Predictions of Molecular Geometries and Electronic Spectra of Complex Unsaturated Molecules from MC-LCAO-MO Method.
II. 1,3-Butadiene and Cyclobutadiene

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A multi-configuration (MC)-LCAO-MO method is applied to 1,3-butadiene and cyclobutadiene, predicting their molecular geometries and electronic spectra. The molecular ground state geometry, electronic spectrum and stabilization energy of the *trans-* to the *cis*-isomer of 1,3-butadiene are predicted to be in good accord with experiments and with those derived from the ordinary semi-empirical SCF-CI method. The results obtained for cyclobutadiene indicate that (a) the Jahn-Teller distortion occurs to favor a rectangular (D_{2h}) form, the stabilization energy being 0.3—0.9 eV depending on approximations, and (b) even in a square (D_{4h}) form a singlet (ground) state is more stable than a triplet state by *ca.* 0.3 eV. It is also shown that the lowest excited singlet and triplet states ($^3A_{2g}$ and $^1B_{1g}$) in the square form are not subjected to the Jahn-Teller effect. A discussion is given on a possible error in a CI treatment arising when degenerate molecular orbitals are expressed by real coefficients of atomic orbitals.

In previous papers,[1-4] a semi-empirical multi-configuration (MC)-LCAO-MO method in which a π-electron approximation is used was proposed in order to predict molecular geometries of ground and excited electronic states of unsaturated hydrocarbons, in particular those having open-shell MO's. The method was found to be useful, when applied to the benzene and triphenylene ions, for the examination of a static Jahn-Teller effect. One of the fruitful results obtained up to the present is that the method can be applied with the same degree of accuracy as the ordinary semi-empirical SCF-CI method to any unsaturated hydrocarbons independently of whether their electronic configurations are made up of closed shells or open shells and whether their MO's are degenerate or non-degenerate. This fact allows one to make use of the method securely for predictions of electronic structures of π-electron systems whose geometrical conformations are unknown.

The purpose of the present paper is twofold. One is to answer whether our MC-LCAO-MO method can be reliably used for predictions of molecular geometries and electronic structures of unsaturated open-chain molecules, thereby we have chosen 1,3-butadiene as a prototype of linear polyenes. As in the preceding paper[4] (called Part I of this series), we will compare the results obtained by our method with those of the usual SCF-CI calculation. We also discuss which isomer, *cis* or *trans*, is more stable.

The other is to complete our study of many years in a Jahn-Teller effect in unsaturated molecules by making use of the present method. We reported previously[5] a study of the effect in cyclobutadiene, which however was somewhat unsatisfactory in the selection of configuration functions taken for CI calculation and in the use of a bond order-bond length relationship that was found later to be not consistent with the whole scheme of the present MC-LCAO-MO method. Noting that there occur complicated CI mixings between different symmetry species of configuration functions when degenerate MO's are expressed by *real* coefficients of atomic orbitals, we carefully analyse the electronic structure of cyclobutadiene. We predict molecular geometry and spin multiplicity of the ground state, molecular geometries of some excited states, stabilization energies due to the Jahn-Teller effect and transition energies and oscillator strengths of square and rectangular cyclobutadiene.

Method of Calculation

In this section we will only give a brief outline of the method, the detail of which has been stated previously.

In order to construct a secular equation from which MO's are determined, we use throughout the calculation the formula

$$\alpha_p = -I_p - \sum_{q \neq p} (q : pp) \qquad (1)$$

for the diagonal elements and the formulas

$$\beta_{pq} = \beta_0 \exp[-(r_{pq} - b)/a] \quad \text{(Approximation (1))} \qquad (2a)$$

and

$$\beta_{pq} = -\frac{1}{2} K S_{pq}(I_p + I_q) \quad \text{(Approximation (2))} \qquad (2b)$$

for the off-diagonal elements. Here I_p is an appropriate valence-state ionization potential of carbon p, (q : pp) the penetration integral, r_{pq} the carbon-carbon distance and S_{pq} is the overlap integral. The constants β_0, a, b, K, and I_p are set equal to the values −2.38 eV, 0.3938 Å, 1.397 Å, 0.86291, and 11.290 eV, respectively. Non-neighbor β_{pq}'s are also included.

