hydration destabilizes the tt conformation relative to both gg and gt, while gt was favored over gg conformer. The hydration free energy simulations reported here indicate that the relative preference of the phosphodiester torsions for gg conformation over gt form in aqueous solutions is to be traced to the $T\Delta S$ term. This is an interesting result and is in accord with the current view of the hydrophobic effect, given that the two methyl groups are closer to each other in the gg conformation. This result also supports the inferences of Jorgensen[32] on conformational evidence for the hydrophobic effect. In his Monte Carlo simulations of *n*-butane in water, the gauche conformer was found to be preferentially solvated. The calculations here establish the relevance of hydrophobic effect to the conformational preferences of biomolecules in aqueous solutions.

Also shown in Table II in the last two rows are the relative free energies of hydration estimated through hydration shell model[5] (row 4) and concentric dielectric continuum calculations[6] (row 5). The conformational preferences predicted by these two models are in agreement with the trends obtained through the free energy simulations here (row 1). The continuum description of hydration appears to overestimate the conformational differences compared with the results obtained from the liquid-state free energy simulations. Continuum representation of the solvent underscores contributions arising solely from the attractive part of the potential of mean force and neglects the nonelectrostatic contributions such as due to shape, size, and packing configurations of the solvent molecules. By way of contrast, the hydration shell model emphasizes the local structural factors and appears to underestimate the free energy differences. Simulations take both these aspects into consideration. The overall picture presented by the conformational differences evaluated through simulations here is that the calculated hydration free energy surface is relatively flat.

The present study yields information for the first time on the relative conformational free energies of hydration of phosphodiester torsions in nucleic acid constituents and also highlights some of the problems to be encountered in complex systems. The series of computations here have shown that qualitative trends in relative hydration free energies evaluated through simulations are reproducible with consistency. Quantitative estimates, however, are more exacting. Thus, caution is to be exercised in drawing inferences based on the assumption that the numerical estimates of hydration free energies of larger systems evaluated through free energy simulations honor the thermodynamic cycle. Thermocycle provides a stringent test on the methodology, and an error estimate of 0.6 kcal obtained here is very encouraging.

Subsequent studies are being undertaken to clarify the sensitivity of results to the assumed change distribution.

VI. Conclusions

The free energy simulations reported here indicate that hydration stabilizes the gg conformation for the phosphodiester torsions in DMP$^-$. The anionic hydration through the solute–solvent interactions and the hydrophobic hydration through the entropic contributions are observed to be the major factors stabilizing the gg conformer of DMP$^-$ in aqueous solutions. The conformational differences in free energies of hydration however suggested that the extended forms (gt and tt) may be thermally accessible to some extent in aqueous solutions at ambient temperature. On the methodological front, the performance of the free energy simulations is satisfactory.

Acknowledgment. This research was supported by NIH Grant GM 24914 and by NSF Grant CHE-8203501.

Registry No. DMP$^-$, 813-78-5.

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Molecular and Electronic Structure of the Low-Lying Electronic States of Cycloalkenylidenes: Cyclopropenylidene

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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 cyclopropenylidene are reported. In addition to the ground state, which is predicted to be the closed-shell singlet $^1A_1$, three open-shell singlets ($^1A_2$, $^1B_1$, $^1B_2$), two triplets ($^3A_2$ and $^3B_1$), and one doubly excited closed-shell singlet (2^1A_1) are described. It is found that at the ab initio SCF level of theory the open-shell states of A_2 symmetry exhibit three imaginary frequencies due to the fact that the wave function of these states is subject to Hartree–Fock instability. As expected, the electron charge distribution, and therefore the electrophilic or nucleophilic character of the carbene center, changes significantly along the seven electronic states considered. However, owing to the large energy differences between the ground state and the calculated excited states, it is unlikely that the latter may play any significant role in the chemistry of (singlet) cyclopropenylidene.

