3344 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 3344—3355 (1980) [Vol. 53, No. 11

Configuration Analysis and Electronic State Properties. III. Ten-π-electron Systems

Giuseppe Buemi
Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania,
Viale A. Doria 8, 95125 Catania, Italy

(Received November 8, 1979)

The electronic state properties of the nonbenzenoid hydrocarbons fulvalene, heptatriafulvalene, dimethylenebenzocyclobutene, [5]radialene, 8-vinylheptafulvene, 1,2-benzofulvene and 2,3-benzofulvene have been studied by means of MIM and PPP-configuration analyses. The resonance integrals evaluated by Kon's equation are satisfactory for the MIM method but not for PPP. On the whole the general spectral trend is fairly predicted by both approximations, the wavefunction composition being in line with the first electronic transitions. The lower energy electronic transitions are found to be a mixture of locally excited and charge transfer states while those computed at higher energy have prevailing charge transfer character.

The electronic state properties of several nonbenzenoid hydrocarbons having four, six and eight π-electrons have been studied[1,2] by means of PPP[3] and MIM methods,[3,4] employing the configuration analysis procedure[5] to interpret the results of PPP calculations directly in terms of the locally excited (Λ) and charge transfer (T_m^k) configurations of the localized orbital model. In this paper the same procedure is extended to the following molecules, having a ten-π-electron system: fulvalene (I), heptatriafulvalene (II), dimethylenebenzocyclobutene (III), [5]radialene (IV), 8-vinylheptafulvene (V), 1,2-benzofulvene (VI) and 2,3-benzofulvene (VII).

Ethylene, *cis*- or *trans*-butadiene and benzene were considered as component systems in MIM model. Their SCF-MOs excited states composition and all the parameters required by the adopted methods are the same as in previous papers.[1,2] The experimental transition energies of ethylene are taken from Ref. 6. Both in MIM and PPP approximations all the monoexcited configurations were considered in the configuration interaction treatment, but in the former method the lowest occupied and highest vacant molecular orbitals of the benzene systems were excluded since they are not necessary for its UV spectrum description.

The topology of the compounds examined is shown in Fig. 1. The ground state charge densities and bond orders obtained are given in Table 1.

Fulvalene (1,1'-Bicyclopentadienylidene) (I). This molecule has been the subject of numerous studies at different level of calculations[7—13] including CNDO/CI;[14] its negative topological resonance energy (TRE) indicates that it is an antiaromatic and very reactive compound.[15] The UV spectrum shows a weak absorption band at 2.9—3.0 eV and an intense band at 3.9—4.0 eV.[7,14] My calculation for which the molecular geometry reported by Brown et Coll.[7] was adopted has been performed by assuming, at MIM level, five ethylene molecules (MIM/A) or two *cis*-butadiene and one ethylene molecules (MIM/B) as component systems. The results obtained are compared with those of PPP-configuration analysis (Table 2). PPP correctly predicts the experimental order of the electronic transitions in contrast to MIM, by which the lowest energy electronic transition was obtained as the most intense one. From the energy order of PPP results, the first electronic transition having prevailing charge transfer character is computed at 3.63 eV (calculated

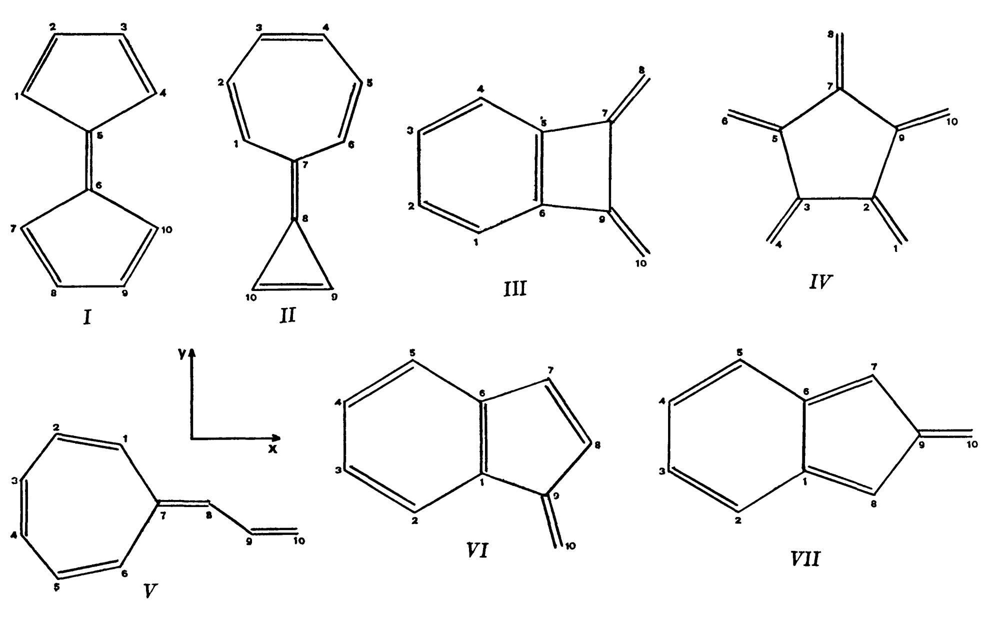

Fig. 1. Topology of the studied molecules,

Table 1. Ground state charge densities (q_i) and bond orders (p_{ij}) of the studied compounds

q_i	PPP	MIM/A	MIM/B	MIM/C	p_{ij}	PPP	MIM/A	MIM/B	MIM/C
					Fulvalene (I)				
1	1.028	1.001a)	1.013b)		1—2	0.926	0.962a)	0.945b)	
2	0.998	1.013	1.007		2—3	0.296	0.179	0.247	
5	0.948	0.971	0.960		1—5	0.244	0.173	0.205	
					5—6	0.882	0.928	0.902	
					Heptatriafulvalene (II)				
1	0.967	1.001a)			1—2	0.898	0.966a)		
2	1.040	1.007			2—3	0.330	0.160		
3	1.002	0.998			3—4	0.893	0.967		
7	1.168	1.141			6—7	0.300	0.166		
8	0.995	0.955			7—8	0.822	0.910		
9	0.910	0.946			8—9	0.299	0.217		
					9—10	0.910	0.946		
					Dimethylenebenzocyclobutene (III)				
1	1.000	1.000c)	1.002d)		1—2	0.662	0.665c)	0.651d)	
2	1.000	1.000	1.002		2—3	0.665	0.656	0.671	
6	1.000	1.000	1.000		1—6	0.658	0.664	0.671	
9	1.000	1.000	1.000		5—6	0.637	0.657	0.651	
10	1.000	1.000	0.996		6—9	0.188	0.129	0.134	
					7—9	0.154	0.166	0.222	
					9—10	0.970	0.971	0.958	
					[5]Radialene (IV)				
1	1.000	1.000a)			1—2	0.945	0.965a)		
					2—3	0.230	0.171		
					8-Vinylheptafulvene (V)				
1(=6)	0.991	1.001a)			1—2(=5—6)	0.939	0.961a)		
2(=5)	0.999	0.997			2—3(=4—5)	0.261	0.185		
3(=4)	0.997	0.997			3—4	0.934	0.960		
7	1.000	1.001			1—7(=6—7)	0.233	0.177		
8	1.022	1.007			7—8	0.920	0.946		
9	0.997	1.000			8—9	0.229	0.171		
10	1.007	1.001			9—10	0.973	0.982		
					1,2-Benzofulvene (VI)				
1	1.010	1.000c)	1.005d)		1—2	0.647	0.664c)	0.663d)	
2	1.002	0.998	0.998		2—3	0.672	0.664	0.663	
3	1.001	1.000	1.006		3—4	0.658	0.654	0.650	
4	1.003	1.006	1.005		4—5	0.674	0.665	0.665	
5	0.997	1.000	0.997		5—6	0.644	0.663	0.661	
6	1.005	1.005	1.004		1—6	0.631	0.654	0.651	
7	1.004	1.008	1.003		6—7	0.255	0.153	0.175	
8	1.014	1.000	1.004		7—8	0.941	0.956	0.950	
9	1.001	1.000	1.003		8—9	0.231	0.213	0.228	
10	0.965	0.982	0.976		1—9	0.230	0.141	0.159	
					9—10	0.944	0.957	0.952	
					2,3-Benzofulvene (VII)				
1	1.004	1.015a)	1.010b)	1.020e)	1—2	0.249	0.168a)	0.216b)	0.238e)
2	0.999	1.000	1.001	1.000	2—3	0.936	0.965	0.942	0.947
3	1.004	1.001	1.001	1.003	3—4	0.273	0.173	0.257	0.212
8	1.024	1.000	1.012	1.002	1—6	0.272	0.184	0.242	0.219
9	1.000	0.999	1.007	0.998	1—8	0.902	0.944	0.918	0.919
10	0.938	0.968	0.947	0.951	8—9	0.238	0.171	0.198	0.194
					9—10	0.940	0.963	0.951	0.952

a) Five ethylene molecules considered as component systems. b) Two *cis*-butadiene molecules and ethylene as component systems. c) Benzene and two ethylenes as component systems. d) Benzene *trans*-butadiene as component systems. e) Two *trans*-butadiene molecules and ethylene as component systems.