The MO's thus obtained for a previously guessed molecular geometry are employed to calculate the matrix elements of the total Hamiltonian operator for CI mixing, in which the matrix elements of the one-electron Hamiltonian operator between MO's ϕ_i and ϕ_j are calculated to be

$$\varepsilon_{ij} = \delta_{ij} U_{ij} - \sum_{p} \sum_{q \neq p} C_{pi} C_{pj} (pp|qq) \qquad (3)$$

where U_{ii} and C_{pi} are the eigenvalues and atomic orbital coefficients, respectively, of MO's ϕ_i. The two-center electronic repulsion integrals (pp|qq) are evaluated by the formula[6]

$$Z^{-1}(pp|qq) = 0.1227 - 0.005093\rho + 0.000070\rho^2 \qquad (4)$$

(in a. u.) with $\rho = Zr_{pq}/a_0$. Here the effective nuclear charge for carbon 2pπ AO's, $Z=3.250$, is assumed to be constant throughout the calculation and a_0 is the Bohr radius.

The π-bond orders P_{pq} obtained after each step of CI computation are used to revise the bond lengths in the next step of calculation through the relationship

$$r_{pq} = 1.523 - 0.193P_{pq} \tag{5}$$

and this process is repeated until a self-consistent solution is obtained with respect to bond lengths.

Electronic Structures of *trans*- and *cis*-1,3-Butadiene

To begin with, the MC-LCAO-MO method is applied to the calculation of the electronic structures of *trans*- and *cis*-1,3-butadiene; all the C–C–C bond angles are assumed to be 123° for both *trans*- and *cis*-butadiene. For comparison, the usual semi-empirical SCF-CI calculation is also carried out with the same atomic integrals, values of constants and species of configuration functions as in the MC-LCAO-MO method. The C–C bond lengths and C–C–C bond angles used in the SCF-CI calculation are taken from the experimental values obtained for the *trans*-isomer7) (see the last column of Table 2), and assumed to be the same for the *cis*-form. The penetration integrals due to the hydrogen atoms are included for only nearest-neighbors, being given a constant value 0.627 eV.6)

As shown in Table 1, the species of configuration functions employed in the CI calculation are classified according to the irreducible representations of the C_{2h} (*trans*) and C_{2v} (*cis*) symmetries. ϕ_i^k, ϕ_{ij}^{kl}, *etc.* are singly-, doubly-excited configuration functions, *etc.* (ϕ_i^k, for example, is constructed by promoting an electron in the occupied MO ϕ_i of the ground configuration ϕ_0 to the unoccupied MO ϕ_k) and are spin-eigenfunctions for the singlet and triplet states belonging to the corresponding symmetries. The explicit formulas of these singly- and doubly-excited configuration functions have been given previously8); triply- and quadruply-excited configuration functions are easily constructed in a similar way.

Table 1. Symmetry classification of configuration functions for *trans*- and *cis*-1,3-butadiene

C_{2h} (*trans*)	C_{2v} (*cis*)	Species of configuration function
^1A_g	$^1A_1$	ϕ_0, ϕ_2^4, ϕ_1^3, ϕ_{22}^{33}, ϕ_{22}^{44}, ϕ_{11}^{33}, ϕ_{11}^{44}, $\phi_{12}^{34}(1)$, $\phi_{12}^{34}(2)$, ϕ_{112}^{334}, ϕ_{122}^{344}, ϕ_{1122}^{3344}.
^3A_g	$^3A_1$	ϕ_2^4, ϕ_1^3, $\phi_{12}^{34}(I)$, $\phi_{12}^{34}(II)$, $\phi_{12}^{34}(III)$, ϕ_{112}^{334}, ϕ_{122}^{344}.
$^{1,3}B_u$	$^{1,3}B_2$	ϕ_2^3, ϕ_1^4, ϕ_{22}^{34}, ϕ_{11}^{34}, ϕ_{12}^{33}, ϕ_{12}^{44}, ϕ_{122}^{334}, ϕ_{112}^{344}.

