

Molecular and Electronic Structure of the Low-Lying Electronic States of Cycloalkenylenes: Cyclopentadienylydene

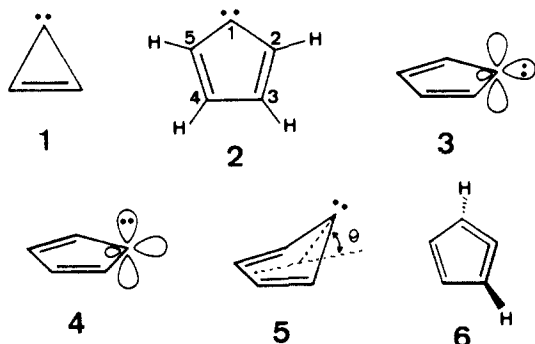
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Abstract: Results of semiempirical (MNDO) and ab initio (at the SCF, TCSCF, and CISD levels of theory) calculations on the low-lying electronic states of cyclopentadienylydene are reported. In addition to the ground state, which is the 3B_1 triplet, three open-shell singlets (1A_2 , 1B_1 , 1B_2), two triplets (3A_2 , 3B_2), and four closed-shell singlets (1^1A_1 , 2^1A_1 , 3^1A_1 , $1^1A'$) are described. The two lower excited states are the 3A_2 triplet and the 1A_2 singlet open-shell diradical, which are predicted, at the CISD/6-31G* level, to lie about 7–8 kcal/mol above the ground state. Neither the antiaromatic (four π electrons) 1^1A_1 nor the aromatic (six π electrons) 2^1A_1 planar singlet states are found to be true potential energy minima. Furthermore, the present ab initio results do not support the existence of any low-lying singlet state (1A) of allenic nature. The lowest energy closed-shell singlet is a $^1A'$ state possessing a nonpolar C_s equilibrium geometry, which is predicted, at the highest ab initio level of theory considered, to lie about 12 kcal/mol above the ground state.

I. Introduction

In a previous paper,² hereafter referred as part 1, as a prelude to a detailed study of the role of low-lying excited states in the chemistry of cycloalkenylenes, the molecular structure and energetics of the lower electronic states of cyclopropenylydene (**1**), the simplest example of *union*³ of methylene with an even-conjugated polyene possessing $4n + 2$ π electrons, were investigated by means of MNDO⁴ and ab initio molecular orbital (MO) calculations.



Cyclopentadienylydene (**2**), a carbocyclic carbene homologous to **1**, may be considered the simplest example of *union* of methylene with an even-conjugated polyene possessing $4n$ π electrons (butadiene). The interaction of the butadiene π system with the carbene center should favor a triplet (3B_1) ground state for **2**.⁵ This prediction is in good agreement with experimental data.⁶

Although the chemistry of **2** in solution appears to be well established and has been ascribed to a closed-shell singlet state,^{7,8} both the molecular and electronic structures of this singlet remain uncertain. Thus, assuming that the molecule adopts a planar geometry (C_{2v} point group symmetry), two alternative electronic configurations have been postulated in the past for singlet **2**.

Structures **3** and **4** are simple pictorial descriptions of these electronic configurations. While configuration **3** possesses four π electrons and can be formally related to the $\sigma^2\pi^0$ ground-state (S_0) configuration of methylene, configuration **4** has six π electrons and can be related to the $\sigma^0\pi^2$ configuration of the doubly excited state (S_2) of methylene. The electrophilicity of the singlet state of **2** appears to be demonstrated experimentally and has been discussed⁹ as an indication that it has the "aromatic" electronic configuration **4**. In contrast, multiconfiguration self-consistent field (MCSCF) calculations,¹⁰ including configurations **3** and **4**, indicate a lower energy value for the singlet state with the largest contribution from the "antiaromatic" electronic configuration **3**.

A recent MNDO study of **2** by Waali and co-workers¹¹ has shown that none of the C_{2v} molecular structures calculated for the singlet states arising from the electronic configurations **3** and **4** are a true potential energy minimum. The force constant calculations proved that the MNDO-optimized structure for the singlet with the electronic configuration **3** has one imaginary vibrational frequency, which corresponds to a normal mode that transforms the C_{2v} geometry into a nonplanar C_s structure (**5**). Such a structure came out to be the lowest energy singlet state ($^1A'$) of **2**. As regards the alternative singlet state with the electronic configuration **4**, the MNDO-optimized structure showed two imaginary vibrational frequencies. While the normal mode of one of these imaginary frequencies corresponds to nuclear movements that would yield the aforementioned structure **5**, the other normal mode would lead to a slightly twisted C_2 structure (**6**). The latter structure corresponds to a singlet state (1A) of allenic nature lying 4.4 kcal/mol above the $^1A'$ singlet. Moreover, according to the MNDO atomic net charges, both the $^1A'$ and 1A singlets could exhibit electrophilic behavior. Therefore, the question concerning the electronic configuration of the singlet state of **2** responsible for its solution chemistry still seems to be open. In addition, experimental results with cyclic conjugated carbenes generated from aza analogues of diazocyclopentadiene suggest that low-lying electronic states other than the methylene S_0 -like singlet might be involved in such cases.¹² In particular, a highly reactive carbene with a strong diradical character has been postulated.¹²

While several theoretical studies of **2** have appeared,^{10,11,13-16} none of them have considered the possible open-shell singlet states

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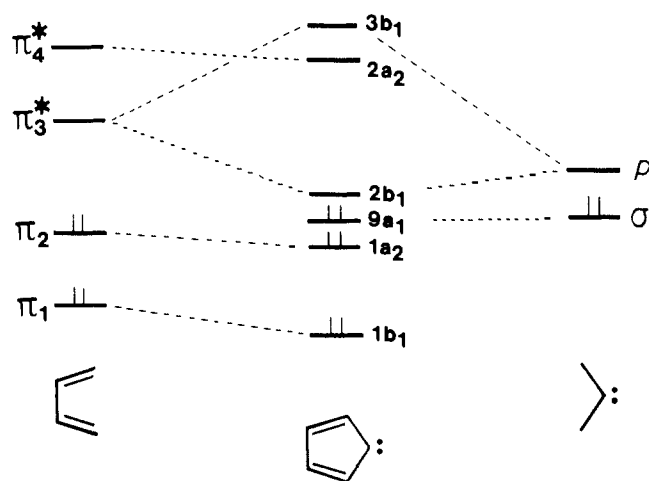


Figure 1. Molecular orbital interaction diagram for the methylene and *cis*-1,3-butadiene fragments of cyclopentadienylidene.

