	0		
	B_{3u}			4.38	0.036			4.519	0.03	4.45	0.58		
	A_g			4.52	0	4.94	0			4.79	0		
	B_{2u}			4.94	0.989	4.70	0.091	5.111	1.08	4.95	1.00		
	B_{3u}			5.11	1.304	5.30	1.17						
	B_{1g}			5.34	0	5.46	0						
	B_{2u}			5.69	1.072	5.49	1.71			5.25	0.44		
XXIII		Ref. 50				Ref. 36a		Ref. 50					
(82)	B_2	1.45≃3.00		1.99	0.089	1.98	0.28	1.52					
	A_1	2.46	2.00										
	A_1	2.86	4.00	3.06	0.417	3.21	1.03	2.93					
	B_2	3.29		3.39	0.086			3.45					
	A_1	3.61	3.60	3.97	0.004	3.83	0.37	3.82					
	B_2	4.09		3.78	0.090	3.88[e]	0.15	3.66					
	A_1	4.25		4.31	0.643	4.33	0.95	3.87					
	B_2	4.45≃4.30		4.78	0.354	4.74	0.65	4.28					
	A_1	4.77≃4.30		4.82	1.019			4.80					
	B_2			4.95	0.297								
	A_1			4.96	0.171	5.06	0.07	4.88					
	B_2	5.13≃4.30		5.25	0.013	5.19[e]		5.18					
	A_1			5.45	0.082			5.33					

TABLE 1. (Continned)

Molecule	Sym-metry	Experimental eV	Experimental log ε (or f)	Present work eV	Present work f[c]	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f[c]
	B_2			5.55	0.084								
	B_2	5.75	4.48	5.79	0.960			5.64					
XXIV		Ref. 45				Ref. 36a		Ref. 52					
(82)		3.40	3.96	3.12	0.064	3.25	0.27	3.26	0.06				
		3.54	3.99	3.44	0.380	3.26	0.78	3.60	0.48				
		4.13	3.58	4.02	0.241	4.18	0.52	4.13	0.03				
		4.59	3.96	4.57	0.017	4.55	0.71	4.55	0.23				
				4.75	0.435			4.74	0.07				
				4.97	0.813			4.96	0.22				
		5.20	4.54	5.17	0.751	5.27	0.43	5.31	0.41				
		5.39	4.58	5.39	0.299	5.36	0.26	5.39	0.17				
								5.53	0.85				
XXV						Ref. 36a		Ref. 44					
(82)	B_2			2.40	0.002	2.05	0.01	2.01					
								3.15					
	A_1			3.24	0.446	3.35	0.88	3.20					
	B_2			3.83	0.099	3.90	0.84	3.87					
								4.62					
	A_1			4.78	0.550	4.63	0.02	4.75					
	A_1			5.18	0.423	5.20	0.51	5.11					
	B_2			5.49	1.404	5.42	0.37	5.48					
XXVI		Ref. 46				Ref. 36a							
		1.84	3.20										
(82)	B_2	1.91	3.17	2.11	0.093	2.26	0.34	1.98[53),f)]					
		2.01	3.14										
	A_1			2.28	0.164			2.21					
	B_2	3.29	4.69	3.08	0.033	3.22	0.30	3.24					
	A_1	3.43	4.51	3.62	1.709	3.52	0.70	3.59	>0.2				
	A_1	3.91	4.04[53),f)]	3.79	0.137			3.76					
								3.80	<0.02				
								3.81					
	B_2	4.23	4.25	4.12	0.035	4.04	0.39	4.27	<0.02				
	B_2	4.38	4.23	4.59	0.672	4.29	0.05	4.33					
	A_1	5.17	4.23	5.09	0.548	4.98	0.02						
	A_1	5.46	4.32	5.24	0.165	5.52	0.45						
	A_1			5.52	0.211								
XXVII						Ref. 36a							
(82)				2.92	0.320	2.97	0.35						
				2.95	0.123								
				3.35	0.027	3.13	0.97						
				3.50	0.084	3.43	0.31						
				3.94	0.187	3.79	0.38						
				4.30	0.088								
				4.35	0.679	4.41	0.55						
				4.43	0.222	4.49	0.32						
				4.80	0.114								
				4.89	0.870	4.84	0.40						
				5.09	0.338								
				5.46	0.153	5.41	0.41						
XXVIII		Ref. 47				Ref. 36a		Ref. 37		Ref. 31			
(82)	B_{3u}	3.02	4.55	3.13	0.696	3.24	1.08	3.06		2.779	1.20		
	B_{2u}	3.38	3.98	3.28	0.035					4.434	0.02		
		3.55	3.58			3.78	0						
	B_{3u}	4.24	5.10	4.21	0.436	4.20	0.89	3.98		4.003	0.07		
	B_{3u}	4.72	4.53	4.85	0.997	4.86	0.62			4.645	0.32		
	B_{2u}	4.90	4.56	4.96	0.260	5.04	1.00	4.85		4.825	0.16		

Table 1. (Continued)

Molecule	Sym-metry	Experimental eV	Experimental log ε (or f)	Present work eV	Present work f[c]	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f	Other work eV	Other work f[a]
XXIX		Ref. 48				Ref. 38							
(82)	B_{3u}	3.22	4.19	3.16	0.718	3.22	0.97						
	B_{3u}	4.26	4.09	4.42	0.001	4.14	0.56						
	B_{2u}	5.07	4.30	4.88	0.509	5.31	0.24						
	B_{3u}			5.11	0.082								
	B_{2u}	5.52	4.72	5.55	1.438	5.52	0.93						

a) *f*-Values quoted in column 8 were not included in Ref. 3a (molecules XIV—XVI and XVIII). b) Figure in the parentheses in the first column indicates the number of configurations. c) Figures in fourth column are *f*-values for molecules I—IV and VII and others they correspond to log ε. d) Values in parentheses in third column refer to shoulder. e) Not included in the Ref. 36a. f) *f*-Values not shown lie between 0.02 to 0.2. g) Not included in the Ref. 3a.