Table 2. Bond lengths of 1,3-butadiene (Å)

Bond	Approximation (1)a)		Approximation (2)a)		Exptl.7) (122.86°)b)
	trans-	*cis*-	*trans*-	*cis*-	
1—2 3—4	1.3454	1.3453	1.3484	1.3479	1.3439
2—3	1.4716	1.4713	1.4648	1.4659	1.4672

a) The columns under Approximation (1) and Approximation (2) are the results calculated with Eqs. 2a and 2b in the text, respectively. b) Observed C-C-C bond angle.7)

In Table 2 are shown the bond lengths finally obtained for the ground states of *trans*- and *cis*-1,3-butadiene together with the corresponding observed values. It is found that the calculated values are in good accord with experiments.

The total energies for the two isomers of 1,3-butadiene are evaluated as

$$E_t = E + V. \tag{6}$$

Here the total electronic energy E is assessed through the formula

$$E = E_\pi + E_\sigma + E_c \tag{7}$$

where E_π and E_σ are, respectively, the π-electron and σ-electron energies to be obtained by the MC-LCAO-MO and/or the SCF-CI methods (the explicit forumla of E_σ depending upon bond lengths is given in Ref. 1; the value of E_σ determined by a fixed molecular geometry is to be just added in a SCF-CI calculation) and E_c is the sum of the effective internuclear interaction between π-electronless carbon cores and assumed to be

$$E_c = \sum_{p<q}\sum (pp|qq). \tag{8}$$

The term V is the sum of the energies due to the internuclear interactions between the non-neighbor carbon and hydrogen atoms (V_{CH}) and between the hydrogen atoms (V_{HH}), each being estimated according to Bartell's formulas9) (in eV):

$$\left.\begin{aligned} V_{CH} &= 5.419[358\exp(-r/0.490)-1]r^{-6} \\ V_{HH} &= 285.9\exp(-r/0.245) - 2.135r^{-6}. \end{aligned}\right\} \tag{9}$$

The C–H bond length is taken to be 1.094 Å.7)

Table 3 gives the energy differences between *trans*- and *cis*-1,3-butadiene in their ground states calculated by the MC-LCAO-MO and the SCF-CI methods. The two methods predict the same result that the *trans*- is energetically more stable than the *cis*-species, though the difference in E appears to be negligibly small and the main term comes from the energy difference in V. The stabilization energies 0.11 eV calculated with Approximation (1) and 0.14 eV with Approximation (2) well compare with the value 0.12 eV obtained by a non-empirical SCF πMO method with a correction for nuclear repulsion10) and with the value 0.22 eV obtained by an *ab initio* SCF-CI method.11) The corresponding observed value is 0.10 eV, which was obtained a long time ago.12)

Table 4 shows the calculated transition energies and oscillator strengths of the singlet and triplet transitions in 1,3-butadiene, together with the observed values. The MO's and the molecular geometries used are those obtained in the ground state calculation and the species of configuration functions listed in Table 1 are employed for the CI calculation. The first excited ^1A_g($^1A_1$ for *cis*) state comes out to be very close to the ^1B_u($^1B_2$ for *cis*) state which is to be expected as the lowest excited state and this is due to a strong interaction of the singly-excited configurations with the doubly-excited configurations, in the main with the configura-

TABLE 3. ENERGY DIFFERENCES BETWEEN *trans*- AND *cis*-1,3-BUTADIENE IN THEIR GROUND STATES (eV)

Method	Approximation (1)			Approximation (2)		
	ΔE_t[a]	ΔE	ΔV	ΔE_t[a]	ΔE	ΔV
MC-LCAO-MO	−0.1082	0.0103	−0.1185	−0.1377	−0.0180	−0.1197
SCF-CI	−0.1179	0.0071	−0.1250	−0.1444	−0.0194	−0.1250

a) $\Delta E_t = E_t(trans\text{-}) - E_t(cis\text{-})$, $E_t = E + V$.