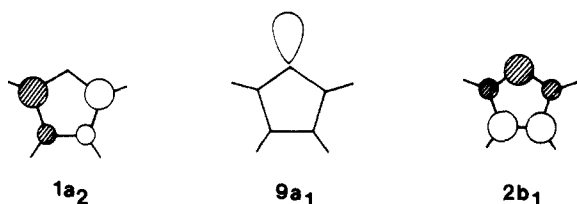


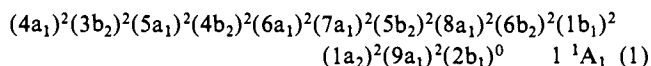
Figure 2. Qualitative drawings of the atomic orbitals that make the largest contribution to the $1a_2$, $9a_1$, and $2b_1$ molecular orbitals.

of this carbene. Here we report the results of our own MNDO and *ab initio* MO calculations on the molecular and electronic structure of *all* low-lying singlet and triplet states of **2**.

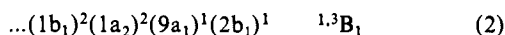
II. Elementary Theoretical Considerations

The first step in the present investigation was to find the possible low-lying electronic states of **2** before performing the corresponding theoretical calculations. For this purpose we carried out an elementary perturbational molecular orbital (PMO)³ analysis, which is similar to that reported in the earlier study of Gleiter and Hoffmann.⁵ A MO interaction diagram for the methylene and butadiene fragments of **2** is given in Figure 1. Assuming C_{2v} molecular symmetry, the lowest unoccupied MO (LUMO) of the diene (π_3^*) has the correct symmetry (b_1) to interact with the methylene out-of-plane p AO. This interaction will stabilize the latter orbital, causing the σ - π splitting in **2** to be smaller than in methylene. Low-lying states of **2** will arise from the occupation with two electrons of the σ -type MO $9a_1$ and the π -type MO $2b_1$. The atomic orbitals making the largest contribution of these MO are shown in Figure 2.

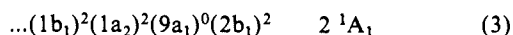
Double occupation of the $9a_1$ orbital gives rise to a 1A_1 singlet; its valence electronic configuration **3** can be written as in (1).



Promotion (relative to configuration 1) of a $9a_1$ electron to the $2b_1$ orbital yields an open-shell electronic configuration, which can be written in short form as in (2). This configuration, which

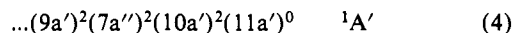


can be formally related to the $\sigma^1\pi^1$ configuration of the S_1 and T_1 states of methylene, gives rise to one singlet and one triplet states of B_1 symmetry. Excitation (relative to configuration 1) of the two $9a_1$ electrons to the $2b_1$ orbital gives rise to a second closed-shell singlet state 1A_1 ; its electronic configuration (4) can be written as in (3).

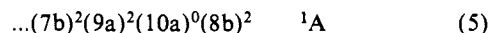


When the molecular symmetry of **2** is lowered from the C_{2v} point group to the C_2 one (5), the former $1b_1$, $9a_1$, and $2b_1$ MOs

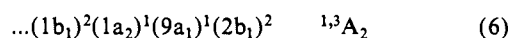
become orbitals of the symmetric irreducible representation $9a'$, $10a'$, and $11a'$, respectively, whereas the former $1a_2$ MO becomes an orbital of the antisymmetric irreducible representation $7a''$. Thus, the closed-shell electronic configuration **1** is transformed into a new configuration, which can be written as in (4). This



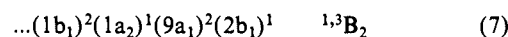
is the electronic configuration of the closed-shell singlet state $^1A'$, which corresponds to the nonplanar structure **5** reported by Waali and co-workers.¹¹ Finally, when the molecular symmetry of **2** is lowered from the C_{2v} point group to the C_2 one (6), the former $1b_1$ and $2b_1$ MOs become orbitals of the antisymmetric irreducible representations $7b$ and $8b$, respectively, whereas the former $1a_2$ and $9a_1$ MOs become orbitals of the symmetric irreducible representations $9a$ and $10a$, respectively. Thus, within C_2 molecular symmetry, the doubly excited electronic configuration **3** is written as in (5). This is the electronic configuration of the closed-shell singlet state 1A corresponding to Waali's allenic structure **6**.



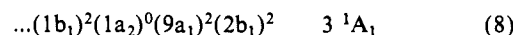
At this point it is noteworthy that the $1a_2$ MO (Figure 1), which is basically the π_2 MO of the butadiene fragment of **2**, should lie energetically close to the $9a_1$ and $2b_1$ orbitals. Consequently, it is likely that, within C_{2v} molecular symmetry, besides the electronic configurations 1–3 there might arise other low-lying electronic configurations involving different occupation of the $1a_2$ orbital. Thus, the nonpaired double excitation (relative to configuration 1) of one electron from $9a_1$ and another from $1a_2$ to the $2b_1$ orbital yields another open-shell configuration written as in (6). This



electronic configuration gives rise to one singlet and one triplet state of A_2 symmetry, with no counterpart in methylene. Promotion (relative to configuration 1) of a $1a_2$ electron to the $2b_1$ orbital yields a third open-shell electronic configuration possessing four π electrons, written as in (7). This configuration gives rise



to one singlet and one triplet state of B_2 symmetry, again having no counterpart in methylene. Finally, excitation (relative to configuration 1) of the two $1a_2$ electrons to the $2b_1$ orbital gives rise to a third closed-shell singlet state 1A_1 with four π electrons. The corresponding electronic configuration can be written as in (8).