TABLE 2. FIRST EXCITED

	Ψ_3		Ψ_4		Ψ_6		Ψ_8	
	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP
							MIM/A: Five ethylene	
Γ	—	—	0.04	0.16	0.04	0.10	—	—
$(1/2)(\Lambda_a+\Lambda_b+\Lambda_d+\Lambda_e)$	—	—	0.12	—	0.04	0.01	—	—
Λ_c	0.27	0.17	—	—	—	—	0.13	0.12
$(1/2)(\Lambda_a+\Lambda_b-\Lambda_d-\Lambda_e)$	0.05	0.03	—	—	—	—	0.01	0.03
$(1/2)(T^b_a+T^a_b+T^e_d+T^d_e)$	—	—	0.28	0.28	0.26	0.08	—	—
$(1/2)(T^b_a+T^a_b-T^e_d-T^d_e)$	0.09	0.11	—	—	—	—	0.85	0.44
$(1/2)(T^c_a+T^c_b+T^c_d+T^c_e)$	0.14	0.09	—	—	—	—	—	0.03
$(1/2)(T^c_a+T^c_b-T^c_d-T^c_e)$	—	—	0.34	0.12	0.06	0.13	—	—
$(1/2)(T^d_a+T^e_b+T^a_d+T^b_e)$	—	—	—	—	0.07	0.09	—	—
$(1/2)(T^d_a+T^e_b-T^a_d-T^b_e)$	0.03	0.03	—	—	—	—	—	—
$(1/2)(T^e_a+T^d_b+T^a_e+T^b_d)$	—	—	—	—	0.08	0.08	—	—
$(1/2)(T^e_a+T^d_b-T^a_e-T^b_d)$	0.02	0.02	—	—	—	—	—	—
$(1/2)(T^a_c+T^b_c+T^d_c+T^e_c)$	—	—	0.22	0.08	0.46	0.20	—	—
$(1/2)(T^a_c+T^b_c-T^d_c-T^e_c)$	0.40	0.30	—	—	—	—	0.01	0.06
Total weight (%)	100	75	100	64	100	69	100	70
E	3.11	4.76	5.31	6.44	6.11	6.83	6.22	7.23
Polarization	y	y	—	—	—	—	y	y
Symmetry	$^1B_{2u}$		$^1A_{1g}$		$^1A_{1g}$		$^1B_{2u}$	
f	0.60	1.13	0	0	0	0	0.16	0.43
					MIM/B: Two *cis*-butadiene molecules			
Γ	—	—	0.01	0.03	0.14	0.15	—	—
$(1/\sqrt{2})(\Lambda_{2a}+\Lambda_{2c})$	—	—	0.37	0.52	0.03	0.03	—	—
$(1/\sqrt{2})(\Lambda_{3a}+\Lambda_{3c})$	—	—	0.07	—	—	0.01	—	—
$(1/\sqrt{2})(\Lambda_{2a}-\Lambda_{2c})$	0.07	0.12	—	—	—	—	0.36	0.49
$(1/\sqrt{2})(\Lambda_{3a}-\Lambda_{3c})$	0.04	0.03	—	—	—	—	0.01	0.03
Λ_b	0.26	0.20	—	—	—	—	0.03	0.15
$(1/\sqrt{2})(T^b_{1a}+T^b_{1c})$	0.15	0.11	—	—	—	—	0.32	0.04
$(1/\sqrt{2})(T^{3c}_{1a}-T^{3a}_{1c})$	0.06	0.06	—	—	—	—	0.01	0.01
$(1/\sqrt{2})(T^{4c}_{2a}-T^{4a}_{2c})$	—	—	—	—	—	—	—	—
$(1/\sqrt{2})(T^{3a}_{b}-T^{3c}_{b})$	0.42	0.33	—	—	—	—	0.27	0.08
$(1/\sqrt{2})(T^{3c}_{1a}+T^{3a}_{1c})$	—	—	—	—	0.42	0.20	—	—
$(1/\sqrt{2})(T^b_{1a}-T^b_{1c})$	—	—	0.25	0.09	0.15	0.15	—	—
$(1/\sqrt{2})(T^{4c}_{2a}+T^{4a}_{2c})$	—	—	—	—	—	—	—	—
$(1/\sqrt{2})(T^{3a}_{b}+T^{3c}_{b})$	—	—	0.30	0.16	0.26	0.19	—	—
Total weight (%)	100	85	100	80	100	73	100	80
ΔE	2.77	4.76	4.66	6.44	6.24	6.83	5.92	7.23
Polarization	y	y	—	—	—	—	y	y
Symmetry	$^1B_{2u}$		$^1A_{1g}$		$^1A_{1g}$		$^1B_{2u}$	
f	0.60	1.13	0	0	0	0	<0.01	0.43

a) a, b, c, d, and e denote the ethylenic fragments $C_1=C_2$, $C_3=C_4$, $C_5=C_6$, $C_7=C_8$, and $C_9=C_{10}$, respectively.

at 3.57—2.91 eV by MIM/A and MIM/B, respectively) and should be assigned to the forbidden $^1B_{1g}\leftarrow{}^1A_{1g}$ transition.

The second electronic transition, polarized along the short molecular axis (x) and computed at 3.81 eV by PPP and at 3.39—3.03 eV (in agreement with experimental result) by MIM/A and MIM/B, is assigned to a $^1B_{3u}\leftarrow{}^1A_{1g}$ transition. It shows noticeable percentage of locally excited states but the largest weights are those due to electronic transfers partially localized inside the two cyclopentadienyl systems and partially directed towards the "external" molecular ethylenic fragment joining the two pentatomic rings. This composition closely resembles that of the lowest energy $^1B_2\leftarrow{}^1A_1$ transition in fulvene, calculated in the range 2.9—3.3 eV.[1)]

The most intense third electronic transition, corresponding to the strong absorption band at $\simeq$4.0 eV, is predicted at 4.76 eV by PPP, very close to the value of 4.93 eV obtained by Marschner and Pohle,[10)] and at 3.11—2.77 eV by MIM/A and MIM/B. It is a $^1B_{2u}\leftarrow{}^1A_{1g}$ transition polarized along the y molecular axis and results principally from the electronic transfer from the "external" ethylene fragment to the two cyclopentadienyl rings. A similar situation is encountered in the $^1A_1\leftarrow{}^1A_1$ transition of fulvene,[1)]

SINGLET STATES OF FULVALENE

	Ψ_1		Ψ_2		Ψ_5		Ψ_7	
	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP
molecules as component systems[a)]								
$(1/2)(\Lambda_a-\Lambda_b+\Lambda_d-\Lambda_e)$	—	—	0.37	0.16	—	—	0.17	0.30
$(1/2)(\Lambda_a-\Lambda_b-\Lambda_d+\Lambda_e)$	0.30	0.20	—	—	0.14	0.28	—	—
$(1/2)(T_a^b-T_b^a+T_e^d-T_d^e)$	0.34	0.14	—	—	0.19	0.08	—	—
$(1/2)(T_a^b-T_b^a-T_e^d+T_d^e)$	—	—	0.32	0.13	—	—	0.11	0.10
$(1/2)(T_a^d-T_b^e+T_d^a-T_e^b)$	—	—	0.01	0.04	—	—	0.14	0.12
$(1/2)(T_a^d-T_b^e-T_d^a+T_e^b)$	0.02	0.04	—	—	0.14	0.09	—	—
$(1/2)(T_a^e-T_b^d+T_e^a-T_d^b)$	0.02	0.03	—	—	0.15	0.11	—	—
$(1/2)(T_a^e-T_b^d-T_e^a+T_d^b)$	—	—	0.02	0.04	—	—	0.15	0.07
$(1/2)(T_a^c-T_b^c+T_d^c-T_e^c)$	0.32	0.26	—	—	0.38	0.17	—	—
$(1/2)(T_a^c-T_b^c-T_d^c+T_e^c)$	—	—	0.28	0.29	—	—	0.43	0.12
$(1/2)(T_c^a-T_c^b+T_c^d-T_c^e)$	—	—	—	—	—	—	—	0.03
$(1/2)(T_c^a-T_c^b-T_c^d+T_c^e)$	—	—	—	—	—	0.01	—	—
	100	67	100	66	100	74	100	74
	3.57	3.63	3.39	3.81	5.86	6.69	5.78	7.02
	—	—	x	x	—	—	x	x
	$^1B_{1g}$		$^1B_{3u}$		$^1B_{1g}$		$^1B_{3u}$	
	0	0	0.08	0.06	0	0	0.15	0.30
(a and c) and ethylene (b) as component systems.								
$(1/\sqrt{2})(\Lambda_{1a}+\Lambda_{1c})$	—	—	0.22	0.33	—	—	0.55	0.42
$(1/\sqrt{2})(\Lambda_{4a}+\Lambda_{4c})$	—	—	—	—	—	—	—	0.03
$(1/\sqrt{2})(\Lambda_{1a}-\Lambda_{1c})$	0.28	0.39	—	—	0.55	0.37	—	—
$(1/\sqrt{2})(\Lambda_{4a}-\Lambda_{4c})$	—	—	—	—	—	0.04	—	—
$(1/\sqrt{2})(T_{1a}^{4c}-T_{1c}^{4a})$	—	—	—	—	—	—	—	—
$(1/\sqrt{2})(T_{2a}^{b}+T_{2c}^{b})$	0.58	0.31	—	—	0.05	0.20	—	—
$(1/\sqrt{2})(T_{2a}^{3c}-T_{2c}^{3a})$	0.14	0.09	—	—	0.40	0.21	—	—
$(1/\sqrt{2})(T_{b}^{4a}-T_{b}^{4c})$	—	—	—	—	—	0.01	—	—
$(1/\sqrt{2})(T_{1a}^{4c}+T_{1c}^{4a})$	—	—	—	—	—	—	—	0.01
$(1/\sqrt{2})(T_{2a}^{3c}+T_{2c}^{3a})$	—	—	0.16	0.10	—	—	0.44	0.22
$(1/\sqrt{2})(T_{2a}^{b}-T_{2c}^{b})$	—	—	0.62	0.36	—	—	0.01	0.14
$(1/\sqrt{2})(T_{b}^{4a}+T_{b}^{4c})$	—	—	—	—	—	—	—	0.03
	100	79	100	79	100	83	100	85
	2.91	3.63	3.03	3.81	5.35	6.69	5.61	7.02
	—	—	x	x	—	—	x	x
	$^1B_{1g}$		$^1B_{3u}$		$^1B_{1g}$		$^1B_{3u}$	
	0	0	0.01	0.06	0	0	0.21	0.30