TABLE 4. TRANSITION ENERGIES (eV) AND OSCILLATOR STRENGTHS FOR 1,3-BUTADIENE

State	Approximation (1)				Approximation (2)				Exptl.
	MC-LCAO-MO		SCF-CI		MC-LCAO-MO		SCF-CI		
	Energy	f	Energy	f	Energy	f	Energy	f	
trans									
^1A_g	0.000	ref.	0.000	ref.	0.000	ref.	0.000		
	5.960		5.972		5.399		5.466		
	7.524		7.545		7.316		7.347		(7.2)[a]
	9.542		9.566		9.273		9.325		
^1B_u	6.073	0.732	6.076	0.733	5.775	0.718	5.809	0.717	5.92[13]
	9.390	0.151	9.430	0.152	9.285	0.130	9.320	0.132	
	10.660	0.001	10.686	0.001	10.140	0.010	10.206	0.010	
^3A_g	4.368		4.395		4.156		4.188		4.91[13]
	7.791		7.809		7.630		7.671		
	11.909		11.958		11.565		11.628		
^3B_u	3.162		3.166		2.795		2.844		3.22[13]
	7.118		7.153		6.737		6.799		
	10.031		10.072		9.836		9.877		
cis									
$^1A_1$	0.000	ref.	0.000	ref.	0.000	ref.	0.000	ref.	
	5.965	0.005	5.976	0.006	5.390	0.012	5.446	0.012	
	7.799	0.531	7.820	0.533	7.515	0.439	7.545	0.441	(7.2)[a]
	9.101	0.017	9.115	0.017	8.778	0.073	8.820	0.073	
$^1B_2$	5.699	0.324	5.697	0.324	5.333	0.315	5.358	0.313	
	9.294	0.001	9.331	0.001	9.230	0.003	9.263	0.003	
	10.624	0.000	10.647	0.000	10.027	0.000	10.082	0.000	
$^3A_1$	4.380		4.406		4.149		4.177		
	7.705		7.720		7.554		7.589		
	11.915		11.961		11.546		11.603		
$^3B_2$	3.146		3.149		2.744		2.782		
	7.134		7.167		6.738		6.794		
	9.812		9.846		9.593		9.626		

a) This assignment appears to be incorrect.[13–15]

tion ϕ_{22}^{33}. A similar situation was found in an *ab initio* calculation.[11] As is well known, such lowering of the ^1A_g state is not obtained in the CI calculation in which only the singly-excited configurations are taken into account. Recent experimental[13] and more elaborate *ab initio*[14,15] studies of the electronic spectrum of *trans*-1,3-butadiene indicate that the transition in the 7.2 eV region should be assigned to a ^1B_u state of Rydberg character. We are not qualified for giving comments on this matter, since Rydberg-type transitions cannot be predicted by a minimal basis calculation such as the present treatment. The rest of the results shown in Table 4 appears to be in good agreement with experiments.

Electronic Structure of Cyclobutadiene

So far we have demonstrated that the present method is credible to reproduce the bond lengths and the electronic spectrum of 1,3-butadiene together with the stabilization energy of the *trans*-form against *cis*-, at least with the same accuracy as the usual SCF-CI method using a fixed molecular geometry. With this and accumulated confidence obtained in a series of papers hitherto, we challenge cyclobutadiene.