Therefore, besides the five electronic states (3B_1 , $^1A'$, 1^1A_1 , 1A , 2^1A_1) reported by Waali and co-workers,¹¹ it appears that there are other six possible low-lying states (1B_1 , 3A_2 , 1A_2 , 3B_2 , 1B_2 , 3^1A_1) for **2**.

III. Computational Methods

The details of the computational methods used have been described in part 1, and only a brief review of the procedures will therefore be given here. All MNDO calculations were performed with the MOPAC¹⁷ program with standard parameters. Calculations for triplet and open-shell singlet states employed the half-electron (HE) version¹⁸ of MNDO. Standard *ab initio* calculations were carried out using locally modified versions¹⁹ of both the GAUSSIAN-80²⁰ and GAMESS²¹ program packages.

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Table I. MNDO-Calculated Heats of Formation (ΔH_f , kcal/mol) and Relevant Geometrical Parameters^{a,b} of the Optimized Molecular Structures for Several Electronic States of Cyclopentadienyliidene^c

state	ΔH_f	C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₂ C ₁ C ₅	θ^d
³ B ₁	119.5	1.418	1.391	1.486	115.5	0
³ A ₂	123.6 (4.1)	1.381	1.485	1.377	115.9	0
¹ A ₂	125.0 (5.5)	1.380	1.485	1.377	116.2	0
¹ B ₁	133.4 (13.9)	1.405	1.403	1.486	117.4	0
¹ A'	140.5 (21.0)	1.462	1.374	1.495	108.6	23.2
1 ¹ A ₁	141.1 (21.6)	1.497	1.359	1.507	104.0	0
¹ A	144.9 (25.4)	1.354	1.492	1.391	123.5	e
2 ¹ A ₁	147.0 (27.5)	1.368	1.447	1.426	129.6	0
³ B ₂	150.8 (31.3)	1.455	1.448	1.400	104.7	0
3 ¹ A ₁	168.2 (48.7)	1.380	1.537	1.350	108.0	0
¹ B ₂	176.7 (57.2)	1.432	1.432	1.436	107.2	0

^aGeometrical parameters defined as in 2. ^bDistances are in angstroms and angles in degrees. ^cRelative energies (kcal/mol) are given in parentheses. ^dFolding angle defined as in 5. ^eHere the relevant dihedral angle is C₃C₂C₁C₅ = 3.4°.

Table II. Relevant Geometrical Parameters^{a,b} of the Optimized Molecular Structures for Several Electronic States of Cyclopentadienyliidene

state	computational method	C ₁ C ₂ C ₂ C ₃ C ₃ C ₄ C ₂ C ₁ C ₅ θ^c				
		C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₂ C ₁ C ₅	θ^c
³ B ₁	ROHF	1.458	1.346	1.486	109.1	0
³ A ₂	ROHF	1.379	1.486	1.343	110.7	0
¹ A ₂	ROHF	1.379	1.485	1.344	110.7	0
¹ B ₁	ROHF	1.407	1.381	1.484	113.5	0
¹ A'	RHF	1.511	1.331	1.522	103.5	20.6
	TCSCF	1.433	1.365	1.492	111.3	22.8
1 ¹ A ₁	RHF	1.540	1.323	1.534	100.8	0
	TCSCF	1.547	1.322	1.529	100.2	0
³ B ₂	ROHF	1.484	1.443	1.364	99.3	0
2 ¹ A ₁	RHF	1.355	1.436	1.401	127.4	0
	TCSCF	1.364	1.425	1.407	125.6	0
3 ¹ A ₁	RHF	1.404	1.572	1.310	99.9	0
¹ B ₂	ROHF	1.519	1.399	1.403	97.0	0

^aGeometrical parameters defined as in 2. ^bDistances are in angstroms and angles in degrees. ^cFolding angle defined as in 5.

Geometries were initially optimized with MNDO within appropriate molecular symmetry constraints and then further optimized at the SCF level of theory with the split-valence 3-21G basis set²² using analytical gradient methods. Singlet closed-shell states ¹A₁, ²A₁, and ¹A' were calculated employing the spin-restricted Hartree-Fock (RHF) method²³ and by use of a two-configuration SCF (TCSCF), or the equivalent generalized valence bond (GVB),^{24a} wave function. For the ¹A₁ and ²A₁ singlet states, the TCSCF wave function included the electronic configurations 1 and 3. In addition to configuration 4, the TCSCF wave function of the ¹A' state included the doubly excited configuration (10a')² → (11a')². Triplet and singlet open-shell states were calculated by the spin-restricted open-shell Hartree-Fock (ROHF) approach.²⁴ Additional single-point calculations were carried out with the larger split-valence 6-31G basis set²⁵ and with the split-valence plus d polarization at the carbon atoms 6-31G* basis set.²⁶

To establish more reliable relative energies, configuration interaction (CI) was used at the SCF and TCSCF optimum geometries with the 6-31G basis set. The CI wave function included all interacting singly and doubly excited configurations (CISD) relative to either the SCF or both TCSCF reference configurations. The Hartree-Fock interacting space^{27,28} of single and double excitations was included for the triplet and open-shell states. All five nonvalence molecular orbitals were frozen. The number of configurations varied from 26 897 for the ¹A₁ state (single-reference CISD) to 93 393 for the ¹A' state (two-reference CISD). Our best ab initio relative energies (CISD/6-31G*) were estimated by assuming additivity of the d-polarization functions and correlation energy effects.²⁹ In part 1, this procedure has been proven to give a reliable

