Theoret. chim. Acta (Berl.) 24, 61–70 (1972)

Configuration Analysis and Electronic States Properties

I. Four- and Six-π-Electron Systems

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Received June 11, 1971

The excited-states electronic properties of unsaturated small-ring hydrocarbons with four- and six-π-electrons have been studied by the "Molecules in Molecules" method and compared with experimental data and PPP results interpreted through a "configuration analysis" procedure. The results show that the MIM method is applicable with good reliability.

Die elektronischen Eigenschaften der angeregten Zustände von ungesättigten kleinen Kohlenwasserstoffringen mit vier und sechs π-Elektronen wurden mit Hilfe der „Molekül- im-Molekül"-Methode untersucht und die Ergebnisse mit experimentellen Daten und PPP Resultaten, die durch eine „Konfigurationsanalyse" interpretiert wurden, verglichen. Die Ergebnisse zeigen, daß die MIM-Methode mit großer Zuverlässigkeit anwendbar ist.

1. Introduction

The semiempirical PPP method [1] has been applied with remarkable success to a large number of organic molecules. One may point out, however, that the wavefunctions finally obtained by this method for electronic states of a molecule are not immediately understandable when an extended configuration interaction is included.

A procedure, tentatively called "configuration analysis", has been developed by Baba, Suzuki and Takemura [2] to interpret the results of PPP calculations directly in terms of the localized orbital model [3] in which the excited states are classified as locally excited or as charge-transfer states. This procedure enables one to compare the results of the PPP method with those of the MIM calculations.

By this correlation it should be possible to obtain informations on the validity of the choise of the reference orbitals used in MIM calculations, on the reliability of the results when an incomplete configuration interaction treatment is adopted, and finally on the effectiveness of the comparison between the electronic transition energies obtained in PPP and MIM calculations.

Aim of the present investigation was to apply this procedure to a series of non-benzenoid hydrocarbons as a mean for the discussion of their spectroscopic properties.

The ground- and excited-states electronic properties of these derivatives were already studied in the PPP approximation [4], by means of a refined ω-technique [5] and by the VESCF method [6].

2. Method

The details of the configuration analysis procedure have been described in the original paper [2], where also the symbols used were defined.

In MIM calculations ethylene and *cis*-butadiene are considered as component systems; a small conjugation between the components is predicted across the "long" bonds in the composite systems.

The SCF–MO and the experimental transition energies of the component molecules are given in Table 1; the values and the data of the cyclopentadiene were adopted for the *cis*-butadiene molecule.

Table 1. SCF–MO's, experimental transition energies (in eV) of the component molecules, and configurations to which they are assigned

Molecule	SCF–MO's	Configuration	$E_{\text{exp.}}$	Refs.
Ethylene	$\varphi_1 = 1/\sqrt{2}(\chi_1 + \chi_2)$	$\varphi_1^{-1}\varphi_2$	6.94[a]	[7, 8]
	$\varphi_2 = 1/\sqrt{2}(\chi_1 - \chi_2)$		6.60[b]	
			6.63[c]	
cis-butadiene[d]	$\varphi_1 = a(\chi_1 + \chi_4) + b(\chi_2 + \chi_3)$	$\Lambda_1 = \varphi_2^{-1}\varphi_3$	5.18	[9, 10]
$a = 0.4361$	$\varphi_2 = b(\chi_1 - \chi_4) + a(\chi_2 - \chi_3)$	$\Lambda_2 = 1/\sqrt{2}(\varphi_1^{-1}\varphi_3 - \varphi_2^{-1}\varphi_4)$	6.20	[11]
$b = 0.5566$	$\varphi_3 = b(\chi_1 + \chi_4) - a(\chi_2 + \chi_3)$	$\Lambda_3 = 1/\sqrt{2}(\varphi_1^{-1}\varphi_3 + \varphi_2^{-1}\varphi_4)$	7.90	[11]
	$\varphi_4 = a(\chi_1 - \chi_4) - b(\chi_2 - \chi_3)$	$\Lambda_4 = \varphi_1^{-1}\varphi_4$	8.53[e]	

[a] For ethylene 1,2-disubstituted.