As for cyclobutadiene, if it exists as a stable entity, there are two problems of theoretical and experimental interest: molecular geometry and spin multiplicity of the ground state. Up to date, various theoretical studies on cyclobutadiene have been carried out with CI[16–18] and without CI[19]; all of these results indicate that the molecule has a singlet ground state of a rectangular (the D_{2h} symmetry) form.[17–19] Recently, several authors[20,21] have reported studies of the photochemical synthesis and the infrared spectrum of cyclobutadiene and inferred its geometrical structure to be a square (the D_{4h} symmetry) form in its ground state. Cyclobutadiene, if it assumes to take a geometry of the D_{4h} symmetry, is considered theoretically to be subjected to the Jahn-Teller effect[†] in the ground and some excited states, because it has a pair of degenerate π-MO's partly occupied in the ground configuration.

In the following CI calculation for cyclobutadiene, we take account of all species of configuration functions which can be constructed by accommodating four π-electrons on four π-MO's, as in the case of 1,3-butadiene. The resulting configuration functions are classified into 20 singlets, 15 triplets and 1 quintuplet, the quintuplet state being not treated in the present study.

The four π-MO's are written, under the zero-differential overlap assumption, for cyclobutadiene of the D_{4h} geometry as in the following:

$$\left.\begin{array}{lll} a_{2u} & & \phi_1 = \frac{1}{2}(\chi_1+\chi_2+\chi_3+\chi_4) \\ e_g & \left\{\begin{array}{l} \\ \\ \end{array}\right. & \begin{array}{l} \phi_2 = a(\chi_1-\chi_3) - b(\chi_2-\chi_4) \\ \phi_3 = c(\chi_1-\chi_3) + d(\chi_2-\chi_4) \end{array} \\ b_{2u} & & \phi_4 = \frac{1}{2}(\chi_1-\chi_2+\chi_3-\chi_4) \end{array}\right\} \qquad (10)$$

where the orbital symmetries are determined by making use of the coordinate system shown in Fig. 1 and the MO's ϕ_2 and ϕ_3 are a pair of degenerate MO's. In the symmetry classification of configuration functions according to which each unit CI calculation is carried out, it should be noted that the irreducible representations to which some functions belong in the D_{4h} point group are varied depending upon whether the degenerate MO's are expressed by complex or real coefficients of atomic orbitals. This situation can be explained by taking up, for example, the singlet configuration functions having a g representation of the D_{4h} point group. If the degenerate MO's are expressed through the *complex* coefficients determined by the symmetry, that is, if the coefficients in Eq. 10 are set as $a=c=1/2$ and $b=d=-i/2$ (i: imaginary), then the species of configuration functions are classified as in Table 5. (Here we assume the ground configuration ϕ_0 as $(\phi_1{}^2\phi_2{}^2)$, and as for the full symmetry classification of the other singlet and triplet configuration species, see Refs. 5 and 16). On the other hand, if the MO's are *real* and all the coefficients a, b, c, and d are set equal to 1/2, then the symmetry species are determined as in Table 6. It should be noted that the species of the A_{1g} and B_{1g} configuration functions shown in Table 5 are different from the corresponding ones listed in Table 6. Furthermore, when the coefficients in the real MO's are set as $a=d$ and $b=c$ but $a \neq b$, the configuration species of the A_{1g} and B_{1g} symmetries shown in Table 6 mix partly with those of A_{2g} and B_{2g}, respectively, and the CI mixings to be allowed become more complicated.

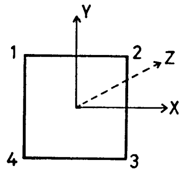

Fig. 1. Coordinate system of cyclobutadiene.

TABLE 5. SYMMETRY CLASSIFICATION OF g-SINGLET CONFIGURATION FUNCTIONS: CASE OF COMPLEX MO'S

B_{2g}: $\phi_0-\phi_{22}^{33}$, $\phi_{12}^{34}(1)$, $\phi_{11}^{44}-\phi_{1122}^{3344}$;
B_{1g}: $\phi_0+\phi_{22}^{33}$, $\phi_{12}^{34}(2)$, $\phi_{11}^{44}+\phi_{1122}^{3344}$;
A_{1g}: ϕ_2^3, $\phi_1^4+\phi_{122}^{334}$, ϕ_{22}^{44}, ϕ_{11}^{33}, ϕ_{112}^{344}; A_{2g}: $\phi_1^4-\phi_{122}^{334}$.