I. Introduction

The chemistry of carbenes is normally interpreted in terms of the relative energies of the lowest singlet (S_0) and triplet (T_1) electronic states of these species.[2] In methylene, the simplest carbene, the above states arise from occupation with two electrons of the lone-pair σ-orbital (which is basically a sp^2 hybrid orbital in the molecular plane) and the out-of-plane p atomic orbital (AO) on the carbon atom. Essentially, the singlet S_0 is fairly well described by the configuration σ^2p^0 whereas the triplet T_1 by the configuration σ^1p^1. In addition to these low-lying states, there are two possible excited singlet states, S_1 and S_2, arising from configurations σ^1p^1 and σ^0p^2, respectively. Both ab initio and semiempirical molecular orbital (MO) calculations[3] indicate that

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[1] (a) Department de Química Orgànica. (b) Departament de Química Física.

[2] Kirmse, W. *Carbene Chemistry*; Academic: New York, 1971. Gaspar, P. P.; Hammond, G. S. In *Carbenes*; Moss, R. A., Jones, M., Eds.; Wiley: New York, 1975; Vol. 2. Moss, R. A.; Jones, M. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2.

[3] For a recent review on theoretical calculations of methylene, see: Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.

0002-7863/88/1510-1694$01.50/0

the S_1 and S_2 states lie high in energy and, therefore, it is very unlikely that they can play any significant role in the chemical behavior of singlet methylene. However, substitution of the methylene hydrogens should affect the relative stability of the above four states (S_0, S_1, S_2, T_1) of methylene. Thus, in a preceding paper,[4] we have shown that, in the case of methylenes with some strong π-acceptor substituents, singlet state S_1 is lowered in energy with regard to singlet S_0 while triplet T_1 is by far the ground state. Consequently, possible contribution of electronic states other than S_0 and T_1 to the chemistry of substituted carbenes cannot be completely ruled out.

Incorporation of the methylene carbon atom into a conjugated ring can also change the relative stability of the low-lying electronic states of methylene. The interaction of the out-of-plane p AO of methylene with a π-electron system was first theoretically investigated in the pioneering work of Gleiter and Hoffmann on the stabilization of singlet methylene.[5] Depending on the number of π electrons ($4n$ or $4n + 2$) in the polyene, such an interaction was analyzed in terms of the symmetry of the highest occupied MO (HOMO) or the lowest unoccupied MO (LUMO) of the polyene, placing particular emphasis on the S_0–T_1 energy separation and the nucleophilic or electrophilic properties of the resulting carbocyclic conjugated carbene. Subsequent theoretical studies on the molecular electronic structure of cycloalkenylidenes[6–19] have mainly dealt with the singlet–triplet energy gap[7–11,13–16,18,19] and the possible allenic structure of the lowest singlet state.[6,9,13,15–17,19] Other singlet states, formally related to either the S_1 or S_2 states of methylene, have received far less attention. For example, the molecular and electronic structure of a singlet state related to the S_2 state of methylene has been reported for cyclopentadienylidene[8,12,19] and cycloheptatrienylidene.[13]

Since in a conjugated polyene the HOMO and LUMO are energetically close to both the lone-pair σ-orbital and out-of-plane p AO of methylene, it is likely that in carbocyclic conjugated carbenes, in addition to the three basic electronic configurations that give place to the aforementioned four states of methylene, there might arise other low-lying configurations involving different occupation of the polyene frontier MOs. As far as we know, only in two cases[13,18] have calculations been reported on electronic states that might be related to such electronic configurations. Specifically, two structures lying very close in energy, corresponding to $^3B_1$ and $^3A_2$ states, were found for both cyclopropenylidene[18] and cycloheptatrienylidene[13] when the molecular geometry was optimized under C_{2v} symmetry constraints. While the $^3B_1$ states are formally related to the T_1 state of methylene, the $^3A_2$ states may be considered to arise formally from S_0 through excitation of an electron from the lone-pair σ-orbital of the carbene center to the LUMO of the polyene moiety in the above cycloalkenylcarbenes.