[b] For ethylene 1,1-disubstituted.

[c] For ethylene tetrasubstituted.

[d] Geometry of cyclopentadiene (*cfr*. Ref. [12]).

[e] Evaluated from E_{Λ_1} plus the energy differences between SCF–MO's $\varphi_4 - \varphi_3$ and $\varphi_2 - \varphi_1$.

First ionization potentials and electron affinities of the component systems are taken from the literature [13]; for butadiene the electron affinity (−0.60 eV) was calculated through the Briegleb's relationship [14]. Second ionization potential (8.58 eV) and electron affinity (−2.55 eV) for butadiene were obtained from the above values minus the energy difference between the relevant SCF orbitals.

Coulomb integrals $\gamma_{\mu\nu}$ were calculated by the previously given formula [15] and the resonance integrals $\beta_{\mu\nu}$ by the Kon's relationship [16].

3. Results

The topology of the molecules studied is shown in Fig. 1.

Triafulvene (Methylenecyclopropene) (I)

The results of PPP method in Ref. [17] were subjected to configuration analysis and compared with our standard MIM calculations (columns A in Table 2); those of PPP method in Ref. [4], after application of the configuration

Fig. 1

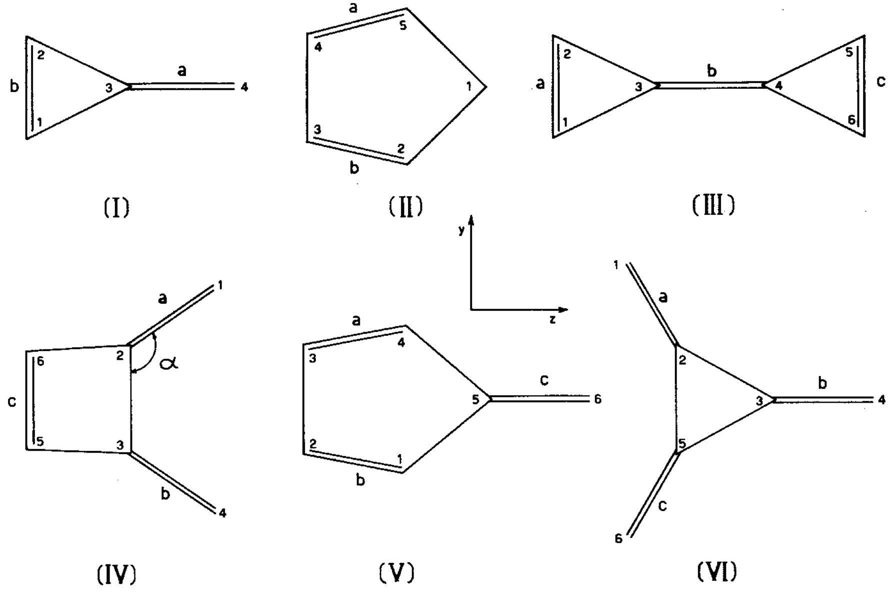

Table 2. Excited singlet states of triafulvene (weights of states; transition energies, oscillator strengths and polarizations)