computed by MIM at 3.6—4.0 eV shifting to lower energy in fulvalene by the higher percentage of charge transfer states.

Three electronic transitions, all with predominant charge transfer character and theoretically forbidden, were calculated at 6.44, 6.69 and 6.83 eV by PPP and at 5.31—4.66 eV, 5.86—5.35 eV and 6.11—6.24 eV by MIM/A and MIM/B, respectively. They are assigned to $^1A_{1g}\leftarrow{}^1A_{1g}$, $^1B_{1g}\leftarrow{}^1A_{1g}$, and $^1A_{1g}\leftarrow{}^1A_{1g}$ transitions, in order of sequence.

Two other allowed transitions follow at 7.02 and 7.23 eV calculated by PPP, and at 5.78—5.69 and 6.22—5.92 eV by MIM (the first figure refers to MIM/A, the second to MIM/B). The former, of $^1B_{3u}\leftarrow{}^1A_{1g}$ type, x-polarized, is the predicted charge transfer if MIM/A results are taken into account, a mixture of locally excited (Λ_{1a}, Λ_{1c}) and charge transfer states if the MIM/B results are considered. In both cases, however, its composition resembles that of the $^1B_2\leftarrow{}^1A_1$ transition in fulvene at 6.45 eV[1)] with some percentage variation due to the presence of two pentatomic rings in fulvalene. The latter, $^1B_{2u}\leftarrow{}^1A_{1g}$, y-polarized transition, is nearly exclusively due to charge transfers between the ethylene molecules constituting the cyclopentadienyl rings (MIM/A results), and to charge transfers involving the whole π-system with a greater percentage of locally excited states (MIM/B results). The composition is similar in the corresponding $^1A_1 \leftarrow {}^1A_1$ transition at 6.28 eV in fulvene.[1)] It is evident that all the allowed transitions found in fulvalene correspond to the electronic transitions of fulvene as well as in energy and composition.

Heptatriafulvalene (II). The PPP results[16)] subjected to configuration analysis are compared with the MIM ones, the energies and oscillator strengths obtained by using Kon's resonance integrals being given (Table 3). Since no experimental spectrum of heptatriafulvalene has been found in the literature a comparison with the theoretical data is not possible, however a discussion about the theoretical transitions is possible with reference to the heptafulvene and triafulvene molecules. The first electronic transition,

TABLE 3. FIRST SINGLET EXCITED STATES OF HEPTATRIAFULVALENE. FIVE ETHYLENE MOLECULES AS COMPONENT SYSTEMS[a)]

States of $^1A_1$ symmetry	Ψ_3		Ψ_5		States of $^1B_2$ symmetry	Ψ_1		Ψ_2		Ψ_4	
	MIM	PPP	MIM	PPP		MIM	PPP	MIM	PPP	MIM	PPP
Γ	0.01	—	0.02	0.15	$(1/\sqrt{2})(\Lambda_a-\Lambda_c)$	0.21	0.09	—	—	0.05	0.11
$(1/\sqrt{2})(\Lambda_a+\Lambda_c)$	0.06	0.02	0.25	0.06	Λ_b	0.15	0.05	—	—	0.14	0.11
Λ_d	0.28	0.14	0.10	0.08	Λ_e	0.01	—	0.33	0.11	—	—
$(1/\sqrt{2})(T_c^a+T_a^c)$	0.06	0.08	—	0.10	$(1/\sqrt{2})(T_c^a-T_a^c)$	0.05	0.04	—	—	0.01	—
$(1/\sqrt{2})(T_a^d+T_c^d)$	0.18	0.10	—	0.02	$(1/\sqrt{2})(T_a^b+T_c^b)$	0.20	0.09	—	—	0.01	—
$(1/\sqrt{2})(T_a^b-T_c^b)$	—	0.02	0.24	0.10	$(1/\sqrt{2})(T_a^e+T_c^e)$	—	—	0.06	0.11	—	—
$(1/\sqrt{2})(T_a^e-T_c^e)$	—	—	—	—	$(1/\sqrt{2})(T_a^d-T_c^d)$	—	—	—	—	0.02	0.05
$(1/\sqrt{2})(T_b^a+T_b^c)$	0.06	0.06	0.14	0.02	$(1/\sqrt{2})(T_b^a-T_b^c)$	0.12	0.05	—	—	0.12	0.13
T_b^d	0.03	0.04	0.03	—	T_b^e	—	—	—	0.03	—	—
$(1/\sqrt{2})(T_d^a+T_d^c)$	0.14	0.10	0.05	—	$(1/\sqrt{2})(T_d^a-T_d^c)$	0.15	0.13	—	—	0.36	0.11
$(1/\sqrt{2})(T_e^a+T_e^c)$	0.05	0.03	—	—	T_d^b	0.06	0.06	—	—	0.09	0.08
T_e^d	0.13	0.06	0.17	0.01	T_d^e	0.01	—	0.61	0.30	—	—
					$(1/\sqrt{2})(T_e^a-T_e^c)$	0.03	0.03	—	—	0.15	0.04
					T_e^b	0.01	0.02	—	—	0.05	0.03
Total weight (%)	100	65	100	54		100	56	100	55	100	66
$\Delta E^{b)}$	3.22	4.27 (5.07)	5.36	5.96 (6.58)		3.37	2.38 (3.68)	4.15	3.45 (5.05)	4.94	5.91 (6.43)
$f^{b)}$	0.53	0.91 (0.97)	0.10	0.74 (0.54)		0.02	0.01 (0.02)	0.09	0.05 (0.07)	0.14	0.13 (0.13)
Polarization	y	y	y	y		x	x	x	x	x	x

a) a, b, c, d, and e denote the fragments $C_1=C_2$, $C_3=C_4$, $C_5=C_6$, $C_7=C_8$, and $C_9=C_{10}$, respectively. b) Values obtained by using Kon's resonance integrals given in parentheses.

TABLE 5. FIRST SINGLET EXCITED STATES OF [5] RADIALENE.