TABLE 6. SYMMETRY CLASSIFICATION OF g-SINGLET CONFIGURATION FUNCTIONS: CASE OF REAL MO'S

B_{2g}: $\phi_0-\phi_{22}^{33}$, $\phi_{12}^{34}(1)$, $\phi_{11}^{44}-\phi_{1122}^{3344}$;
B_{1g}: ϕ_2^3, $\phi_1^4+\phi_{122}^{334}$, ϕ_{112}^{344};
A_{1g}: $\phi_0+\phi_{22}^{33}$, $\phi_{12}^{34}(2)$, ϕ_{22}^{44}, ϕ_{11}^{33}, $\phi_{11}^{44}+\phi_{1122}^{3344}$;
A_{2g}: $\phi_1^4-\phi_{122}^{334}$.

In the previous study on cyclobutadiene,[5] we have carried out each unit CI computation by making use of the symmetry species of configurations classified as in Table 5, despite of the fact that the degenerate MO's used are real. This probably led to an unsatisfactory result not only in the symmetry assignment of the electronic states but also in the magnitudes of the transition energies. In the present study, therefore, we have chosen all the 12 configuration functions having a g representation for a unit CI calculation, from which the eigenvalues and eigenfunctions of the singlet A_{1g}, A_{2g}, B_{1g}, and B_{2g} states are obtained. As for the other states, 7 and 8 configuration functions are taken for the triplet g state and the singlet and triplet u states, respectively.

Table 7 shows the bond lengths obtained for the square and rectangular forms together with the corresponding π-bond orders. It is found that the lowest $^3A_{2g}$ and $^1B_{1g}$ states in the square form are not subjected to the Jahn-Teller distortion; that is, self-consistent solutions do not converge to a rectangular form but to the square form. A similar situation has been seen in the lowest excited states of the benzene anion and cation.[1,2] This is caused by the fact that the configuration $\phi_2{}^3$ shown in Table 6 is the main term in the CI mixing and gives a bond-order distribution which favors a square geometry.

[†] A word "second-order" or "pseudo" Jahn-Teller effect is sometimes used for the stabilization due to the second-order terms of an expanded Hamiltonian operator for the electronic motion in the field of nuclei. The ground state ($^1B_{1g}$) of cyclobutadiene is actually the case. On the other hand, the excited states ^1E_u and ^3E_u of cyclobutadiene receive the "first-order" Jahn-Teller effect. We hereafter use only the word "Jahn-Teller effect" for both ground and excited states of cyclobutadiene.

TABLE 7. CALCULATED BOND LENGTHS (Å) AND π-BOND ORDERS IN CYCLOBUTADIENE

State	D_{4h}-geometry				State	D_{2h}-geometry$^{a)}$			
	Approx. (1)		Approx. (2)			Approx. (1)		Approx. (2)	
	Bond length	Bond order	Bond length	Bond order		Bond length	Bond order	Bond length	Bond order
$^1B_{2g}$	1.432	0.472	1.432	0.473	^1A_g	1.519	0.019	1.515	0.041
$^3A_{2g}$	1.431	0.478	1.430	0.479		1.341	0.941	1.346	0.915
$^1A_{1g}$	1.434	0.459	1.435	0.457	$^1B_{2u}$	1.523	0.000	1.523	0.000
$^1B_{1g}$	1.427	0.499	1.427	0.499		1.430	0.484	1.430	0.480
^1E_u	1.477	0.240	1.477	0.238	$^3B_{2u}$	1.523	0.000	1.523	0.000
^3E_u	1.479	0.229	1.478	0.234		1.433	0.468	1.432	0.474

a) The upper and lower figures in these column are the values for the 1—2 and 2—3 bonds, respectively.