States	$^1B_2$				$^1A_1$				$^1B_2$				$^1A_1$			
	MIM		PPP		MIM		PPP		MIM		PPP		MIM		PPP	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Γ	—	—	—	—	0.08	0.13	0.07	0.08	—	—	—	—	0.04	0.06	0.01	0.08
Λ_a	—	—	—	—	0.54	0.57	0.23	0.62	—	—	—	—	0.46	0.42	0.72	0.29
Λ_b	0.38	0.40	0.63	0.29	—	—	—	—	0.62	0.60	0.33	0.63	—	—	—	—
T_b^a	—	—	—	—	0.38	0.30	0.63	0.18	—	—	—	—	0.50	0.52	0.22	0.51
T_a^b	0.62	0.60	0.32	0.59	—	—	—	—	0.38	0.40	0.60	0.25	—	—	—	—
Total weight (%)	100	100	95.1	87.8	100	100	92.6	88.1	100	100	92.8	87.6	100	100	95.4	88.0
ΔE (eV)	4.83	4.19	5.48	4.33	5.38	5.16	6.37	6.15	8.23	8.77	9.49	9.10	8.50	9.27	9.61	10.34
f	0.13	0.10	0.27	0.10	0.50	0.49	0.41	0.74	0.36	0.32	0.25	0.44	0.02	<0.01	0.23	0.02
Polar.	*y*	*y*	*y*	*y*	*z*	*z*	*z*	*z*	*y*	*y*	*y*	*y*	*z*	*z*	*z*	*z*

analysis treatment, were compared with the results of a MIM procedure carried with the same parameters as in Ref. [4] (columns B in Table 2). In this table are given the weights of the individual locally excited states (Λ_n) or charge transfer states (T_m^k), together with the total weight of the $V_{\sigma'}^0$ and the data on the electronic transitions; the ground state is indicated by the symbol Γ.

Cyclopentadiene (II)

The structure of the molecule has been recently discussed [12, 18] and a planar configuration with C_{2v} symmetry has been confirmed. The π-electronic states were obtained by the PPP method starting from the SCF–MO's of Table 1 and using the standard parameters; the configuration analysis was applied to the results of the above calculation and a comparison with the results of the MIM procedure is shown in Table 3.

Table 3. Excited singlet states of cyclopentadiene

States	$^1B_2$		$^1A_1$		$^1A_1$		$^1B_2$	
	MIM	PPP	MIM	PPP	MIM	PPP	MIM	PPP
Γ	—	—	0.06	0.06	—	—	–	—
$\Lambda_a(\Lambda_b)$	0.25	0.295	—	—	0.50	0.485	0.25	0.19
$T_b^a(T_a^b)$	0.25	0.19	0.47	0.43	—	—	0.25	0.295
Total weight (%)	100	97	100	92	100	97	100	97
ΔE (eV)	4.44	5.85	6.62	7.65	7.69	8.55	7.91	9.20
f	0.16	0.21	0	0	1.01	1.13	<0.01	<0.01
Polar.	y	y	—	—	z	z	y	y

Triafulvalene (Bis-Cyclopropenylidene) (III)

The results of the PPP method in Ref. [4], after application of the configuration analysis treatment, were compared with the results of MIM calculations; the same geometry was adopted and the resonance integrals were evaluated by the Kon's formula [16] (columns A in Table 4) or by the exponential formula of Ref. [4] (columns B in Table 4).

Dimethylenecyclobutene (IV)

The results of the PPP method in Ref. [19] were subjected to configuration analysis and compared in Table 5 with the MIM calculations obtained for the observed geometry [20] (columns B) by considering three ethylene fragments; columns A relate to a procedure in which the same parameters and geometry as

Table 4. Excited singlet states of triafulvalene (allowed transitions)