	Ψ_1		Ψ_2		Ψ_3		Ψ_4	
	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP
Γ	—	—	—	—	—	—	—	—
$(1/\sqrt{2})(\Lambda_a+\Lambda_b)$	0.03	0.03	0.25	0.22	0.01	—	0.01	0.02
$(1/\sqrt{2})(\Lambda_c+\Lambda_e)$	0.24	0.21	0.04	0.03	0.03	0.01	—	—
Λ_d	0.18	0.17	0.19	0.17	0.02	0.01	0.01	0.02
$(1/\sqrt{2})(T_a^b+T_b^a)$	—	—	—	—	0.21	0.18	0.28	0.21
$(1/\sqrt{2})(T_a^c+T_b^e)$	—	—	0.02	0.02	0.08	0.07	0.08	0.08
$(1/\sqrt{2})(T_a^e+T_b^c)$	0.05	0.04	0.16	0.10	0.16	0.12	0.03	0.02
$(1/\sqrt{2})(T_c^a+T_e^b)$	0.02	0.01	0.01	0.01	0.17	0.13	0.01	—
$(1/\sqrt{2})(T_e^a+T_c^b)$	0.08	0.06	0.17	0.12	0.12	0.11	0.02	0.02
$(1/\sqrt{2})(T_c^e+T_e^c)$	0.03	0.02	0.02	0.02	0.03	0.03	0.02	0.02
$(1/\sqrt{2})(T_a^d+T_b^d)$	0.01	0.01	—	—	—	—	0.06	0.05
$(1/\sqrt{2})(T_c^d+T_e^d)$	0.15	0.12	0.08	0.06	0.03	0.02	0.18	0.13
$(1/\sqrt{2})(T_d^a+T_d^b)$	0.04	0.02	0.01	0.01	0.13	0.10	0.11	0.09
$(1/\sqrt{2})(T_d^c+T_d^e)$	0.17	0.12	0.05	0.03	0.01	0.02	0.19	0.14
Total weight (%)	100	81	100	79	100	80	100	80
ΔE	3.57	5.09	4.81	5.95	5.32	6.24	6.04	7.05
f	0	0	0.84	1.34	0	0	0.03	0.08
Polarization	—	—	y	y	—	—	y	y

a) a, b, c, d, and e denote the $C_1=C_2$, $C_3=C_4$, $C_5=C_6$, $C_7=C_8$, and $C_9=C_{10}$ fragments respectively.

Table 4. First singlet excited states of dimethylenebenzocyclobutene

States of $^1A_1$ symmetry	Ψ_1		Ψ_3		Ψ_5		States of $^1B_2$ symmetry	Ψ_2		Ψ_4	
	MIM	PPP	MIM	PPP	MIM	PPP		MIM	PPP	MIM	PPP
MIM/A: Benzene (a) and two ethylenes (b, c) as component systems											
Γ	—	—	—	—	0.01	0.02	Λ_{2a}	0.01	0.78	0.53	0.02
Λ_{1a}	0.82	0.84	—	—	0.12	0.03	Λ_{4a}	—	0.01	0.10	0.46
Λ_{3a}	—	—	0.25	0.46	—	—	$(1/\sqrt{2})(\Lambda_b-\Lambda_c)$	0.54	0.01	—	0.02
$(1/\sqrt{2})(\Lambda_b+\Lambda_c)$	—	—	0.23	0.18	—	—	$(1/\sqrt{2})(T^{b}_{1a}+T^{c}_{1a})$	0.08	0.01	—	0.05
$(1/\sqrt{2})(T^{b}_{1a}-T^{c}_{1a})$	0.03	0.02	0.03	0.04	—	—	$(1/\sqrt{2})(T^{b}_{2a}-T^{c}_{2a})$	0.01	0.03	0.15	0.05
$(1/\sqrt{2})(T^{b}_{2a}+T^{c}_{2a})$	0.05	0.01	0.22	0.09	0.28	0.27	$(1/\sqrt{2})(T^{3a}_{b}+T^{3a}_{c})$	0.01	0.03	0.15	0.05
$(1/\sqrt{2})(T^{4a}_{b}+T^{4a}_{c})$	0.03	0.02	0.04	0.04	—	—	$(1/\sqrt{2})(T^{4a}_{b}-T^{4a}_{c})$	0.08	0.01	—	0.05
$(1/\sqrt{2})(T^{3a}_{b}-T^{3a}_{c})$	0.05	0.01	0.23	0.09	0.28	0.27	$(1/\sqrt{2})(T^{c}_{b}-T^{b}_{c})$	0.27	0.01	0.07	0.18
$(1/\sqrt{2})(T^{c}_{b}+T^{b}_{c})$	0.02	—	—	—	0.31	0.26					
Total weight (%)	100	90	100	90	100	85		100	89	100	88
ΔE	4.34	4.60	4.93	6.08	5.65	6.73		4.68	4.84	5.36	6.38
f	$\simeq 0$	$\simeq 0$	1.17	1.67	$\simeq 0$	$\simeq 0$		0.46	0.03	0.10	0.31
Polarization	—	—	x	x	—	—		y	y	y	y
MIM/B: Benzene (a) and *cis*-butadiene (b) as component systems											
Γ	—	—	0.01	—	0.03	0.07	Λ_{2a}	0.06	0.79	0.33	0.02
Λ_{1a}	0.60	0.86	0.12	—	0.20	0.03	Λ_{4a}	0.02	0.01	0.12	0.47
Λ_{3a}	—	—	0.11	0.46	0.04	—	Λ_{1b}	0.40	—	0.09	0.17
Λ_{2b}	0.07	—	—	—	0.29	0.22	Λ_{4b}	—	0.02	0.06	0.04
Λ_{3b}	—	—	0.10	0.18	0.02	—	T^{3b}_{1a}	0.08	0.01	—	0.05
T^{4b}_{1a}	0.04	0.02	—	0.04	0.01	—	T^{4b}_{2a}	—	0.03	0.13	0.05
T^{3b}_{2a}	0.02	0.01	0.19	0.09	0.32	0.25	T^{3a}_{1b}	0.01	0.04	0.27	0.05
T^{4a}_{1b}	0.04	0.02	0.06	0.04	0.01	—	T^{4a}_{2b}	0.43	0.01	—	0.05
T^{3a}_{2b}	0.23	0.01	0.41	0.09	0.08	0.25					
Total weight (%)	100	92	100	90	100	82		100	90	100	90
ΔE	4.16	4.60	4.57	6.08	5.22	6.73		4.56	4.84	4.92	6.67
f	0.04	$\simeq 0$	0.82	1.67	0.14	$\simeq 0$		0.15	0.03	0.08	0.31
Polarization	x	x	x	x	x	x		y	y	y	y

Five ethylenes as component systems[a)]

	Ψ_1		Ψ_2		Ψ_3		Ψ_4	
	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP
$(1/\sqrt{2})(\Lambda_a-\Lambda_b)$	0.33	0.31	0.13	0.12	0.04	0.02	0.01	0.01
$(1/\sqrt{2})(\Lambda_c-\Lambda_e)$	0.13	0.12	0.35	0.31	0.02	0.01	0.02	0.03
$(1/\sqrt{2})(T^{b}_{a}-T^{a}_{b})$	0.18	0.13	0.19	0.12	—	—	—	—
$(1/\sqrt{2})(T^{c}_{a}-T^{e}_{b})$	0.03	0.02	—	—	0.08	0.06	0.03	0.02
$(1/\sqrt{2})(T^{e}_{a}-T^{c}_{b})$	0.14	0.09	0.03	0.02	0.06	0.06	0.25	0.19
$(1/\sqrt{2})(T^{a}_{c}-T^{b}_{c})$	0.02	0.01	0.02	0.03	—	—	0.11	0.09
$(1/\sqrt{2})(T^{a}_{e}-T^{b}_{c})$	0.10	0.08	0.01	—	0.09	0.06	0.26	0.19
$(1/\sqrt{2})(T^{e}_{c}-T^{c}_{e})$	—	—	—	0.01	0.13	0.11	0.09	0.08
$(1/\sqrt{2})(T^{d}_{a}-T^{d}_{b})$	0.03	0.01	0.02	0.02	0.16	0.13	0.05	0.05
$(1/\sqrt{2})(T^{d}_{c}-T^{d}_{e})$	0.03	0.02	0.11	0.06	0.18	0.16	0.10	0.08
$(1/\sqrt{2})(T^{a}_{d}-T^{b}_{d})$	—	—	0.01	0.01	0.03	0.03	—	—
$(1/\sqrt{2})(T^{c}_{d}-T^{e}_{d})$	0.01	0.01	0.13	0.10	0.21	0.16	0.08	0.06
	100	80	100	80	100	80	100	80
	3.57	5.09	4.81	5.95	5.32	6.24	6.04	7.05
	0	0	0.84	1.34	0	0	0.03	0.08
	—	—	x	x	—	—	x	x

having $^1B_2$ symmetry, is calculated by PPP at 2.38 eV[16] or at 3.68 eV (2.09 eV according to CNDO/CI calculations[14]), whilst MIM predicts it at 3.37 eV. Its prevailing charge transfer tendency is evident, but the ethylenic fragment *e* (component of the cyclopropenyl ring) does not appreciably participate to the wavefunction composition. The transition seems to be the same as that at 3.46—3.98 eV (MIM-PPP)[2] and experimentally observed at 2.91 eV[16] in heptafulvene. It would lie at *ca.* 2.8—2.9 eV in the heptatriafulvalene absorption spectrum, probably as a shoulder.

The second electronic transition, computed at 4.15 eV by MIM, at 3.45 eV[16] or 5.05 eV by PPP and at 3.45 eV by CNDO/CI[14] corresponds to the analogous $^1B_2 \leftarrow {}^1A_1$ transition found in triafulvene at 4.83—5.48 eV (standard MIM and PPP calculations respectively[1]) and at 4.08 eV in calicene.[2] Even if a consistent percentage of the locally excited state Λ_e is present, the remarkable electronic transfer from ethylene *d* to ethylene *e* determines a spectral shift of about 2 eV with respect to the component molecules.