As a prelude to a detailed study of the role of low-lying excited states in the chemistry of cycloalkenylidenes, we present herein a comprehensive examination of the molecular electronic structure and energetics of *all* low-lying singlet and triplet states of the simplest carbocyclic conjugated carbene, cyclopropenylidene (**1**),

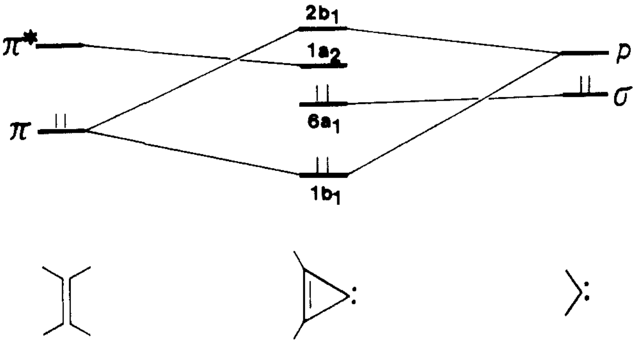


Figure 1. Molecular orbital interaction diagram for the methylene and ethylene fragments of cyclopropenylidene.

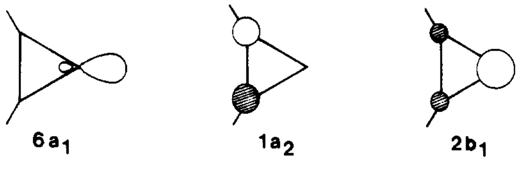
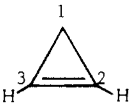
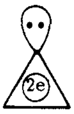


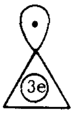
Figure 2. Qualitative drawings of the atomic orbitals that make the largest contribution to the $6a_1$, $1a_2$, and $2b_1$ molecular orbitals.



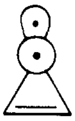
1



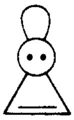
2 ($1\,^1A_1$)



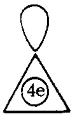
3 ($^1A_2$, $^3A_2$)



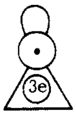
4 ($^1B_1$, $^3B_1$)



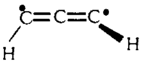
5 ($2\,^1A_1$)



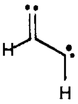
6 ($3\,^1A_1$)



7 ($^1B_2$, $^3B_2$)



8



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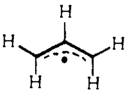

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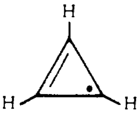

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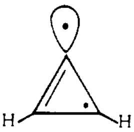

12

using appropriate semiempirical (MNDO) and ab initio MO methods. Although some previous MNDO calculations of the ground-state singlet and the lowest triplet state of **1** have been reported,[19] it should be noted that other potential low-lying electronic states were ignored. Regarding previous ab initio calculations performed at a high level of theory comparable to that used in this paper, it should be noted that the recent investigation of Schaefer and co-workers[18] has not dealt with possible open-shell singlet states of **1**.

In section II a qualitative perturbational MO (PMO) analysis of the possible low-lying electronic states of **1** is presented. The details of the computational methods used are given in section III. The quantitative results of the MNDO and ab initio calculations are presented and discussed in section IV. Finally, our conclusions are presented in section V.

II. Elementary Theoretical Considerations

The first step in the present research was to find out the possible low-lying electronic states of **1** before performing the corresponding theoretical calculations. For this purpose we carried out an elementary PMO analysis that is similar to that reported in the earlier study of Gleiter and Hoffmann.[5] According to the PMO

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approach, **1** is derived conceptually by *union*[20] of methylene with ethene, the simplest even-conjugated polyene with $4n + 2$ π-electrons. A MO interaction diagram is given in Figure 1. Assuming C_{2v} molecular symmetry, the HOMO of ethene (π) has the correct symmetry (b_1) for interaction with the methylene out-of-plane p AO. This interaction will push the latter orbital above its σ-orbital partner, this causing the σ–p splitting to be larger than in methylene. Low-lying states will arise from occupation with two electrons of the $6a_1$, $1a_2$, and $2b_1$ MOs shown in Figure 2. Simple pictorial descriptions of the resulting electronic states, along with their symmetry specifications, are summarized in structures **2**–**7**.