States	$^1B_{1u}$			$^1B_{2u}$			$^1B_{2u}$			$^1B_{1u}$			$^1B_{2u}$		
	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP
$1/\sqrt{2}(\Lambda_a+\Lambda_c)$	—	—	—	0.25	0.26	0.17	0.63	0.61	0.64	—	—	—	0.12	0.14	0.01
$1/\sqrt{2}(T_b^a+T_b^c)$	—	—	—	0.64	0.63	0.48	0.08	0.06	0.09	—	—	—	0.28	0.31	0.20
$1/\sqrt{2}(T_a^c+T_c^a)$	—	—	—	0.11	0.11	0.12	0.29	0.33	0.12	—	—	—	0.60	0.55	0.59
$1/\sqrt{2}(T_a^b+T_c^b)$	0.55	0.55	0.38	—	—	—	—	—	—	0.45	0.45	0.50	—	—	—
Λ_b	0.45	0.45	0.50	—	—	—	—	—	—	0.55	0.55	0.38	—	—	—
Total weight (%)	100	100	87.8	100	100	77.1	100	100	85.1	100	100	87.8	100	100	79.7
ΔE (eV)	3.58	3.20	5.58	4.04	3.68	3.55	7.80	7.84	8.93	9.09	9.46	11.09	10.12	10.45	11.53
f	0.45	0.43	0.85	0.12	0.11	0.13	0.60	0.56	0.92	<0.01	<0.01	0.02	0.15	0.17	0.05
Polar.	z	z	z	y	y	y	y	y	y	z	z	z	y	y	y

Table 5. First excited singlet states of dimethylenecyclobutene (three ethylenes as component systems)

States	$^1B_2$			$^1A_1$			$^1A_1$			$^1B_2$		
	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP
Γ	—	—	—	—	—	0.01	0.02	0.03	0.04	—	—	—
$1/\sqrt{2}(\Lambda_a+\Lambda_b)$	—	—	—	0.25	0.32	0.24	—	—	~ 0	—	—	—
$1/\sqrt{2}(T_c^a+T_c^b)$	—	—	—	0.37	0.34	0.31	0.27	0.26	0.13	—	—	—
$1/\sqrt{2}(T_a^c-T_b^c)$	—	—	—	0.37	0.34	0.26	0.27	0.26	0.31	—	—	—
$1/\sqrt{2}(T_a^b+T_b^a)$	—	—	—	—	—	0.01	0.44	0.45	0.32	—	—	—
$1/\sqrt{2}(\Lambda_a-\Lambda_b)$	0.02	0.30	0.01	—	—	—	—	—	—	0.62	0.35	0.55
Λ_c	0.30	0.19	0.21	—	—	—	—	—	—	0.08	0.23	~ 0
$1/\sqrt{2}(T_c^a-T_c^b)$	0.18	0.05	0.12	—	—	—	—	—	—	0.06	0.20	0.04
$1/\sqrt{2}(T_a^c+T_b^c)$	0.18	0.05	0.21	—	—	—	—	—	—	0.06	0.20	0.10
$1/\sqrt{2}(T_a^b-T_b^a)$	0.31	0.41	0.26	—	—	—	—	—	—	0.18	0.02	0.16
Total weight (%)	100	100	81.5	100	100	83.3	100	100	80.1	100	100	85.5
ΔE (eV)	5.01	4.29	4.68	5.00	4.43	6.02	5.08	4.77	4.77	4.63	4.99	6.31
f	0.06	0.02	0.12	0.41	0.45	0.77	0	0	0.01	0.64	0.72	0.89
Polar.	y	y	y	z	z	z	—	—	z	y	y	y

Table 6. First excited singlet states of dimethylenecyclobutene (ethylene(E) and *cis*-butadiene(B) as component systems)

States	$^1B_2$		$^1A_1$		$^1A_1$		$^1B_2$	
	MIM/B	PPP	MIM/B	PPP	MIM/B	PPP	MIM/B	PPP
Γ	—	—	0.04	0.12	0.05	0.02	—	—
$(\Lambda_2)_B$	—	—	0.11	0.26	0.35	0.01	—	—
$(\Lambda_3)_B$	—	—	0.09	0.01	0.05	0.24	—	—
T_E^{3B}	—	—	0.06	0.11	0.55	0.33	—	—
T_{2B}^E	—	—	0.70	0.28	~ 0	0.27	—	—
Λ_E	0.31	0.24	—	—	—	—	~ 0	~ 0
$(\Lambda_1)_B$	0.01	0.19	—	—	—	—	0.98	0.66
$(\Lambda_4)_B$	0.13	0.09	—	—	—	—	~ 0	0.07
T_{1B}^E	0.35	0.22	—	—	—	—	0.01	0.11
T_E^{4B}	0.20	0.13	—	—	—	—	~ 0	0.04
Total weight (%)	100	87.3	100	77.3	100	87.4	100	88.2
ΔE (eV)	4.17	4.68	4.50	4.77	4.98	6.02	5.18	6.31
f	0.25	0.12	0.27	0.01	0.13	0.77	0.45	0.89
Polar.	y	y	z	z	z	z	y	y^-