The third theoretical transition, of $^1A_1 \leftarrow {}^1A_1$ type, polarized along the y axis, is the most intense, showing conjugative character. It was calculated at 3.91 eV by CNDO/CI[14] and at 4.27 eV[16] or 5.07 eV by PPP. By MIM it is predicted at 3.22 eV as the lowest energy transition with a strong bathochromic shift with respect to the corresponding transition in heptafulvene (3.94 eV[2]).

The fourth ($^1B_2 \leftarrow {}^1A_1$) and fifth ($^1A_1 \leftarrow {}^1A_1$) electronic transitions, computed by PPP at 5.91 and 5.96 eV[16] or 6.43 and 6.58 eV (Kon's resonance integrals) and by MIM at 4.94 and 5.36 eV, still have predominating charge transfer character involving the whole π-system shifted at lower energy with respect to the analogous transitions found in heptafulvene.

As in calicene,[2] the triatomic ring is positively charged and the total weight of the PPP-CA states is found to be rather low.

Dimethylenebenzocyclobutene (III). Theoretical and experimental geometrical data concerning the dimethylenebenzocyclobutene molecule are lacking. An improved LCAO method,[17] taking into account both σ and π energy applied to determine the molecular structure and the UV spectrum, shows that the benzene bond lengths are not appreciably different from their standard value of 1.397 Å, the cyclobutene ring being nearly square. The PPP-SCF-MO-LCAO method, modified to take into account the effect of neighbouring atoms[18] gives different results depending on the starting geometry. Since in planar molecules slight differences in bond angles of bond lengths do not appreciably affect the calculated spectra, the benzene ring was chosen as a regular hexagon with all bond lengths equal to 1.4 Å while the values found by electron diffraction studies[19] were taken for the remaining bond lengths and bond angles relative to the dimethylenecyclobutane fragment. At MIM level benzene and two ethylene molecules (MIM/A), or benzene and *cis*-butadiene (MIM/B) were considered as component systems. Similar results obtained in the two cases are compared with the PPP ones (after application of configuration analysis) in Table 4.

The experimental UV absorption spectrum in ethanol[20] exhibits very close maxima in the range 3.7—4.0 eV which would be partially due to bond vibrations. The first weak electronic transition, calculated at 4.34—4.16 eV by MIM and at 4.60 eV by PPP, could be correlated with the absorption in the above region. It closely resembles the bonzenic α band as supported by the large weight relative to the benzenic configuration Λ_{1a} and it is assigned to a $^1A_1 \leftarrow {}^1A_1$ transition.

The second, $^1B_2 \leftarrow {}^1A_1$, y-polarized transition, calculated at 4.68—4.56 eV by MIM/A and MIM/B, respectively, and at 4.84 eV by PPP, corresponds to the absorption band experimentally observed at 4.52 eV.[20] According to MIM results the predominating weights in its wavefunction composition are those due to locally excited ethylenic (MIM/A) or butadienic (MIM/B) configurations together with electronic transfers between the two ethylenic component systems (MIM/A) or from butadiene to benzene (MIM/B). PPP results, on the contrary, attributes to this transition a benzenic nature. This on the basis that the predominant weight in the relative wavefunction is that of the Λ_{2a} configuration which corresponds to the benzenic p-band.

The third electronic transition is predicted as the most intense transition and is polarized along the x-axis ($^1A_1 \leftarrow {}^1A_1$). It is estimated by MIM at 4.93—4.57 eV and by PPP at higher energy (6.08 eV) as a mixture of locally excited and charge transfer states and should be correlated with the intense absorption band observed at 5.4 eV ($\log \varepsilon = 4.8$).

The fourth is a $^1B_2 \leftarrow {}^1A_1$, y-polarized, weak transition calculated at 5.36—4.92 eV (MIM/A and MIM/B) and 6.38 eV (PPP). It originates from locally excited and charge transfer configurations involving all the component systems.

The fifth $^1A_1 \leftarrow {}^1A_1$ transition is predicted at 5.65—5.22 eV (MIM) and 6.76 eV (PPP) as a forbidden transition, even though an oscillator strength of 0.14 is given by MIM/B. MIM/A points out the charge transfer character of this transition in contrast with MIM/B results predicting an equilibrium between charge transfer and locally excited configurations. The transitions having $^1B_2$ symmetry show different compositions in MIM and PPP approaches. Particularly, while the $^1B_2 \leftarrow {}^1A_1$ transitions exhibit a comparable energy calculated by the MIM and PPP methods, the composition of their wavefunctions seem to be interchanged, *i.e.* the composition calculated by the MIM for the transition at 4.56—4.84 eV agrees better with the one calculated by PPP for the transition at $\simeq$6.6 eV, and *vice versa.* In any case however, the agreement is scarcely satisfactory. The second and third electronic transitions of $^1A_1$ symmetry have a composition approximatively comparable with that of the corresponding ones of dimethylenecyclobutene.

The biexcited configurations calculated by configuration analysis (not included in PPP and MIM calculations) have negligible weight (each of them appears with a percentage lower than 1%) so that they should not affect the results. From PPP results, in which all the monoexcited configurations were included some wavefunctions relative to transitions at energies higher than those given in Table 4, show a noticeable percentage of configurations involving the lowest occupied and the highest vacant benzenic molecular orbitals. A calculation at MIM level in which these configurations were taken into account gave no appreciable variation in energy or composition of the first excited states.

[5]Radialene(Pentamethylenecyclopentane) (IV). The [5]radialene molecule, not known as yet, has been assumed as a regular pentagon with single bond lengths of 1.467 Å and double bonds of 1.366 Å.[21)]

The first degenerate electronic transition calculated at 3.57—5.09 eV (MIM-PPP) is a mixture of locally excited and charge transfer configurations (Table 5). Calculations show it is forbidden.

The second ($E_1' \leftarrow A_1'$) transition has a strong intensity and a composition similar to that of the first one. It is predicted at 4.81—5.95 eV (MIM-PPP), *i.e.* very near the theoretical value found for [4]radialene[2)] (4.77—6.41 eV (MIM-PPP)) and experimentally observed at 4.59 eV.

The third (forbidden) and fourth (weak) electronic transitions are calculated at 5.32—6.24 eV and 6.04—7.05 eV (MIM-PPP) and originate exclusively from charge transfer configurations. On the whole the results confirm what Heilbronner predicted for this compound.[22)]

8-Vinylheptafulvene(7-Methylene-1,3,5-cycloheptatriene) (V). The geometry postulated by Lo and Whitehead was adopted for calculations.[23)] The results are given in Table 6.

The UV trend is fairly reproduced by MIM and PPP, even though the latter method gives rather high energy values. The first electronic transition, roughly polarized along the short axis (y), is computed at 3.55—4.17 eV (MIM-PPP) and is to be associated with the weak absorption band experimentally observed at 2.8 eV.[24)] PPP predicts it is prevailingly due to charge transfer states while MIM indicates it is a mixture of locally excited and charge transfer configurations. However both methods show that it is localized in the seven-membered ring, corresponding

Table 6. First singlet excited states of 8-vinylheptafulvene
Five ethylene molecules as component systems.[a)]

	Ψ_1		Ψ_2		Ψ_3		Ψ_4		Ψ_5	
	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP
Γ	—	—	—	0.03	0.01	0.08	—	—	—	—
Λ_a	0.11	0.09	0.06	0.02	0.06	0.01	0.05	0.06	0.02	0.02
Λ_b	0.19	0.11	—	—	—	—	0.03	0.09	0.12	0.05
Λ_c	0.13	0.09	0.03	0.02	0.04	0.02	0.06	0.05	0.03	0.02
Λ_d	—	—	0.25	0.17	0.07	0.06	—	—	—	—
Λ_e	—	—	0.04	0.05	0.14	0.09	—	—	—	—
T_a^b	0.11	0.07	0.01	—	0.01	0.05	0.01	—	—	—
T_a^c	0.03	0.03	0.02	0.03	0.03	0.07	0.08	0.03	0.02	0.06
T_a^d	—	—	0.09	0.07	0.02	—	0.19	0.09	0.10	0.11
T_a^e	—	—	0.01	0.01	—	—	0.01	0.01	0.01	0.01
T_b^c	0.08	0.05	0.01	0.02	0.11	0.04	0.01	0.03	0.08	0.10
T_b^d	—	—	0.03	0.05	0.05	0.04	—	—	—	—
T_b^e	—	—	—	0.01	—	—	—	—	—	—
T_c^d	0.01	—	0·09	0.07	0.01	—	0.19	0.09	0.10	0.11
T_c^e	—	—	0.01	0.01	—	—	0.01	0.01	0.01	0.01
T_d^e	—	—	0.04	0.04	0.20	0.07	—	—	—	—
T_b^a	0.07	0.04	0.03	0.02	0.10	0.05	0.01	0.02	0.09	0.10
T_c^a	0.03	0.03	0.03	0.03	0.02	0.06	0.08	0.04	0.01	0.06
T_d^a	0.03	0.06	0.10	0.05	—	—	0.08	0.08	0.16	0.03
T_e^a	—	—	0.01	0.01	—	—	0.01	0.01	0.01	0.01
T_c^b	0.11	0.07	—	—	0.02	0.06	0.01	0.01	—	—
T_d^b	0.04	0.06	—	—	—	—	0.07	0.08	0.07	0.05
T_e^b	—	0.01	—	—	—	—	0.01	0.02	0.01	0.01
T_d^c	0.05	0.07	0.07	0.04	—	—	0.08	0.09	0.14	0.04
T_e^c	—	0.01	0.01	0.01	—	—	0.01	0.02	0.02	0.01
T_e^d	—	—	0.06	0.05	0.10	0.04	—	—	—	—
Total weight (%)	100	79	100	81	100	75	100	83	100	80
ΔE	3.55	4.17	3.69	4.97	5.28	6.43	5.51	6.51	5.76	7.32
f	0.07	0.05	0.82	1.24	0.01	0.58	<0.01	0.02	0.32	0.42
Polarization[b)]	−70	−85	−0.2	−2	−28	−3	70	73	88	89