TABLE 8. ENERGY LEVELS OF THE LOWER ELECTRONIC STATES OF CYCLOBUTADIENE IN D_{4h}-GEOMETRY (eV)

State	Approximation (1)			Approximation (2)		
	$\Delta E^{a)}$	ΔE_π	ΔE_σ	$\Delta E^{a)}$	ΔE_π	ΔE_σ
$^1B_{2g}$	0.000	0.000	0.000	0.000	0.000	0.000
$^3A_{2g}$	0.272	0.247	0.025	0.306	0.250	0.056
$^1A_{1g}$	1.291	1.339	−0.048	1.195	1.336	−0.141
$^1B_{1g}$	1.616	1.502	0.114	1.766	1.535	0.231

a) Energy difference referred to the $^1B_{2g}$ state, $E=E_\pi+E_\sigma$.

In Table 8 are shown the energy levels obtained for the lower electronic states of cyclobutadiene in the D_{4h} geometry given in Table 7. The energy differences due to the term E_c in Eq. 7 were omitted, since they were found to be negligibly small. Table 8 shows that the $^1B_{2g}$ state is more stable than the $^3A_{2g}$ state by *ca.* 0.3 eV, that is, the ground state of cyclobutadiene is likely to be the singlet state in the D_{4h} geometry rather than a triplet state. This result is consistent with what obtained by Buenker and Peyerimhoff,[17)] except that in their prediction the $^3A_{2g}$ state has a slightly rectangular equilibrium form, but conflicts with that of Dewar *et al.*;[19)] the latter authors have predicted the triplet to be more stable than the singlet in a square form.

The instability due to the Jahn-Teller effect is calculated for the ground ($^1B_{2g}$) state and the lowest excited states (^1E_u and ^3E_u) in the D_{4h} geometry. The entries in Table 9 are the energy differences, $\Delta E=\Delta E_\pi+\Delta E_\sigma$, between the corresponding species of the D_{2h} and D_{4h} geometries. The table shows that cyclobutadiene is no doubt subjected to the Jahn-Teller distortion in the ground and some excited states and the singlet ground state of the rectangular form is energetically most favorable. The latter conclusion agrees with those of all the other theoretical studies in the past,[17—19)] but is not in accord with the recent experimental inferences[20,21)] which indicate that the molecule should prefer a square rather than a rectangular form, probably in its ground state.

The previous study on cyclobutadiene,[5)] in which the CI treatment was considered to be incomplete as mentioned above, misassigned the singlet A_{1g} and B_{1g} states of D_{4h}-cyclobutadiene and predicted the lowest $^1B_{1g}$ state to be slightly lower than the lowest $^1A_{1g}$ state. However, the conclusion on the Jahn-Teller effect in cyclobutadiene obtained in the previous study is essentially consistent with that mentioned above, though the previously obtained stabilization energy for the ground state is less than the present value by 0.2 eV.

Lastly, we show the calculated results for transition energies and oscillator strengths of the D_{4h} and D_{2h} species of cyclobutadiene. The MO's and the molecular geometries used are those obtained for the singlet ground states of both species. Table 10 lists a part of the results obtained from the full CI calculation. There can be seen a fairly definite difference between the energies of the lower excited states calculated under Approximations (1) and (2) in the D_{2h} geometry. This difference is mainly caused by the fact that Approximation (1) leads the ground state of cyclobutadiene to receive a more remarkable Jahn-Teller distortion in its molecular geometry and energy than Approximation (2) (*cf.* Tables 7 and 9).