Double occupation of the in-plane $6a_1$ orbital gives rise to the 1^1A_1 singlet (**2**), which is expected to be aromatically stabilized since the ring contains $4n + 2$ ($n = 0$) π-electrons. This state is formally related to the lowest singlet state of methylene (S_0). Promotion (relative to **2**) of one $6a_1$ electron to the $1a_2$ orbital yields the singlet and triplet diradical states of A_2 symmetry (**3**). These states cannot be related to any of the electronic states of methylene. They may be considered to arise formally from S_0 through excitation of one electron from the lone-pair σ-orbital of the carbene center to the π^*-orbital of the ethylenic moiety of **1**.

Alternatively, excitation of one $6a_1$ electron to the $2b_1$ orbital gives rise to the singlet and triplet states of B_1 symmetry (**4**), which are formally related to the S_1 and T_1 states of methylene. Excitation of the two $6a_1$ electrons to either the $2b_1$ or $1a_2$ orbital gives rise to two closed-shell singlet states of A_1 symmetry (**5** and **6**, respectively), which are expected to lie very high in energy above **2** since the ring contains $4n$ ($n = 1$) π-electrons, this causing an antiaromatic destabilization. Finally, the nonpaired double excitation of two $6a_1$ electrons to the $1a_2$ and $2b_1$ orbitals yields the singlet and triplet states of B_2 symmetry (**7**).

III. Computational Methods

All MNDO[21] calculations were performed with the IBM/CMS version[22] of MOPAC[23] program with standard parameters. Calculations for triplet and open-shell singlet states were carried out with the "half-electron" (HE) version of MNDO (MNDO-HE), based on the half-electron approximation[24] to Roothaan's spin-restricted open-shell Hartree–Fock (ROHF) formalism.[25] The desired electronic states were obtained by starting with a density matrix generated from an orbital guess in which selected orbitals were occupied. During the iteration to self-consistency, the selected orbital occupation was maintained by either the level-shift technique[26] or Pulay's direct inversion in the iterative subspace (DIIS) method.[27] The optimized structures of the studied electronic states were determined by minimizing the respective energy with respect to all geometrical parameters within appropriate molecular symmetry constraints with the DFP algorithm.[28]

Standard ab initio MO calculations were carried out with modified versions[29] of either GAUSSIAN-80[30] system of programs or GAMESS[31] program package. Singlet closed-shell states were calculated at the self-consistent-field (SCF) level with a spin-restricted Hartree–Fock (RHF) single-configuration wave function[32] and, for comparison, by use of a two-configuration SCF (TCSCF) wave function in the case of the lowest singlet state (1^1A_1, **2**). The latter method should be more reliable for the description of singlet carbenes.[33] According to a recent ab initio study of **1** by Schaefer and co-workers,[18] the most satisfactory TCSCF description of the 1^1A_1 state can be written in short form as shown in eq 1. Consequently, this is the wave function that was adopted in the

$$\Phi = c_1|...(3b_2)^2(6a_1)^2\rangle + c_2|...(3b_2)^2(2b_1)^2\rangle \qquad (1)$$

present investigation. Regarding the second singlet state of A_1 symmetry (2^1A_1, **5**), it must be noted that the results calculated by making use of the normal single-configuration SCF wave function may be of limited significance and should be considered with great caution. This arises from the fact that such a wave function is nonvariational in the sense that the calculated energy is not an upper bound for the true energy of the excited state. In order to obtain a true variationally optimized wave function for an excited state in such cases, it is necessary to ensure that the function is orthogonal to that of the ground state. The simplest and most obvious solution is to use a multiconfiguration SCF (MCSCF) wave function and optimize the appropriate root. Therefore, in this study the 2^1A_1 state was recalculated utilizing the second root of the TCSCF wave function **1**. Triplet and singlet open-shell states were calculated at the SCF level by the ROHF method.[34] Geometry optimizations were performed subject to specified symmetry constraints at the SCF or TCSCF level with the small split-valence 3-21G basis set[35] by use of analytic gradient methods.[36,37]