a) a, b, c, d, and e denote fragments $C_1=C_2$, $C_3=C_4$, $C_5=C_6$, $C_7=C_8$, and $C_9=C_{10}$ respectively. b) Angles with respect to x axis.

TABLE 7. FIRST EXCITED SINGLET STATES OF 1,2-BENZOFULVENE. BENZENE (a) AND TWO

MIM/A	MIM/B	Ψ_1				Ψ_2			
		MIM/A	PPP	MIM/B	PPP	MIM/A	PPP	MIM/B	PPP
Γ	Γ	—	—	—	—	—	—	—	—
Λ_{1a}	Λ_{1a}	0.22	0.09	0.30	0.10	0.11	0.58	0.11	0.62
Λ_{2a}	Λ_{2a}	—	0.30	0.01	0.32	0.17	0.08	0.13	0.08
Λ_{3a}	Λ_{3a}	0.03	0.03	0.04	0.03	0.06	—	0.04	—
Λ_{4a}	Λ_{4a}	0.02	—	0.01	—	0.02	0.01	0.02	0.01
Λ_{b}	Λ_{1b}	0.10	0.08	0.15	0.11	0.09	0.01	0.01	—
Λ_{c}	Λ_{2b}	0.11	—	—	0.03	0.02	0.01	0.07	0.01
T^{b}_{1a}	Λ_{3b}	0.01	0.02	—	0.02	0.20	0.06	0.02	—
T^{c}_{1a}	Λ_{4b}	0.01	0.05	—	—	0.16	0.04	—	—
T^{b}_{2a}	T^{3b}_{1a}	0.06	0.05	0.01	0.07	0.04	—	0.49	0.10
T^{c}_{2a}	T^{4b}_{1a}	0.06	0.04	—	—	0.01	0.02	—	—
T^{c}_{b}	T^{3b}_{2a}	0.11	0.07	0.24	0.10	0.03	—	0.05	0.01
T^{3a}_{b}	T^{4b}_{2a}	0.02	0.03	—	—	0.05	0.01	0.01	0.01
T^{3a}_{c}	T^{3a}_{1b}	0.02	0.01	—	—	—	0.01	0.02	0.02
T^{4a}_{b}	T^{3a}_{2b}	0.10	0.05	0.05	0.03	0.02	0.01	0.01	—
T^{4a}_{c}	T^{4a}_{1b}	0.06	—	0.02	0.04	0.01	0.01	0.02	—
T^{b}_{c}	T^{4a}_{2b}	0.07	—	0.17	0.01	0.01	0.01	—	0.03
Total weight (%)		100	82	100	86	100	86	100	89
ΔE		3.80	4.35	3.82	4.35	4.35	4.47	4.10	4.47
f		0.41	0.06	0.30	0.06	0.08	0.03	0.08	0.03
Polarization[a]		−39	−3	−22	−3	59	−63	73	−63

a) Angle with respect to x-axis.

in energy as well in composition and intensity, to the first electronic transition found in heptafulvene at 3.46—3.98 eV (MIM-PPP) and experimentally observed at 2.9 eV.[2)]

The most intense second absorption band occurs at 3.81 eV,[24)] the corresponding band in heptafulvene lying at 4.4 eV.[8,24)] The bathochromic shift was fairly predicted by calculations. The associated electronic transition, in fact, computed at 3.69—4.97 eV (MIM-PPP) and polarized along the x axis (3.94—5.31 eV in heptafulvene[2)]) has prevailing charge transfer character involving the whole π-system with consistent interaction of the vinyl group with the heptafulvene nucleus.

A very similar composition is found for the weak third theoretical electronic transition, computed at 5.28—6.43 eV (where Λ_e is the most consistent among the locally excited states) which appears shifted at lower energy with respect to the corresponding one in heptafulvene (5.62—6.66 eV, MIM-PPP).[2)] A lower bathochromic shift is predicted by PPP approach because less interaction is predicted between the vinyl group and the remaining heptafulvene fragment.

Next two transitions, both roughly polarized along the y-axis, are calculated at 5.51—6.51 eV (weak) and 5.76—7.32 eV (intense) by MIM and PPP respectively, being nearly exclusively originated by charge transfers involving principally the heptafulvene π-system.

*1,2-Benzofulvene(1-Methylene-1*H*-indene) (VI).* The bond lengths calculated by the LCAO-MO-SCF-PPP ($\pi+\sigma$) method[23)] were adopted for the fulvene ring, benzene being assumed to be a regular hexagon. The most recent UV spectrum[25)] shows a great number of absorption bands and shoulders, often very near each other, giving results very difficult to interpret. Three distinct absorption bands were reported by Bloor *et al.*,[13)] where reference is made to the spectrum in heptane solution reported by Pullman *et al.*[26)] My MIM and PPP-CA results are discordant (Table 7) principally as regards the composition and oscillator strengths of the first and fourth electronic transitions so that the relative assignment is uncertain. Probably this situation is partially due to the molecular asymmetry of this compound. However, the first electronic transition computed at 3.80—3.82 eV by MIM and at 4.35 eV by PPP seems to be associated with the experimental absorption observed at ≃3.6 eV. The second theoretical transition at 4.35—4.10 eV (MIM/A-MIM/B) and 4.47 eV (PPP) corresponds to the absorption band at about 4 eV. The third and fourth calculated transitions might be correlated with the strong absorption at about 4.8 eV. If a comparison is made between the composition of these transitions and the composition of the transitions found in fulvene[1] no resemblance is observed.

*2,3-Benzofulvene(2-Methylene-2*H*-indene) (VII).* As regards 2,3-benzofulvene no spectroscopic data seem to have appeared. Calculations have been performed adopting the molecular geometry of Lo and Whitehead.[23)] Three different approaches at MIM level were examined. The molecule was considered to be five interacting ethylene molecules (MIM/A) or two *cis*-butadienes and ethylene (MIM/B) or two *trans*-butadienes and ethylene (MIM/C). The results are given in Tables 8 and 9, together with those of PPP-CA for comparison. In each case a y-polarized $^1B_2 \leftarrow {}^1A_1$

ETHYLENES (b, c) OR BENZENE (a) AND *trans*-BUTADIENE (b) AS COMPONENT SYSTEMS

Ψ_3				Ψ_4				Ψ_5			
MIM/A	PPP	MIM/B	PPP	MIM/A	PPP	MIM/B	PPP	MIM/A	PPP	MIM/B	PPP
—	—	0.01	0.01	—	0.01	—	—	0.01	0.06	0.05	0.05
0.53	0.06	0.42	0.06	—	0.03	—	0.03	—	—	0.02	—
0.03	0.23	0.02	0.24	0.14	0.13	0.08	0.14	—	—	—	—
—	0.11	0.02	0.11	0.04	—	0.04	—	0.10	0.04	0.02	0.04
0.04	0.01	0.07	0.01	0.05	0.16	0.03	0.17	0.15	0.11	0.05	0.11
0.02	0.08	0.14	0.29	0.01	—	—	0.06	0.02	—	0.01	0.04
0.15	0.09	0.01	—	—	0.12	0.01	0.08	—	—	—	—
—	0.01	—	0.01	0.04	0.07	0.03	0.06	—	0.01	—	0.01
0.06	—	0.01	—	0.04	0.11	—	—	0.04	0.01	—	0.01
0.01	0.01	0.07	—	0.03	—	0.06	0.19	0.26	0.19	0.03	—
0.02	0.02	0.04	0.01	0.01	—	—	—	0.12	0.13	—	0.02
0.02	0.10	—	0.02	0.03	0.01	—	—	0.10	0.02	0.46	0.34
0.01	0.01	—	—	0.21	0.05	—	—	—	0.03	—	—
0.01	—	0.03	0.01	0.15	0.02	—	—	0.11	0.05	0.01	—
—	0.03	0.05	—	0.11	—	0.49	0.07	0.04	0.08	0.16	0.08
0.06	0.06	0.02	—	0.10	0.02	—	0.02	—	0.01	0.03	0.02
0.04	0.02	0.09	0.09	0.04	0.06	0.26	—	0.05	0.04	0.16	0.08
100	83	100	86	100	79	100	82	100	78	100	80
4.50	5.36	4.71	5.36	5.34	5.75	5.00	5.75	5.77	6.54	5.50	6.54
0.33	0.41	0.55	0.41	0.09	0.72	0.02	0.72	0.39	0.24	0.04	0.24
−50	−23	−34	−23	−60	−50	−68	−50	25	21	14	21