The results listed in Table 10 are partly in agreement with those obtained by Allinger and Tai;[18)] in particular, the singlet spectrum of the square form resembles each other. Though we have no experimental datum to compare with our prediction, we feel confident that

TABLE 9. STABILIZATION ENERGIES DUE TO THE JAHN-TELLER EFFECT IN CYCLOBUTADIENE (eV)

Reference state	Approximation (1)			Approximation (2)		
	$\Delta E^{a)}$	ΔE_π	ΔE_σ	$\Delta E^{a)}$	ΔE_π	ΔE_σ
$^1A_g-{}^1B_{2g}$	−0.921	−2.095	1.174	−0.300	−1.248	0.948
$^1B_{2u}-{}^1E_u$	−0.283	−0.537	0.254	−0.156	−0.410	0.254
$^3B_{2u}-{}^3E_u$	−0.319	−0.560	0.241	−0.170	−0.424	0.254

a) $\Delta E=E(D_{2h})-E(D_{4h})$, $E=E_\pi+E_\sigma$.

Table 10. Calculated transition energies (eV) and oscillator strengths for cyclobutadiene

	D_{4h}-geometry					D_{2h}-geometry			
	Approx. (1)		Approx. (2)			Approx. (1)		Approx. (2)	
State	Energy	f	Energy	f	State	Energy	f	Energy	f
Singlet					Singlet				
B_{2g}	0.000	ref.	0.000	ref.	A_g	0.000	ref.	0.000	ref.
A_{1g}	1.204		1.175		B_{1g}	3.299		2.667	
B_{1g}	1.821		1.804		A_g	4.124		2.879	
E_u	5.698	0.052	5.394	0.072	B_{2u}	6.363	0.142	5.667	0.159
A_{1g}	7.515		7.208		B_{3u}	8.241	0.003	6.933	0.008
E_u	8.089	0.315	8.682	0.309	B_{2u}	8.597	0.670	8.833	0.597
A_{2g}	9.971		10.266		A_g	9.281		8.182	
B_{1g}	11.131		11.426		B_{1g}	10.219		10.378	
					B_{3u}	10.755	0.011	10.319	0.023
Triplet					Triplet				
A_{2g}	0.317		0.313		B_{1g}	1.787		1.173	
E_u	3.236		3.028		B_{2u}	3.863		3.289	
E_u	6.448		6.926		B_{3u}	5.827		4.592	
A_{2g}	8.888		9.178		B_{2u}	7.180		7.291	
B_{1g}	9.971		10.266		B_{3u}	8.923		8.360	
A_{1g}	9.971		10.266		B_{1g}	9.223		9.352	
B_{2g}	9.971		10.266		A_g	11.529		11.044	

the electronic spectra calculated for the square and rectangular forms of cyclobutadiene are about right from the viewpoint that the same method has been successful in reproducing the observed data for 1,3-butadiene and other unsaturated hydrocarbons.

Conclusion

The results obtained so far are summarized as in the following:

(a) The MC-LCAO-MO method can be applied, with about the same degree of accuracy as the usual semi-empirical SCF-CI method with fixed molecular geometry, to predictions of molecular geometries and electronic spectra of linear polyenes as well as cyclic polyenes, independently of whether configurations are made up of closed-shells or open-shells and whether MO's are degenerate or non-degenerate.

(b) The *trans*-1,3-butadiene is predicted to be stable than the *cis*- by 0.11—0.14 eV.

(c) The ground $^1B_{2g}$ state of square cyclobutadiene lies below the $^3A_{2g}$ state by 0.3 eV.

(d) The lowest $^3A_{2g}$ and $^1B_{1g}$ states in the square form are not subjected to the Jahn-Teller distortion.

(e) The Jahn-Teller distortion occurs to favor rectangular cyclobutadiene which has a singlet ground state, bond length expansion and contraction being 0.09 Å for the ground state and 0.04 Å for the lowest excited degenerate singlet and triplet states.

(f) The stabilization energy due to the Jahn-Teller effect for the ground state of cyclobutadiene is predicted to be 0.6 eV on the average, depending upon the approximation for the two-center core resonance integral.

An additional remark is as follows: When one uses degenerate MO's expressed by *real* coefficients of atomic orbitals, all the g (or u) state functions having the same multiplicity are recommended to be taken together in each unit CI calculation.

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