Table I. MNDO-Calculated Heats of Formation (kcal/mol) and Optimized Geometries[a,b] for Several Electronic States of Cyclopropenylidene[c]

state	ΔH_f	C_1C_2	C_2C_3	CH	$C_3C_1C_2$	C_1C_2H
1^1A_1	152.3 (0)	1.458	1.365	1.065	55.8	150.3
$^3A_2$	180.5 (28.2)	1.362	1.533	1.057	68.5	156.9
$^1A_2$	185.7 (33.4)	1.361	1.523	1.057	68.1	155.8
$^3B_1$	187.3 (35.0)	1.432	1.372	1.063	57.3	148.8
$^1B_1$	218.4 (66.1)	1.424	1.393	1.064	58.7	150.5
$^1B_2$	277.6 (125.3)	1.357	1.633	1.054	74.0	162.2
2^1A_1	296.3 (144.0)	1.417	1.420	1.062	60.2	151.3

[a] Atom numbering as in **1**. [b] Distances are in angstroms and angles in degrees. [c] Relative energies (kcal/mol) are given in parentheses.

To furnish more accurate ab initio SCF energies, additional single-point calculations were carried out with the larger split-valence 6-31G basis set[38] and with the split-valence plus d polarization at the carbon atoms 6-31G* basis set.[39] Configuration interaction (CI) was used to account for the anticipated large differences in electron correlation energies for closed- and open-shell states. The CI wave function of the closed-shell singlet states included all interacting singly and doubly excited configurations (CISD) relative to the RHF or both TCSCF (for the 1^1A_1 and 2^1A_1 states) reference configurations. The Hartree–Fock interacting space[40,41] of single and double excitations was included for the triplet and open-shell singlet states. The CI calculations were carried out with the 6-31G basis set at the SCF/3-21G or TCSCF/3-21G optimum geometries and did not involve the nonvalence orbitals (frozen core approximation). The number of configurations varied from 3014 for the 2^1A_1 state (one-reference configuration) to 6080 for the $^1A_1$ state (two-reference configuration). Our best ab initio relative energies (CISD/6-31G*) were *estimated* by assuming additivity.[42] That is, the CI correction calculated with the 6-31G basis set was added to the SCF/6-31G* energies.

To assess whether the stationary-point structure calculated for a given electronic state is physically meaningful, this structure must be identified as a true energy minimum on the potential energy hypersurface of this state. For a ground-state structure, such an identification is performed by calculating and diagonalizing the Cartesian force constant matrix

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(20) In perturbation molecular orbital (PMO) theory, *union* is defined as a process in which two conjugated molecules combine in a such a way that their two π-systems unit into one larger one. See: Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1968; p 194.

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Table II. Ab Initio SCF/3-21G-Optimized Geometries[a,b] for Several Electronic States of Cyclopropenylidene

state	computational method	C_1C_2	C_2C_3	CH	$C_3C_1C_2$	C_1C_2H
1^1A_1	RHF	1.441	1.317	1.059	54.4	149.0
	TCSCF	1.448	1.314	1.058	53.9	148.8
$^3A_2$	ROHF	1.343	1.579	1.053	72.1	157.9
$^1A_2$	ROHF	1.343	1.564	1.054	71.3	155.9
$^3B_1$	ROHF	1.477	1.311	1.059	52.7	149.7
$^1B_1$	ROHF	1.484	1.334	1.060	53.4	152.4
$^1B_2$	ROHF	1.409	1.752	1.055	76.9	169.7
2^1A_1	RHF	1.516	1.345	1.062	52.7	155.2
	TCSCF	1.514	1.348	1.062	52.8	155.3

[a] Atom numbering as in **1**. [b] Distances are in angstroms and angles in degrees.