Table III. Calculated Total Energies (Hartrees) for Several Electronic States of Cyclopentadienyliidene^a

state	computational method	basis set		
		3-21G	6-31G	6-31G*
³ B ₁	ROHF	-190.459 87	-191.463 61	-191.533 35
	CISD		-191.840 02	
³ A ₂	ROHF	-190.441 30	-191.444 91	-191.516 21
	CISD		-191.825 19	
¹ A ₂	ROHF	-190.437 92	-191.441 54	-191.512 54
	CISD		-191.827 20	
¹ B ₁	ROHF	-190.420 48	-191.425 10	-191.497 92
	CISD		-191.802 19	
¹ A'	RHF	-190.407 53	-191.409 98	-191.487 83
	TCSCF ^b	-190.428 02	-191.432 68	-191.510 50
	CISD ^c		-191.796 75	
	CISD ^{b,d}		-191.812 48	
1 ¹ A ₁	RHF	-190.406 41	-191.408 18	-191.484 31
	TCSCF ^b	-190.420 86	-191.422 20	
	CISD ^c		-191.791 69	
	CISD ^{b,d}		-191.798 18	
³ B ₂	ROHF	-190.400 96	-191.406 63	-191.484 37
	CISD		-191.777 98	
2 ¹ A ₁	RHF	-190.375 78	-191.382 08	-191.456 46
	TCSCF ^b	-190.378 61	-191.385 04	
	CISD ^c		-191.774 48	
	CISD ^{b,d}		-191.775 68	
3 ¹ A ₁	RHF	-190.345 99	-191.349 38	-191.435 24
	CISD		-191.743 63	
¹ B ₂	ROHF	-190.341 80	-191.347 45	-191.428 13
	CISD		-191.727 72	

^aAll calculations at the SCF/3-21G-optimized geometries. ^bAt the TCSCF/3-21G-optimized geometry. ^cBased on the RHF reference configuration. ^dBased on both TCSCF reference configurations.

Table IV. Calculated Relative Energies (kcal/mol) for Several Electronic States of Cyclopentadienyliidene^a

state	SCF/3-21G	SCF/6-31G	SCF/6-31G*	CISD/6-31G	CISD/6-31G**
³ B ₁	0	0	0	0	0
³ A ₂	11.7	11.7	10.8	9.3	8.4
¹ A ₂	13.8	13.8	13.1	8.0	7.3
¹ A'	20.0 ^c	19.4 ^c	14.3 ^c	17.3 ^d	12.2 ^d
¹ B ₁	24.7	24.2	22.2	23.7	21.7
1 ¹ A ₁	33.5	34.7	30.8	30.3	26.4
³ B ₂	37.0	35.8	30.7	38.9	33.8
2 ¹ A ₁	52.8	51.2	48.3	41.1	38.2
3 ¹ A ₁	71.5	71.7	61.6	60.5	50.4
¹ B ₂	74.1	72.9	66.0	70.5	63.6

^aAll calculations at the SCF/3-21G-optimized geometries except for the ¹A' state, for which the TCSCF/3-21G-optimized geometry was used. ^bEstimated assuming additivity of the electron correlation and d-polarization functions corrections. ^cAt the TCSCF level of theory. ^dBased on both TCSCF reference configurations.

approximation to the vastly more computer time consuming CI calculations with the 6-31G* basis set.

Both the MNDO and ab initio 3-21G stationary point structures determined for each electronic state were characterized by their harmonic

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Table V. Mulliken Atomic Net Charges and Dipole Moments (μ , Debyes) for Several Electronic States of Cyclopentadienylidene at the SCF/6-31G* Level of Theory^{a-c}

state	C ₁	C ₂	C ₃	μ
³ B ₁	+0.052 (+0.071)	-0.246 (-0.166)	-0.193 (-0.048)	0.52 (0.88)
³ A ₂	-0.047 (-0.176)	-0.186 (+0.044)	-0.213 (-0.118)	0.72 (0.74)
¹ A ₂	-0.047 (-0.177)	-0.185 (+0.044)	-0.214 (-0.118)	0.69 (0.74)
¹ B ₁	+0.104 (+0.065)	-0.310 (-0.168)	-0.164 (-0.045)	1.14 (0.95)
¹ A ₂ ^d	+0.071 (+0.069)	-0.284 (-0.165)	-0.174 (-0.051)	1.47 (1.83)
1 ¹ A ₁	+0.082 (+0.076)	-0.326 (-0.187)	-0.137 (-0.026)	3.16 (2.83)
³ B ₂	-0.037 (-0.201)	-0.233 (-0.004)	-0.184 (-0.068)	3.56 (3.64)
2 ¹ A ₁	+0.137 (+0.219)	-0.261 (-0.185)	-0.247 (-0.132)	1.46 (1.45)
3 ¹ A ₁	-0.224 (-0.552)	-0.117 (+0.253)	-0.218 (-0.142)	4.22 (3.76)
¹ B ₂	-0.213 (-0.236)	-0.160 (+0.013)	-0.184 (-0.067)	4.75 (3.81)

^aSee footnote a in Table IV. ^bAtom numbering as in 2. ^cThe quantities in parentheses are the MNDO-calculated values. ^dBased on the TCSCF wave function.

vibrational frequencies as minima, saddle points, or higher extrema, from the Cartesian force constants matrix calculated numerically by finite differences of numerical (MNDO) or analytical (3-21G) gradients.³⁰

IV. Results and Discussion

The MNDO-computed heats of formation and the most relevant geometrical parameters of the 11 electronic states of 2 predicted in section II are summarized in Table I according to the predicted energy ordering. The same geometrical parameters of the 3-21G-optimized structures found for all these states, except for the allenic ¹A singlet, are given in Table II. It did not prove possible to perform a geometry optimization on the latter closed-shell singlet state. Thus, geometry optimizations performed within C₂ symmetry constraints, starting at the MNDO-optimized geometry, led invariably to a C_{2v} structure, which corresponds to the 2 ¹A₁ state. The total and relative ab initio energies, calculated at different levels of theory, are shown in Tables III and IV, respectively. Finally, the net atomic charges, determined from the Mulliken population analysis,³¹ and the dipole moments calculated at the SCF/6-31G* level of theory are shown in Table V. For comparison, Table V also includes the MNDO-computed values.