$(\Lambda_n)_B$: locally excited states of *cis*-butadiene.

T_E^{nB} and T_{nB}^E: charge transfer configuration from ethylene to *cis*-butadiene and from *cis*-butadiene to ethylene respectively.

in Ref. [19] were applied. Finally in Table 6 are shown the results obtained when ethylene and *cis*-butadiene are considered as component systems.

Fulvene (V)

The electronic system of fulvene has been the subject of a large number of studies by various methods [21]. In MIM calculations we used the molecular geometry based upon the crystallographic data on dimethylfulvene [22]. The coplanarity of the carbon skeleton has been recently confirmed by electron diffraction study and nearly equal geometrical parameters were found [23]. The resonance integrals were evaluated by the Kon's formula or by the exponential formula of Ref. [4] (columns A and B respectively in Tables 7 and 8). The configuration analysis procedure was applied to the results of the PPP method [4] by considering as component systems three molecules of ethylene or, alternatively, one molecule of ethylene and one molecule of *cis*-butadiene; a comparison with the MIM results is shown in Tables 7 and 8 respectively.

Trimethylenecyclopropane ([3]-Radialene) (VI)

Standard parameters and observed geometry [24] were used in the calculations; the results of the configuration analysis treatment for the first three excited states are compared with those of the MIM procedure in Table 9.

Table 7. First excited singlet states of fulvene (three ethylenes as component systems)

States	$^1B_2$			$^1A_1$			$^1A_1$			$^1B_2$		
	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP	MIM/A	MIM/B	PPP
Γ	—	—	—	0.04	0.04	0.10	~0	~0	0.01	—	—	—
$1/\sqrt{2}(\Lambda_a+\Lambda_b)$	—	—	—	0.08	0.09	0.02	~0	~0	0.01	—	—	—
Λ_c	—	—	—	0.29	0.29	0.22	0.08	0.08	0.21	—	—	—
$1/\sqrt{2}(T_a^c+T_b^c)$	—	—	—	0.21	0.22	0.12	0.11	0.11	0.05	—	—	—
$1/\sqrt{2}(T_c^a+T_c^b)$	—	—	—	0.30	0.29	0.18	0.14	0.14	0.07	—	—	—
$1/\sqrt{2}(T_a^b+T_b^a)$	—	—	—	0.08	0.07	0.11	0.67	0.67	0.41	—	—	—
$1/\sqrt{2}(\Lambda_a-\Lambda_b)$	0.36	0.36	0.25	—	—	—	—	—	—	0.01	0.06	0.04
$1/\sqrt{2}(T_a^c-T_b^c)$	0.27	0.27	0.34	—	—	—	—	—	—	0.36	0.14	0.07
$1/\sqrt{2}(T_c^a-T_c^b)$	~0	~0	~0	—	—	—	—	—	—	0.30	0.48	0.29
$1/\sqrt{2}(T_a^b-T_b^a)$	0.37	0.37	0.19	—	—	—	—	—	—	0.33	0.32	0.42
Total weight (%)	100	100	77.5	100	100	75.0	100	100	75.9	100	100	82.1
ΔE (eV)	3.29	2.93	3.27	3.95	3.64	5.05	6.28	6.28	6.98	6.45	6.45	8.21
f	0.06	0.05	0.05	0.57	0.55	0.67	0.12	0.12	0.31	0.13	0.12	0.29
Polar.	y	y	y	z	z	z	z	z	z	y	y	y