(Hessian matrix) and determining that it has no negative eigenvalues (imaginary frequencies). Problems arise, however, in the case of electronic excited states since some of these states may be subject to variational collapse.[43] In the MOPAC program, the Hessian is obtained by finite differences of gradients that in turn have been calculated by finite differences of energies, which are evaluated, for each nuclear coordinate, at molecular geometries slightly displaced from the equilibrium nuclear configuration. Since these geometries are of lower symmetry than the equilibrium one, the SCF procedure may converge to another solution if a lower lying electronic state of the same multiplicity and symmetry does exist. Consequently, the negative eigenvalues obtained by diagonalizing the Hessian evaluated by means of the above method may be physically meaningless. At first sight this problem could be avoided by computing the Hessian by analytic second derivatives[43,44] since all matrix elements are calculated simultaneously at the equilibrium geometry. Unfortunately, the coupled perturbed Hartree–Fock method,[45,46] used in determining analytically the energy second derivatives with respect to the nuclear coordinates, is not physically meaningful if a lower energy wave function of the same multiplicity does exist. Therefore, in the present investigation, we have calculated the Hessian numerically by finite differences of analytic gradients[47] to characterize the ab initio 3-21G-optimized structures. It must be emphasized, of course, that such a procedure, although less widely appreciated, suffers from the theoretical objections above mentioned and, therefore, the uncertainty in the physical meaning of the negative eigenvalues of the Hessian calculated for some of the electronic excited states does not vanish.

IV. Results and Discussion

Geometrical Structures and Energetics. The MNDO-computed heats of formation and optimized structures for most of the electronic states predicted in section II are listed in Table I according to the calculated energy ordering. It did not prove possible to perform geometry optimizations on either the $^1A_1$ state **6** or the $^3B_2$ state **7**, because these invariably led to linear geometries corresponding to the breaking of the C_2C_3 bond. The 3-21G-optimized geometries calculated for the seven low-lying electronic states of **1** found in the preliminary MNDO study are given in Table II. Corresponding total and relative energies at different levels of theory are shown in Tables III and IV, respectively.

In good qualitative agreement with earlier theoretical studies,[5,7,8,10,11,18,19] the present MNDO and ab initio calculations predict the electronic ground-state of **1** to be a closed-shell singlet $^1A_1$ (**2**). The harmonic vibrational analysis proved in each case that the geometry calculated for this state is a true minimum on the C_3H_2 potential energy hypersurface. A recent matrix isolation of **1** by Hoffmann and Maier[48] appears to confirm these predictions.

A comparison between the optimized geometries at the SCF and TCSCF levels of theory with the 3-21G basis set for this state shows only minor differences. This result is a consequence of the small contribution ($c_1 = -0.131$) of the $(6a_1)^2 \rightarrow (2b_1)^2$ configuration in the TCSCF wave function **1**. In addition, the energy lowering of the TCSCF description with respect to the SCF one is only 7.2 kcal/mol. On these bases, therefore, it appears that the (single-configuration) SCF description of the ground-state single cyclopropenylidene is qualitatively acceptable. Furthermore, when the geometrical parameters shown in Tables I and II for the 1^1A_1 state are compared, it is readily noticeable that the SCF/3-21G-optimized structure is remarkably close to the MNDO-predicted geometry for this state.