To facilitate discussion, the results obtained for the open-shell and closed-shell states are presented separately.

Open-Shell States. In good qualitative agreement with earlier theoretical studies^{5,11,13-15} and experimental data,⁶ the present MNDO and ab initio calculations predict the electronic ground state of 2 to be the ³B₁ triplet. The harmonic vibrational analysis proved that the 3-21G-optimized structure obtained for this state is a true potential energy minimum. When the geometrical parameters shown in Tables I and II for the ³B₁ state are compared, it is found that MNDO predicts the C₂C₁C₅ bond angle to be somewhat wider. This observation is consistent with the MNDO tendency to exaggerate the bond angle at the carbene center of triplet carbenes.³²

One of the most interesting results of the present MNDO and ab initio calculations is the prediction regarding the existence of a triplet ³A₂ and an open-shell singlet ¹A₂ state, which lie lower in energy than any of the other excited states, including the open-shell singlet ¹B₁ arising from the same electronic configuration of the ground state ³B₁. Indeed, *the diradical open-shell singlet ¹A₂ is predicted to be the lowest energy singlet state of 2.* As mentioned above, these open-shell states of A₂ symmetry have no counterpart in methylene and may be considered to arise formally from the excitation, relative to the ground-state configuration 2, of one electron from the highest occupied MO of the butadiene moiety of 2 (1a₂) to the highest singly occupied MO (2b₁). Interestingly, the absolute energies of the ³A₂ and ¹A₂ states switch in order on going from the SCF to the CISD ab initio levels of theory. The ³A₂-¹A₂ energy separation is never large, and this precludes a definitive statement as to establish which is the first excited electronic state of 2. It is to be noted that the ³B₁-³A₂ and ³B₁-¹A₂ energy gaps estimated at the CISD/6-31G* level

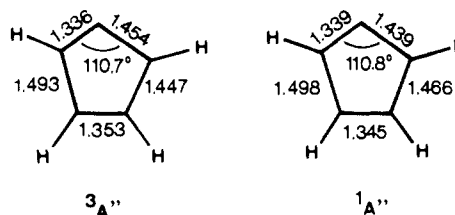


Figure 3. ROHF/3-21G equilibrium geometries after C_s symmetry constrained reoptimization of the structures calculated for the ³A₂ and ¹A₂ electronic states of cyclopentadienylidene. All bond distances are in angstroms.

of theory (8.4 and 7.3 kcal/mol, respectively) are in reasonable agreement with the values predicted by MNDO (4.1 and 5.5 kcal/mol, respectively). Moreover, it is noteworthy that the SCF/3-21G-optimized geometries for these excited states are close to those calculated with MNDO. Once again, the main difference is found for the C₂C₁C₅ bond angles, which are predicted to be somewhat wider by MNDO. As regards the charge distribution, the 6-31G*-calculated atomic net charges differ appreciably from those predicted by MNDO. In particular, while the latter method predicts a considerable negative net charge on the carbene center (C₁) of the two A₂ states, the 6-31G* calculations give a weak negative net charge on this atom of both states. However, the 6-31G*-computed dipole moments of these states are nearly identical with the MNDO values.

The harmonic vibrational analysis showed that the SCF/3-21G optimized structures for both ³A₂ and ¹A₂ states have one imaginary frequency (2990i and 2156i cm⁻¹, respectively). Curiously, the normal modes associated with these imaginary frequencies are of b₂ symmetry and suggest a concerted shortening and lengthening of the two equivalent C₁C₂ and C₁C₅ bonds. This normal mode breaks the C_{2v} molecular symmetry and should lead to a planar structure (C_s) with unequal C₁C₂ and C₁C₅ bond lengths. In fact, subsequent geometry reoptimization (at the SCF/3-21G level) within the C_s symmetry constraints of the calculated ³A₂ and ¹A₂ structures, slightly modified according to the nuclear displacements indicated by the normal mode of imaginary frequency, yielded the molecular geometries shown in Figure 3, which correspond to one triplet and one open-shell singlet state of A'' symmetry. As expected, these C_s geometries show one short and one long C₁C₂₍₅₎ bond relative to the C₁C₂ distance predicted for the corresponding C_{2v} geometries. The force constant analysis proved these C_s structures to be true potential energy minima. Interestingly, the decrease in energy accompanying the symmetry lowering from the C_{2v}- to the C_s-optimized structures is only 2.7 kcal/mol for the triplet and 1.1 kcal/mol for the singlet.

A plausible explanation of the above unexpected results, concerning the broken-symmetry (C_s) equilibrium geometries predicted for the two lowest excited states of 2, can be given on the basis of the analogous results found for the ³A₂ and ¹A₂ states of 1. As noted in part 1, the electronic wave function calculated at the SCF level of theory for open-shell configurations involving single occupation of the 1a₂ MO are subject to the Hartree-Fock instability.³³ Due to this phenomenon, a ROHF calculation tends

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to locate the odd $1a_2$ electron at one end of the $C_2C_1C_5$ fragment of the molecule, while a double bond is localized at the other end. This spurious localization compensates for the inadequacy of the SCF single configuration in providing correlation of the two opposite-spin $2b_1$ and $1a_2$ electrons. It has been recently shown³⁴ that an appropriate MCSCF wave function averts the symmetry-breaking problem in analogous molecular geometry calculations. It is likely, therefore, that such a model should predict for the lowest triplet (3A_2) and singlet (1A_2) states of **2** a C_{2v} equilibrium geometry. Restrictions imposed by the size of the molecule and the limitations of computer sources have prevented the use of such a MCSCF wave function to confirm the latter hypothesis.