Table 8. First excited singlet states of fulvene (ethylene(E) and *cis*-butadiene(B) as component systems)

States	$^1B_2$		$^1A_1$		$^1A_1$		$^1B_2$	
	MIM/A	PPP	MIM/A	PPP	MIM/A	PPP	MIM/A	PPP
Γ	—	—	0.02	0.05	0.01	0.01	—	—
$(\Lambda_2)_B$	—	—	0.14	0.19	0.69	0.49	—	—
$(\Lambda_3)_B$	—	—	0.06	0.02	0.01	0.01	—	—
Λ_E	—	—	0.23	0.25	0.22	0.24	—	—
T_{1B}^E	—	—	0.21	0.12	0.02	0.04	—	—
T_E^{3B}	—	—	0.34	0.23	0.05	0.06	—	—
$(\Lambda_1)_B$	0.39	0.38	—	—	—	—	0.61	0.31
$(\Lambda_4)_B$	—	~0	—	—	—	—	—	0.11
T_{2B}^E	0.61	0.47	—	—	—	—	0.39	0.36
T_E^{4B}	—	~0	—	—	—	—	—	0.07
Total weight (%)	100	85.4	100	85.8	100	84.9	100	85.0
ΔE (eV)	3.26	3.27	3.55	5.05	6.23	6.98	6.44	7.26
f	0.02	0.05	0.51	0.67	0.16	0.31	0.18	0.11
Polar.	y	y	z	z	z	z	y	y

Table 9. First excited singlet states of [3]-radialene (three ethylenes as component systems)

States	$^1E'_1$		$^1E'_1$		$^1A'_1$	
	MIM	PPP	MIM	PPP	MIM	PPP
$1/\sqrt{2}(\Lambda_a-\Lambda_c)$	0.44	0.45	0.31	0.27	—	—
$1/\sqrt{2}(T_b^a-T_b^c)$	~0	~0	0.27	0.22	—	—
$1/\sqrt{2}(T_a^c-T_c^a)$	0.29	0.24	0.02	0.02	—	—
$1/\sqrt{2}(T_a^b-T_c^b)$	0.27	0.22	0.40	0.37	—	—
$1/\sqrt{6}(T_a^b+T_b^c+T_c^a-T_b^a-T_c^b-T_a^c)$	—	—	—	—	1.00	0.88
Total weight (%)	100	91	100	88	100	88
ΔE	3.86	5.89	6.70	7.98	6.97	8.38
f	0.46	0.81	0.15	0.17	0	0
Polar.	y, z	y, z	y, z	y, z	—	—
	(degenerate transition)		(degenerate transition)			

4. Discussion

For the triafulvene, in which strong bond fixation exists, the calculated results for both the ground state and the excited states are sensitive to the dependence of the resonance integrals on bond length and to the choice of empirical values for the repulsion integrals. The results in Table 2 reveal clearly that the dependence is more remarkable in PPP calculations than in MIM calculations. Unfortunately, the triafulvene spectrum is not available for a direct comparison between theory and experiment; however, by the configuration analysis treatment a better agreement between the theoretical results is found for the case B in Table 2. In the first transition $^1B_2 \leftarrow {}^1A_1$ the effect of a charge transfer from ethylene *a* to ethylene *b* is remarkable and it determines a spectral shift of about 2 eV respect to the component molecules.

For the cyclopentadiene the results of the configuration analysis and of the MIM technique are similar in the excited state composition, in spite of the differences in transition energies. The first absorption band observed at 5.18 eV [9, 10] is intermediate between the values calculated for the $^1B_2 \leftarrow {}^1A_1$ transition, in the two procedures. The second band of moderate intensity observed at 6.20 eV corresponds to the $^1A_1 \leftarrow {}^1A_1$ transition found at 6.62 eV in MIM calculation (forbidden in the π-approximation). The very strong band at 7.90 eV is assigned to the next $^1A_1 \leftarrow {}^1A_1$ transition ($\Delta E = 7.69$ eV and $f = 1.01$ in MIM calculations). These results are congruent with the values obtained by the CNDO treatment of the molecule [11].