In qualitative agreement with the MNDO results, the lowest excited electronic state of **1**, at either the CISD/6-31G or CISD/6-31G* level, is a triplet of A_2 symmetry (**3**). The 3-21G-optimized structure calculated for this state closely resembles to that obtained with MNDO. The main differences are found for the $C_3C_1C_2$ bond angle and the C_1C_2 bond length, which are predicted to be somewhat wider and shorter, respectively, by the 3-21G calculation. The 1^1A_1–$^3A_2$ energy separation of 66.4 kcal/mol estimated at the CISD/6-31G* level is about twice as big as the value (28.2 kcal/mol) predicted by MNDO. A recent study of Dewar and co-workers[49] on the performance of MNDO in calculating excited states has shown that the MNDO-HE energies of the lower triplet and open-shell singlet states of the n,π* type are systematically too negative. As regards the 1^1A_1–$^3A_2$ energy gap, it is gratifying to note that the value (66.4 kcal/mol) *estimated* with the 6-31G* basis set at the CISD level, assuming additivity of the d-polarization and energy correlation effects, is

Table III. Calculated Total Energies (Hartrees) for Several Electronic States of Cyclopropenylidene[a]

state	computational method	basis set 3-21G	6-31G	6-31G*
1^1A_1	RHF	−113.945 89	−114.550 48	−114.618 59
	TCSCF[b]	−113.957 26	−114.561 51	−114.633 24
	CISD[c]		−114.788 89	
	CISD[b,d]		−114.792 66	
$^3A_2$	ROHF	−113.852 11	−114.455 90	−114.513 66
	CISD		−114.700 75	
$^1A_2$	ROHF	−113.844 26	−114.448 12	−114.505 31
	CISD		−114.695 49	
$^3B_1$	ROHF	−113.863 95	−114.467 85	−114.521 31
	CISD		−114.699 37	
$^1B_1$	ROHF	−113.766 11	−114.370 59	−114.428 49
	CISD		−114.616 81	
$^1B_2$	ROHF	−113.635 63	−114.243 93	−114.291 21
	CISD		−114.501 36	
2^1A_1	RHF	−113.577 75	−114.183 49	−114.231 00
	TCSCF[b]	−113.574 39	−114.180 38	−114.228 63
	CISD		−114.435 53	
	CISD[b,d]		−114.440 59	

[a] All calculations at the SCF/3-21G-optimized geometries. [b] At the TCSCF/3-21G-optimized geometry. [c] Based on the RHF reference configuration. [d] Based on both TCSCF reference configurations.

Table IV. Calculated Relative Energies (kcal/mol) for Several Electronic States of Cyclopropenylidene[a]

state	SCF/3-21G	SCF/6-31G	SCF/6-31G*	CISD/6-31G	CISD/6-31G*[b]
1^1A_1	0[c]	0[c]	0[c]	0[d]	0
$^3A_2$	66.0	66.3	75.0	57.7	66.4
$^1A_2$	70.9	71.2	80.3	61.0	70.1
$^3B_1$	58.6	58.8	70.2	58.5	69.9
$^1B_1$	119.9	119.8	128.5	110.3	119.0
$^1B_2$	201.8	199.3	214.6	182.8	198.1
2^1A_1	240.2[c]	239.1[c]	253.9[c]	220.9[d]	235.7[d]

[a] All calculations at the SCF/3-21G-optimized geometries except for the 1^1A_1 and 2^1A_1 states, for which the TCSCF/3-21G-optimized geometry was used. [b] Estimated assuming additivity of the electron correlation and polarization corrections. [c] At the TCSCF level of theory. [d] Based on both TCSCF reference configurations.

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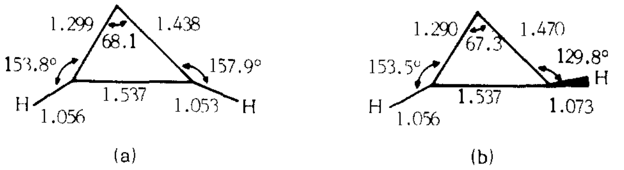

Figure 3. ROHF/3-21G geometries after C_s (a) and C_1 (b) symmetry-constrained reoptimization of the structure calculated for the $^3A_2$ electronic state of cyclopropenylidene. All bond distances are in angstroms.

in remarkably good agreement with the value (65.3 kcal/mol) *calculated* with a DZ+P basis set at the same level of theory.[18]