Regarding the open-shell singlet state 1B_1 , at the CISD/6-31G* level, it is estimated to lie 21.7 kcal/mol above the ground state. This 1B_1 - 3B_1 energy splitting is substantially larger than the value (13.9 kcal/mol) predicted by MNDO. A similar discrepancy was found for such a singlet-triplet energy splitting in the study of **1**. On the other hand, besides the $C_2C_1C_5$ bond angle, the geometrical parameters optimized with the 3-21G basis set are in very good agreement with the MNDO-calculated values. As in the case of the corresponding triplet state (3B_1), MNDO predicts a somewhat larger value for the latter bond angle. However, the increase in the $C_2C_1C_5$ bond angle calculated at the SCF/3-21G level in passing from the 3B_1 triplet to the 1B_1 singlet is qualitatively reproduced by the MNDO calculations. As regards the charge distribution computed with the 6-31G* basis set for the 1B_1 singlet, it is worth noting that both the net atomic charge at the carbene center and dipole moment are twice the values calculated for the triplet of the same symmetry. In sharp contrast, MNDO predicts nearly the same charge distribution and dipole moment for both states of B_1 symmetry.

The force constant analysis of the 3-21G-optimized structure for the 1B_1 singlet could not be performed due to the fact that, at molecular geometries (e.g., C_s and C_1) slightly displaced from the optimized C_{2v} geometry, the SCF procedure^{24a} converged to a GVB solution of lower energy, which is related to the TCSCF wave function of a geometrically distorted structure derived from the 1^1A_1 closed-shell singlet.

A comparison of the geometrical parameters calculated for the states of A_2 symmetry with those calculated for the states of B_1 symmetry shows substantial lengthening of the C_2C_3 and C_4C_5 bond distances and shortening of the C_3C_4 bond length. These structural changes are easily understood on the grounds of the different nodal planes of the $1a_2$ and $2b_1$ MOs (Figure 2). As found in the case of carbene **1**,² at the SCF level of theory, the 1A_2 - 3A_2 energy splitting is small, as compared with the notable singlet-triplet splitting calculated for the states of B_1 symmetry. The different spatial localization (Figure 2) of the singly occupied MOs $1a_2$ and $2b_1$, which distinguish these states, accounts for the noted differences in the singlet-triplet energy splittings. In fact, the exchange integral, causing the energy splitting between the singlet and triplet states arising from the same electronic configuration, is expected to be larger for the orbital pair $9a_1$ - $2b_1$ than for the $9a_1$ - $1a_2$ one.

Regarding both the triplet and open-shell singlet states of B_2 symmetry, the most notable geometrical feature is the relatively small value of the $C_2C_1C_3$ bond angle, which is predicted to be remarkably close to the value obtained for the closed-shell singlet 1^1A_1 . This is ascribed to the fact that the double occupation of the $9a_1$ MO favors small $C_3C_1C_2$ bond angles. The geometries calculated with the 3-21G basis set for the two states of B_2 symmetry differ appreciably from those optimized with MNDO. As noted for the open-shell states of B_1 and A_2 symmetries, MNDO predicts wider bond angles at the carbene carbon. In addition, while the MNDO-optimized structures of these B_2 states show a similar bond length for the five CC bonds, the 3-21G-optimized geometries show different values for these CC bonds. The 3-21G-optimized structures of the 3B_2 and 1B_2 states could not be

characterized as true equilibrium geometries due to nonconvergence to self-consistency problems arisen in the calculation of the force constant matrices.

At the estimated CISD/6-31G* level of theory, the 3B_2 state is predicted to lie 33.8 kcal/mol above the ground state. This energy separation is in very good agreement with the 31.3 kcal/mol energy gap predicted by MNDO. Moreover, the 3B_2 - 1B_2 energy splitting estimated at the latter level of theory (29.5 kcal/mol) is similar to that predicted by MNDO (25.9 kcal/mol). It is worth noting that this energy splitting between the singlet and triplet states arising from the same electronic configuration is the largest one of all open-shell electronic configuration considered for carbene **2**. This result is a consequence of the spatial localization on the carbon atoms (except the C_1) of the singly occupied MOs $1a_2$ and $2b_1$, which leads to a large exchange integral between these orbitals. Finally, it is worth noting the large dipole moments calculated for both states of B_2 symmetry with the 6-31G* basis set. As noted in the case of the open-shell states of B_1 symmetry, comparison of the atomic net charges for the 3B_2 and 1B_1 states shows that the singlet is substantially more polarized.

Closed-Shell Singlet States. First we present the results obtained at the single configuration SCF level of theory. Beginning with the lowest energy singlet state arising from the electronic configuration 1, namely 1^1A_1 , it is worth noting that the geometry optimized with the 3-21G basis set shows alternating (short/long) bond distances, thus indicating two localized double bonds. In fact, the calculated C_2C_3 and C_4C_5 bond distances have been lengthened by only 0.003 Å with respect to the SCF/3-21G-predicted CC double-bond distance (1.320 Å) in *cis*-1,3-butadiene.³⁵ Furthermore, the orbital charge in the out-of-plane p AO of atom C_1 was calculated (from the Mulliken population analysis with the 6-31G* basis set) to be 0.166e, proving that there is only a very weak delocalization of the four π electrons away from the two π orbitals of the butadiene fragment of **2** into the empty p AO at the carbene center. These results are a consequence of the expected antiaromatic nature of the electronic configuration 1. When the structure optimized with the 3-21G basis set is compared with that optimized by MNDO, it is found that both methods give similar geometries; the CC bond lengths differ by up to 0.04 Å while the bond angle at the carbene center is calculated to be 3.2° wider by MNDO.