TABLE 8. FIRST SINGLET EXCITED STATES OF 2,3-BEAZOFULVENE. MIM/A—FIVE ETHYLENE MOLECULES AS COMPONENT SYSTEMS[a)]

States of $^1A_1$ symmetry	Ψ_2		Ψ_5		States of $^1B_2$ symmetry	Ψ_1		Ψ_3		Ψ_4	
	MIM	PPP	MIM	PPP		MIM	PPP	MIM	PPP	MIM	PPP
Γ	0.02	0.11	0.01	0.04	$(1/\sqrt{2})(\Lambda_a-\Lambda_b)$	0.08	0.04	0.30	0.29	—	—
$(1/\sqrt{2})(\Lambda_a+\Lambda_b)$	0.01	0.01	0.12	0.03	$(1/\sqrt{2})(\Lambda_c-\Lambda_d)$	0.25	0.18	0.09	0.03	0.02	0.03
$(1/\sqrt{2})(\Lambda_c+\Lambda_d)$	0.10	0.01	0.09	0.05	$(1/\sqrt{2})(T_a^b-T_b^a)$	0.06	0.03	0.26	0.15	—	—
Λ_e	0.20	0.10	—	0.13	$(1/\sqrt{2})(T_a^c-T_b^d)$	0.06	0.04	0.01	0.01	0.17	0.11
$(1/\sqrt{2})(T_a^b+T_b^a)$	—	0.01	0.04	0.14	$(1/\sqrt{2})(T_a^b-T_b^c)$	0.10	0.06	0.03	0.04	0.28	0.16
$(1/\sqrt{2})(T_a^c+T_b^d)$	0.01	0.02	0.06	0.08	$(1/\sqrt{2})(T_a^e-T_b^e)$	0.03	0.04	—	—	0.09	0.10
$(1/\sqrt{2})(T_a^d+T_b^c)$	0.06	0.01	0.08	0.04	$(1/\sqrt{2})(T_c^a-T_d^b)$	0.04	0.03	0.02	0.01	0.14	0.11
$(1/\sqrt{2})(T_a^e+T_b^e)$	0.01	0.01	—	—	$(1/\sqrt{2})(T_c^b-T_d^a)$	0.07	0.04	0.03	0.04	0.28	0.21
$(1/\sqrt{2})(T_c^a+T_d^b)$	0.01	0.04	0.05	0.06	$(1/\sqrt{2})(T_c^d-T_d^c)$	0.21	0.11	0.12	0.07	0.01	0.01
$(1/\sqrt{2})(T_c^b+T_d^a)$	0.01	0.01	0.30	0.01	$(1/\sqrt{2})(T_c^e-T_d^e)$	0.10	0.17	0.14	0.09	0.01	—
$(1/\sqrt{2})(T_c^d+T_d^c)$	0.11	0.11	0.21	0.04	$(1/\sqrt{2})(T_e^a-T_e^b)$	—	—	—	—	—	—
$(1/\sqrt{2})(T_c^e+T_d^e)$	0.16	0.07	0.03	—	$(1/\sqrt{2})(T_e^c-T_e^d)$	—	—	—	—	—	—
$(1/\sqrt{2})(T_e^a+T_e^b)$	0.02	0.04	0.01	—							
$(1/\sqrt{2})(T_e^c+T_e^d)$	0.28	0.13	—	0.09							
Total weight (%)	100	68	100	71		100	74	100	73	100	73
ΔE	3.83	5.31	5.30	6.56		2.67	3.79	4.18	5.44	5.18	6.36
f	0.69	0.62	0.46	0.99		0.09	0.12	0.05	0.12	0.01	0.02
Polarization	x	x	x	x		y	y	y	y	y	y

a) a, b, c, d, and e denote fragments C_2=C_3, C_4=C_5, C_6=C_7, C_1=C_8, and C_9=C_{10}, respectively.

transition of weak intensity is predicted as first electronic transition at 2.67, 2.40 and 2.38 eV (MIM/A, MIM/B and MIM/C respectively) and at 3.79 eV (PPP). With respect to the first calculated electronic transition in 1,2-benzofulvene a greater charge transfer character is found, the calculated transition shifting at lower energy. Moreover the composition of the wavefunction relative to this transition is very similar to that of the first transition in fulvene,[1)] where it was computed at 3.3 eV.

The second ($^1A_1 \leftarrow {}^1A_1$) transition is predicted to be very intense and polarized towards the long molecular axis (x). It is calculated by MIM in the range 3.4—3.8 eV and by PPP at 5.32 eV, the result being pre-