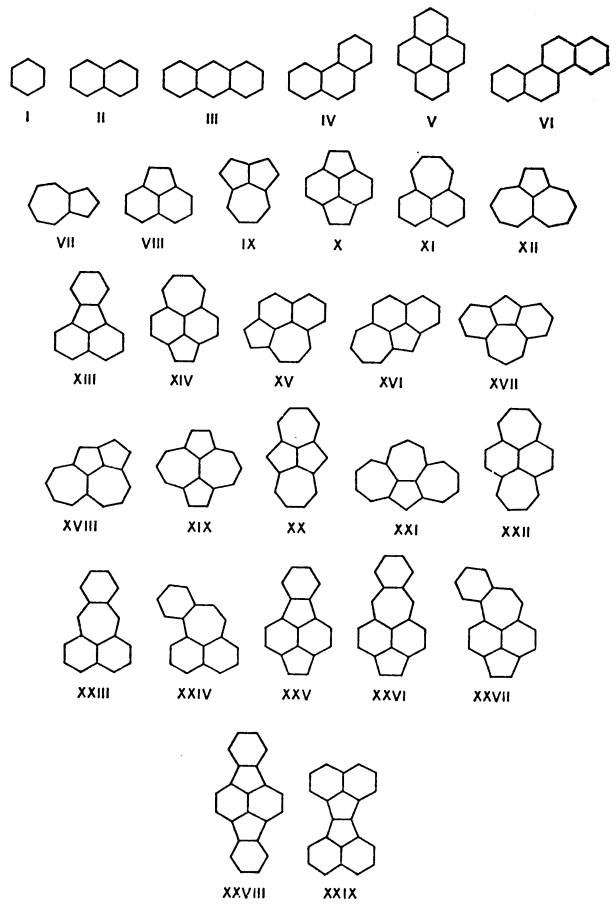

Fig. 1. Molecules studied.
I: Benzene, II: naphthalene, III: anthracene, IV: phenanthrene, V: pyrene, VI: chrysene, VII: azulene, VIII: acenaphthylene, IX: aceazulylene, X: pyracylene, XI: pleiadiene, XII: acheptylene, XIII: fluoranthene, XIV: acepleiadylene, XV: naphth[*cde*]-azulene, XVI: cyclohept[*bc*]acenaphthylene, XVII: cyclohept[*def*]fluorene, XVIII: pentaleno[*def*]heptalene, XIX: azupyrene, XX: dicyclohepta[*cd,gh*]-pentalene, XXI: azuleno[8,8a,1,2-*def*]heptalene, XXII: dipleiadadiene, XXIII: benzopleiadiene, XXIV: benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene, XXV: acefluoranthylene, XXVI: benzo[6,7]acepleiadylene, XXVII: benzo[5,6]acepleiadylene, XXVIII: indeno[1,2,3-*cd*]fluoranthene, XXIX: acenaphth[1,2-*a*] acenaphthylene.

standardization molecules are included in Table 1.

Results and Discussion

The calculated electronic spectra are given in Table 1, along with any available experimental data and other theoretical predictions. The standard deviation of the differences between observed and calculated transition energies for the bands chosen for the standardization of β_0 is 0.08 eV. For these benzenoid systems the agreement between theory and experiment is generally very good, with an overall fit as good as, or better than, that achieved by other workers. The results of azulene, a subsidiary test molecule, are also of good quality.

We have reported elsewhere[3,36,38] and included here for comparison, the predicted transitions for some non-benzenoid hydrocarbons (molecules VII to XXIX) using a different parameterization and the self-consistent field method. In almost all cases the present results achieved a consistently better correlation with experiment. The comparison with the results of other workers[8,12,17,31,33–35,37] yields the same general conclusion.

In most cases there is not only reasonable agreement for the transition energies but also a definite, if rough, agreement in the trends followed by the intensities. There are, however, notable exceptions, when the theoretical intensity is reasonably large. Examples of this are the 4.5 eV transition of acenaphthylene and the 3.8 eV transition of acepleiadylene. An experimental study of such transitions to determine whether their intesity may be due to vibronic coupling would be worthwhile.

In recent years Michl *et al.*[49–53] studied the electronic structure of the excited states of some of the molecules studied here (VIII, XI, XIII, XX, XXIII, XXIV, and XXVI). If we consider single excitations then it would be clear from the table that our results are in better agreement with the experiment than those of Michl *et al.*

Conclusion. It has been found that by slight modification of the method of Yamaguchi *et al.* by making the value of β_0 dependent on the size of the molecules $\pi^* \leftarrow \pi$ spectral transitions of a large number of conjugated systems can be predicted with reasonably

good accuracy.

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