In good agreement with previous MNDO results,¹¹ the harmonic vibrational analysis showed that the structure determined for the 1^1A_1 state with the 3-21G basis set has one imaginary frequency (222i cm^{-1}), which corresponds to a vibrational mode of b_1 symmetry. This normal mode breaks the C_{2v} molecular symmetry and should lead to a nonpolar C_s structure (**5**). In fact, subsequent geometry reoptimization (at the SCF/3-21G level) within the C_s symmetry constraints of the structure calculated for the 1^1A_1 state, slightly modified according to the nuclear displacements indicated by the normal mode of imaginary frequency, yielded the structure calculated for the $^1A'$ singlet state (fifth row in Table II). The force constant analysis proved this C_s structure to be a true potential energy minimum. Therefore, *our ab initio SCF/3-21G calculations agree with Waali's MNDO results predicting the lowest energy closed-shell singlet state of 2 to prefer a nonplanar C_s equilibrium geometry*. The decrease in energy accompanying the "folding" of the planar five-membered ring of singlet state 1^1A_1 to yield the $^1A'$ singlet is calculated to be small at all levels of theory (Table III). However, both the d-polarization functions and electron correlation effects enhance the 1^1A_1 - $^1A'$ energy separation. This is predicted to be 4.3 kcal/mol at the estimated single-reference CISD/6-31G* level of theory. According to the results in Table I, MNDO gives an energy gap of only 0.6 kcal/mol.

It is readily seen in Table II that the geometrical differences, other than the folding angle θ , between the planar (C_{2v}) and folded (C_s) structures of the lowest closed-shell singlet state of **2** are very

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small, the most significant one being the $C_2C_1C_3$ angle, which is found to be 2.7° larger in the latter structure. The same trend is observed in comparing the MNDO-optimized geometries for these states (Table I).

Regarding the geometrical structure optimized at the SCF/3-21G level for the closed-shell singlet state arising from the electronic configuration 3, namely 2^1A_1 , it is worth noting that the differences between the five CC bond lengths are somewhat smaller than in the structure determined for the 1^1A_1 state. A comparison of the geometrical parameters obtained for the 2^1A_1 state with those calculated for the lower 1^1A_1 state reveals a substantial lengthening and shortening of the C_2C_3 and C_1C_3 bond distances, respectively, and a very larger increment of the $C_2C_1C_3$ bond angle. These changes in the CC bond lengths are consistent with the expected (aromatic) delocalization of the six π electrons of the electronic configuration 3; thus, the orbital charges in the out-of-plane p AO of atoms C_1 , C_2 , and C_3 were calculated (at the SCF/6-31G* level) to be 1.319, 1.208, and 1.133e, respectively. The increment of the bond angle at the carbene carbon is ascribed to the electron energy vacancy of the $9a_1$ MO.

At variance with a previous MNDO force constant analysis,¹¹ the structure optimized with the 3-21G basis set for the 2^1A_1 state of **2** did show *only one* imaginary harmonic frequency ($785i$ cm^{-1}), which corresponds to a vibrational mode of b_1 symmetry. This normal mode, as found for the 1^1A_1 singlet, breaks the C_{2v} molecular symmetry and should lead to a nonplanar structure **5**. Not unexpectedly, a subsequent geometry reoptimization (at the SCF/3-21G level) within the C_s symmetry constraints of the structure calculated for the 2^1A_1 state, slightly modified according to the nuclear displacements indicated by the above normal mode of imaginary frequency, led to the structure calculated for the $1A'$ singlet. Therefore, it appears that at the SCF/3-21G level of theory neither the antiaromatic (four π electrons) 1^1A_1 nor the aromatic (six π electrons) 2^1A_1 closed-shell singlet states of **2** have a true C_{2v} equilibrium geometry. Of course, within the nonplanar C_s symmetry, it is not possible to distinguish between σ and π electrons and, therefore, the conventional SCF procedure gives an unique $1A'$ solution for both states.

Finally, within the framework of the single-configuration SCF approach, it is worth mentioning that the structure optimized for the 3^1A_1 state (arising from the electronic configuration 8) with the 3-21G basis set agrees fairly well with the geometry predicted by MNDO, except the bond angle at the carbene center, which is predicted 8.1° wider by the latter method. It should be recalled that the conventional SCF procedure, employed here in the geometry optimization to calculate the electronic wave function, does not warrant that the calculation energy is an upper bound for the true energy of this state. Nevertheless, it is interesting to note that at the estimated CISD/6-31G* level of theory this singlet state is calculated to lie 50.4 kcal/mol above the ground state, which is in excellent agreement with the value (48.7 kcal/mol) predicted by MNDO. Owing to nonconvergence to self-consistency problems in the calculation of the force constants matrix, the structure optimized with the 3-21G basis set could not be characterized as a true equilibrium geometry.

Since closed-shell singlet carbenes are more properly described in zeroth order by TCSCF wave functions,³⁶ the 1^1A_1 , 2^1A_1 , and $1A'$ states were reexamined at this higher level of theory. The most relevant parameters of the TCSCF/3-21G-reoptimized geometries are included in Table II, and the single-point total energies calculated with both larger basis sets (at the TCSCF level) and the two-reference CISD/6-31G wave function are included in Table III.

As regards the 1^1A_1 state, at the TCSCF/3-21G-optimized geometry, the mixing coefficients of the configurations **1** and **2** were calculated to be 0.986 and -0.169 for C_1 and C_2 , respectively, and the TCSCF/3-21G energy was calculated to be 9.3 kcal/mol lower than single-configuration SCF/3-21G value. The SCF/3-21G- and TCSCF/3-21G-optimized geometries of 1^1A_1 are essentially superposable. In good qualitative agreement with the

SCF/3-21G force constant analysis results, the TCSCF/3-21G-optimized structure showed an imaginary frequency ($191i$ cm^{-1}) corresponding to a vibrational mode of b_1 symmetry. This normal mode should lead to a nonplanar C_s structure as **5**. On the basis of the above results, therefore, it appears that the single-configuration SCF description of the 1^1A_1 state of **2** is qualitatively acceptable. Moreover, it is interesting to note that the difference between the single-reference and two-reference CISD/6-31G total energies (4.1 kcal/mol) is relatively small.