In the case of triafulvalene a remarkable difference in energy is found for the first $^1B_{1u} \leftarrow {}^1A_{1g}$ transition which should be appear as charge transfer band in the longest wave-length region (about 350 nm) if the MIM results are reliable and as ethylenic band at about 220 nm if one look at PPP calculations. Unfortunately a choice is not possible since experimental data are lacking.

The results obtained for the dimethylenecyclobutene are rather contradictory. A comparison between PPP and MIM states is possible; however, in PPP calculations two electronic transitions with different polarization and low intensity are found at about 4.7 eV and other two transitions with different polarization and high intensity are found at about 6 eV, whilst in MIM calculations the four corresponding transitions range from 4.2 to 5.2 eV with different sequence according to the component systems considered and the parameters chosen.

The interpretation of the UV spectra of this compound by the simple method applied to other derivatives is not acceptable; it is necessary probably to include the doubly excited configurations in the CI treatment and the core resonance integral between the opposite carbon atoms in the ring which are only about 2.0 Å apart [6].

The electronic absorption spectrum of fulvene in the gas phase has been recently investigated [25] and four electronic transitions have been identified. The lowest energy (3.42 eV) transition of weak intensity ($f = 0.008$) is assigned to a ${}^1B_2 \leftarrow {}^1A_1$ transition in which a remarkable charge transfer occurs from butadiene to exocyclic ethylene. The second transition is strong ($f = 0.34$) and extends from 267 to 205 nm with a maximum at 235 nm (5.28 eV); it is assigned to a ${}^1A_1 \leftarrow {}^1A_1$ transition and the PPP transition energy agrees with the maximum frequency, whilst the MIM transition energy results lower than the observed $0-0$ frequency (4.65 eV); the excited states composition shows an overestimation in MIM calculations of the contribution of the charge transfer configuration from ethylene to butadiene responsible of the bathochromic shift of the ethylenic band. The third and fourth bands observed at 201.7 nm (6.15 eV) and at 178 nm (6.95 eV) are assigned on the basis of our MIM calculation to an ${}^1A_1 \leftarrow {}^1A_1$ transition at 6.23–6.28 eV and to a ${}^1B_2 \leftarrow {}^1A_1$ transition at 6.44–6.45 eV. It is interesting to remark that the molecule behaves both like a weakly coupled *cis*-butadiene plus ethylene entity and like three ethylene entities as suggested by Heilbronner and coworkers [26].

The trimethylenecyclopropane spectrum [24] is well interpreted by the results of MIM calculation. The first (4.20 eV) and the second (6.70 eV) absorption bands are assigned to allowed degenerate transitions ${}^1E'_1 \leftarrow {}^1A'_1$ at 3.86 and 6.70 eV respectively. The energies of these transitions can not be reproduced by simple PPP calculations including only single excited configurations, also when the composition of the two excited states, as results by configuration analysis, is in agreement with that obtained in MIM calculations.

The results obtained for the above four- and six-π-electron systems of unsaturated small-ring hydrocarbons seem to suggest these general conclusions:

a) it is confirmed the validity of the MIM method for compounds in which alternanting single and double bonds occur, also by different choice of the component systems when allowed by molecular symmetry;

b) the additional informations drawn from the results of the calculations of the PPP type through the configuration analysis treatment justify, except for the dimethylenecyclobutene, the inclusion of only single excited configurations in MIM calculations of electronic transition energies;

c) remarkable differences in transition energies related to same electronic excited states may occur in PPP and MIM calculations with the same parameters; MIM energies should be the most reliable.

Financial aid from the Italian C.N.R. is gratefully acknowledged.

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