Table 9. First excited singlet states of 2,3-benzofulvene

States of $^1A_1$ symmetry	Ψ_2		Ψ_5		States of $^1B_2$ symmetry	Ψ_1		Ψ_3		Ψ_4	
	MIM	PPP	MIM	PPP		MIM	PPP	MIM	PPP	MIM	PPP
MIM/B: Two *cis*-butadiene (a, b) and ethylene (c) as component systems											
Γ	0.01	0.04	—	—	$(1/\sqrt{2})(\Lambda_{1a}-\Lambda_{1b})$	0.08	0.07	0.22	0.46	—	—
$(1/\sqrt{2})(\Lambda_{1a}+\Lambda_{1b})$	0.01	0.01	0.08	0.03	$(1/\sqrt{2})(\Lambda_{2a}-\Lambda_{2b})$	—	—	—	0.01	—	—
$(1/\sqrt{2})(\Lambda_{2a}+\Lambda_{2b})$	0.01	0.03	0.06	0.20	$(1/\sqrt{2})(\Lambda_{3a}-\Lambda_{3b})$	0.25	0.33	0.06	0.11	0.06	0.04
$(1/\sqrt{2})(\Lambda_{3a}+\Lambda_{3b})$	0.08	0.02	0.06	0.05	$(1/\sqrt{2})(\Lambda_{4a}-\Lambda_{4b})$	—	—	0.01	0.01	—	—
$(1/\sqrt{2})(\Lambda_{4a}+\Lambda_{4b})$	0.14	0.19	0.12	0.08	$(1/\sqrt{2})(T_{1a}^{3b}-T_{1b}^{3a})$	—	—	—	—	—	—
Λ_c	0.15	0.12	—	0.15	$(1/\sqrt{2})(T_{1a}^{4b}-T_{1b}^{4a})$	0.30	0.12	0.02	0.06	0.46	0.31
$(1/\sqrt{2})(T_{1a}^{3b}+T_{1b}^{3a})$	0.08	0.04	0.02	—	$(1/\sqrt{2})(T_{1a}^{c}-T_{1b}^{c})$	0.06	0.04	0.01	—	0.05	0.12
$(1/\sqrt{2})(T_{1a}^{4b}+T_{1b}^{4a})$	0.02	0.01	—	—	$(1/\sqrt{2})(T_{2a}^{3b}-T_{2b}^{3a})$	0.17	0.20	0.38	0.11	0.07	0.01
$(1/\sqrt{2})(T_{1a}^{c}+T_{1b}^{c})$	—	—	0.34	0.15	$(1/\sqrt{2})(T_{2a}^{4b}-T_{2b}^{4a})$	0.14	0.07	0.29	0.06	0.35	0.34
$(1/\sqrt{2})(T_{2a}^{3b}+T_{2b}^{3a})$	0.15	0.07	0.01	—	$(1/\sqrt{2})(T_{2a}^{c}-T_{2b}^{c})$	—	—	0.01	0.01	0.01	0.01
$(1/\sqrt{2})(T_{2a}^{4b}+T_{2b}^{4a})$	0.05	0.06	0.08	0.02	$(1/\sqrt{2})(T_{c}^{3a}-T_{c}^{3b})$	—	—	—	—	—	—
$(1/\sqrt{2})(T_{2a}^{c}+T_{2b}^{c})$	0.02	0.04	—	—	$(1/\sqrt{2})(T_{c}^{4a}-T_{c}^{4b})$	—	—	—	—	—	—
$(1/\sqrt{2})(T_{c}^{3a}+T_{c}^{3b})$	—	0.01	0.22	0.05							
$(1/\sqrt{2})(T_{c}^{4a}+T_{c}^{4b})$	0.28	0.18	0.01	0.03							
Total weight (%)	100	82	100	82		100	83	100	83	100	83
ΔE	3.42	5.32	4.61	6.56		2.40	3.79	3.85	5.44	3.97	6.35
f	0.62	0.70	0.39	0.98		0.05	0.12	0.04	0.12	$\simeq 0$	0.02
Polarization	x	x	x	x		y	y	y	y	y	y
MIM/C: Two *trans*-butadienes (a, b) and ethylene (c) as component systems											
Γ	0.05	0.10	0.02	0.02	$(1/\sqrt{2})(\Lambda_{1a}-\Lambda_{1b})$	0.30	0.31	0.04	0.15	0.02	0.02
$(1/\sqrt{2})(\Lambda_{1a}+\Lambda_{1b})$	0.06	0.04	0.01	0.13	$(1/\sqrt{2})(\Lambda_{2a}-\Lambda_{2b})$	0.01	0.03	0.31	0.28	—	0.01
$(1/\sqrt{2})(\Lambda_{2a}+\Lambda_{2b})$	0.02	—	—	—	$(1/\sqrt{2})(\Lambda_{3a}-\Lambda_{3b})$	—	—	—	—	0.22	0.40
$(1/\sqrt{2})(\Lambda_{3a}+\Lambda_{3b})$	—	0.01	—	0.02	$(1/\sqrt{2})(\Lambda_{4a}-\Lambda_{4b})$	—	0.01	—	—	—	0.01
$(1/\sqrt{2})(\Lambda_{4a}+\Lambda_{4b})$	—	—	—	—	$(1/\sqrt{2})(T_{1a}^{3b}-T_{1b}^{3a})$	0.01	—	0.21	0.12	0.30	0.14
Λ_c	0.18	0.12	0.06	0.14	$(1/\sqrt{2})(T_{1a}^{4b}-T_{1b}^{4a})$	0.01	—	—	—	0.02	—
$(1/\sqrt{2})(T_{1a}^{3b}+T_{1b}^{3a})$	0.04	0.02	0.01	0.01	$(1/\sqrt{2})(T_{1a}^{c}-T_{1b}^{c})$	0.01	0.02	0.06	0.06	—	0.04
$(1/\sqrt{2})(T_{1a}^{4b}+T_{1b}^{4a})$	—	—	—	—	$(1/\sqrt{2})(T_{2a}^{3b}-T_{2b}^{3a})$	0.51	0.22	0.06	0.22	0.08	—
$(1/\sqrt{2})(T_{1a}^{c}+T_{1b}^{c})$	0.04	0.02	—	—	$(1/\sqrt{2})(T_{2a}^{4b}-T_{2b}^{4a})$	0.02	0.01	0.24	0.12	0.06	0.10
$(1/\sqrt{2})(T_{2a}^{3b}+T_{2b}^{3a})$	0.13	0.17	0.68	0.36	$(1/\sqrt{2})(T_{2a}^{c}-T_{2b}^{c})$	0.13	0.21	0.08	0.04	0.23	0.07
$(1/\sqrt{2})(T_{2a}^{4b}+T_{2b}^{4a})$	0.04	0.01	—	—	$(1/\sqrt{2})(T_{c}^{3a}-T_{c}^{3b})$	—	—	—	—	0.06	0.01
$(1/\sqrt{2})(T_{2a}^{c}+T_{2b}^{c})$	0.17	0.07	0.02	—	$(1/\sqrt{2})(T_{c}^{4a}-T_{c}^{4b})$	—	—	—	—	0.01	—
$(1/\sqrt{2})(T_{c}^{3a}+T_{c}^{3b})$	0.23	0.18	0.13	0.06							
$(1/\sqrt{2})(T_{c}^{4a}+T_{c}^{4b})$	0.04	0.02	0.07	0.04							
Total weight (%)	100	76	100	78		100	81	100	79	100	80
ΔE	3.54	5.32	4.70	6.56		2.38	3.79	3.94	5.44	5.33	6.35
f	0.50	0.70	0.17	0.98		0.10	0.12	0.05	0.12	0.04	0.02
Polarization	x	x	x	x		y	y	y	y	y	y

valently charge transfer in nature.

Next transition, $^1B_2 \leftarrow ^1A_1$, found at *ca.* 4.2 eV by MIM and at 5.44 eV by PPP shows charge transfer character if MIM results are taken into account, in contrast with PPP composition where the greatest contribution is given by locally excited states. Since the calculated energy values for the second and the third transition are very close each other it is probable that the third transition (weak) might appear as a shoulder of the second one on higher energy side.

The fourth electronic transition is predicted having $^1B_2$ symmetry with very low intensity and exclusively charge transfers configurations. Both MIM/A and PPP predict that it is lying very near to the fifth $^1A_1 \leftarrow ^1A_1$ intense electronic transition, probably as a shoulder on lower energy side. On the contrary MIM/C results predict the fourth transition to be forbidden and lying at about 4 eV, in disagreement with the above results.

Conclusion

If [5]radialene and the two benzofulvenes are excluded, the spectra of the molecules studied can be correlated with those of the smaller cyclic compounds which constitute them, by means of the nature, energy and intensity as well as the composition of the corresponding electronic transitions. The principal feature which can be noted by analysing the theoretical electronic transitions energies is the difference between MIM and PPP results. The latter gives values higher than those of MIM and experiment, even if the general spectral trend is acceptable. The main cause seems to be the resonance integrals. When β_{ij} values are evaluated by the exponential formula

$$\beta_{ij} = -2.38 \exp 1.586 (r_0 - r_{\mu\nu})$$

where r_0 is the C–C bond length in benzene (for details Ref. 16, method I), the energy values calculated by PPP are lower than those obtained with Kon's resonance integrals and nearer to the experimental ones. On the other hand MIM values became too low. For a more reliable comparison of the theoretical results we have chosen Kon's integrals in both methods since calculations on some compounds showed that wavefunction compositions do not appreciably differ in the two cases. The nature of the first electronic transitions, among which those experimentally observed are included, are generally concordant in the two methods while mutual shifts are noted for higher energy wavefunctions. However this behaviour is usual and independent of the molecules. Generally the lowest energy transitions are a mixture of locally excited and charge transfer configurations with nearly exclusively Λ character in compounds including benzene ring, while prevalently charge transfer transitions are found at higher energy values. For all the compounds the calculated ground state bond orders are satisfactory.

References

1) G. Favini and G. Buemi, *Theor. Chim. Acta (Berl.)*, **24**, 61 (1972).

2) G. Buemi, *Z. Phys. Chem. Neue Folge*, **119**, 1 (1980).

3) R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York (1963).

4) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).

5) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).

6) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theor. Chim. Acta (Berl.)*, **8**, 101 (1967).

7) R. D. Brown, F. R. Burden, and G. R. Williams, *Aust. J. Chem.*, **21**, 1939 (1968).

8) Z. Yoshida and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **45**, 316 (1972).

9) T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Jpn.*, **35**, 910 (1962).

10) F. Marschner and H. Pohle, *Tetrahedron*, **34**, 105 (1978).

11) K. D. Warren and J. R. Yandle, *Theor. Chim. Acta (Berl.)*, **12**, 279 (1968).

12) O. W. Adams and R. L. Miller, *Theor. Chim. Acta (Berl.)*, **12**, 151 (1968).

13) J. E. Bloor, B. R. Gilson, and N. Brearley, *Theor. Chim. Acta (Berl.)*, **8**, 35 (1967).

14) A. Tajiri, N. Ohmichi, and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 2347 (1971).

15) I. Gutman, M. Milun, and N. Trinajstic, *J. Am. Chem. Soc.*, **99**, 1692 (1977).

16) H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta (Berl.)*, **12**, 349 (1968).

17) P. Francois, *J. Chim. Phys. Phys. Chim. Biol.*, **67**, 1063 (1970).

18) A. Skancke and P. N. Skancke, *Acta Chem. Scand.*, **22**, 175 (1968).

19) A. Skancke, *Acta Chem. Scand.*, **22**, 3239 (1968).

20) M. P. Cava, R. J. Pohl, and M. J. Mitchell, *J. Am. Chem. Soc.*, **85**, 2080 (1963).

21) V. Buss and H. D. Försterilng, *Tetrahedron*, **29**, 3001 (1973).

22) E. Heilbronner, *Theor. Chim. Acta (Berl.)*, **4**, 64 (1966).

23) D. H. Lo and M. A. Whitehead, *Tetrahedron*, **25**, 2615 (1969).

24) D. J. Bertelli, *J. Am. Chem. Soc.*, **86**, 3320 (1964).

25) M. Neuenschwander, R. Vögeli, H. P. Fahrni, H. Lehmann, and J. P. Ruder, *Helv. Chim. Acta*, **60**, 1073 (1977).

26) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, Y. Hirshberg, and Y. Spirinzak, *Bull. Soc. Chim. Fr.*, **1951**, 702.