Regarding the 2^1A_1 state, at the TCSCF/3-21G-optimized geometry, the mixing coefficients of configurations **1** and **2** were found to be -0.153 and 0.988 for C_1 and C_2 , respectively, and the TCSCF/3-21G energy was 1.8 kcal/mol below the single-configuration SCF/3-21G value. The TCSCF/3-21G-optimized geometry of 2^1A_1 is very similar to the single-configuration SCF/3-21G-optimized structure, the largest difference being in the $C_2C_1C_3$ bond angle, which is predicted 1.8° larger by the last method. The difference between the single-reference and two-reference CISD/6-31G total energies is only 0.8 kcal/mol.

For the nonplanar singlet state $1A'$, at the TCSCF/3-21G equilibrium geometry, the mixing coefficients of the main configuration **4** and the doubly excited configuration $(10a')^2 \rightarrow (11a')^2$ were calculated to be 0.948 and -0.317 for C_1 and C_2 , respectively, and the TCSCF/3-21G energy was calculated to be 20.6 kcal/mol below the single-configuration SCF/3-21G value. As a consequence of the significant contribution of the second configuration in the TCSCF wave function, in comparison with the 1^1A_1 and 2^1A_1 states, the equilibrium geometries determined at the TCSCF level of theory differ appreciably from that calculated at the SCF level. For example, at the TCSCF level, the C_1C_2 bond length is 1.433 Å and the $C_2C_1C_3$ bond angle is 111.3° , whereas at the SCF level these geometrical parameters are 1.511 Å and 103.5° , respectively. Moreover, the TCSCF/6-31G*-calculated dipole moment is about half of the value calculated at the SCF level with the same basis set. Therefore, the present results indicate that *a proper description of the $1A'$ state cannot be obtained within the single-configuration approach*.

From the calculated atomic net charges in Table V, it is observed that the positive net charge at the carbene center in the nonplanar $1A'$ singlet is smaller than that predicted for the planar 1^1A_1 and 2^1A_1 singlet states. In any case, on the basis of the predicted atomic net charges at the carbene carbon, the lowest energy closed-shell singlet state of **2**, namely $1A'$, might exhibit a moderate electrophilic behavior, whereas the lowest open-shell singlet, namely $1A_2$, is a diradical with a little negative net charge at the carbene center.

Regarding the relative energies of the singlet states, it is worth noting that the one-reference CISD/6-31G energy places the $1A'$ state 3.4 kcal/mol above the open-shell singlet $1B_1$, while the two-reference CISD/6-31G energy places $1A'$ 6.5 kcal/mol below $1B_1$. This result stresses the importance of using a two-configuration description for the zero-order wave function of the lower closed-shell singlet state in the CISD approach, to evaluate the electron correlation effects on the relative energy ordering of the closed-shell and open-shell states of **2**. Finally, from the relative energies given in the last column of Table IV, we note that, at the highest level of theory considered here, the lowest energy closed-shell singlet state of **2** is predicted to lie 12.2 kcal/mol above the ground state. In spite of this small energy separation, there is another singlet state in between, which is the overall lowest energy singlet state of **2**, namely the diradical open-shell singlet $1A_2$.

V. Conclusions

In this paper, results of MNDO and ab initio calculations have been reported for ten low-lying states of cyclopentadienylidene. Analysis of these results suggests several points of potential value in understanding and interpreting the chemistry of this carbocyclic conjugated carbene:

(1) In agreement with earlier semiempirical calculations and experimental data, the electronic ground state is predicted to be a $3B_1$ triplet.

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(2) The two lower excited electronic states are a 3A_2 triplet and a 1A_2 singlet open-shell diradical lying about 7-8 kcal/mol above the ground state. None of these excited states can be formally related with any electronic state of methylene. Formally these states of A_2 symmetry may be considered to arise from the excitation (relative to the ground state 3B_1) of one electron from the HOMO of the butadiene fragment to the out-of-plane p AO of the carbene carbon atom of cyclopentadienylidene. The electronic wave functions calculated at the ab initio SCF level of theory for the 3A_2 and 1A_2 states are subjected to Hartree-Fock instability. This causes the geometries optimized at the SCF level to show one short (double) and one long (single) CC bond length adjacent to the carbene carbon.

(3) The lowest energy closed-shell singlet is a $^1A'$ state possessing a nonplanar C_2 equilibrium geometry, which is predicted to lie about 12 kcal/mol above the ground state. Neither the antiaromatic (four π electrons) 1^1A_1 nor the aromatic (six π electrons) 2^1A_1 planar singlet states are true potential energy minima. Moreover, the present ab initio calculations do not give support to the existence of a closed-shell singlet state of allenic nature (1A) such as that found by Waali and co-workers in its MNDO study.

(4) On the basis of the predicted atomic net charges at the carbene carbon, the lowest energy closed-shell singlet state ($^1A'$) might exhibit moderate electrophilic behavior, whereas the lowest open-shell singlet (1A_2) might show weak nucleophilic character.

The chemical implications concerning the predicted existence of two low-lying singlet states of cyclopentadienylidene, one of strong diradical nature and the other of standard closed-shell nature exhibiting a moderate electrophilic character, are far reaching. One point of special interest that emerges from this theoretical study is the possibility that the singlet diradical state 1A_2 may be responsible for some unexpected products obtained

from photochemically generated carbenes related to cyclopentadienylidene.^{8b,12,37,38}

Finally, as a practical remark (from the computational point of view), we mention that the present study shows once again that though MNDO has been parametrized to reproduce experimental values of ground-state molecular properties, this method predicts for the low-lying excited states of cycloalkenylidenes molecular geometries and a relative energy ordering that are in qualitative agreement with the results of high-level ab initio calculations. Nevertheless, MNDO systematically underestimates the energy of the open-shell states relative to that of the closed-shell singlets. Therefore, to furnish more accurate evaluations of the energy separation between these states, appropriate high-level ab initio calculations appear to be more recommendable.

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Registry No. Cyclopentadienylidene, 4729-01-5.

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