The force constant matrix analysis proved the MNDO-optimized $^3A_2$ structure to be a true potential energy minimum. In sharp contrast, the 3-21G-optimized structure showed three imaginary frequencies corresponding to normal modes of b_2, a_2, and b_1 symmetries, in good agreement with Schaefer's results.[18] This implies that the $^3A_2$ state does not have a stable equilibrium geometry of C_{2v} symmetry. Since the largest imaginary frequency (which corresponds to a normal mode of b_2 symmetry) suggests the breaking of one of the two equivalent CC bonds, most likely by yielding propenediylidene (**9**), Schaefer and co-workers[18] concluded that the $^3A_2$ state will not be observable for cyclopropenylidene-like geometries. In view of the MNDO and ab initio results predicting the $^3A_2$ state to be the lowest triplet state of **1**, we have reinvestigated the question concerning the possible existence of an equilibrium geometry for this state. For this purpose, additional calculations on the molecular structure of the $^3A_2$ state were carried out. A C_s-constrained geometry optimization (at the SCF/3-21G level) was performed, with as initial geometry the C_{2v} structure previously found for the $^3A_2$ state slightly modified according to the normal mode (b_2 symmetry) corresponding to the largest imaginary frequency. This optimization did not lead to the geometry expected for the triplet state of **9** but to a structure (Figure 3a) that was shown to be a $^3A''$ state lying 2.5 kcal/mol below the $^3A_2$ triplet. Curiously, this planar structure shows three unequal CC bonds, with one short (1.299 Å) and one long (1.438 Å) C_1CH bond relative to the C_1CH bond distance (1.342 Å) predicted for the C_{2v} structure. The force constant analysis of this C_s structure revealed that it has one imaginary frequency that essentially corresponds to an out-of-plane bending of the hydrogen atom adjacent to the longest C_1CH bond. A subsequent unconstrained geometry optimization (at the SCF/3-21G level) was performed starting at the latter C_s geometry slightly modified according to the normal mode (a'' symmetry) of imaginary frequency. A highly unsymmetrical (C_1 point group) structure (Figure 3b) was obtained, which was shown to be a ^3A state lying 13.1 kcal/mol below the $^3A_2$ triplet. Surprisingly, in addition to the short (1.290 Å) and long (1.470 Å) C_1CH bonds, this structure has one hydrogen atom (i.e., that adjacent to the longest C_1CH bond) bent 46.4° out of the plane of the ring, but the other hydrogen atom is very close to the plane. The force constant analysis proved this C_1 structure to be a true minimum on the triplet C_3H_2 potential energy hypersurface.

A plausible explanation to the above unexpected results will be approached in two steps. First, we note the obvious analogy that exists between the π-electron system of the $^3A_2$ state of **1** and that of the allyl radical (**10**). Indeed, both π-systems have the electron configuration ...$(b_1)^2(a_2)^1$ and, therefore, a single-configuration SCF wave function description of such a π-system will be plagued by the so-called "doublet instability" phenomenon.[50] This phenomenon, a particular case of the most general Hartree–Fock instability problem,[51] causes radicals like **10** to be computed to have unequal bond lengths at the ROHF level of theory. An ROHF calculation tends to locate the odd electron at one end of the molecule, while a double bond is localized at the other end. This spurious localization compensates for the inadequacy of the spin-restricted single-configuration wave function in providing correlation of the two opposite-spin π-electrons. Although the doublet instability problem usually has been reported for three-center radicals containing three π-electrons,[52] it should be recalled that analogous symmetry-breaking problems due to the Hartee–Fock instability phenomenon have also been reported in molecular calculations of triplet states.[53] On the basis of the above π-electron structure features, the largest imaginary frequency exhibited by the C_{2v} structure of the $^3A_2$ state of **1** is ascribed to the Hartree–Fock instability shown by the corresponding SCF wave function. Second, we note the apparent similarity that exists between the π-electron system of the $^3A''$ state of **1** and that of the $^2B_1$ state of cyclopropenyl radical (**11**). In fact, a simple localized-bond picture of the $^3A''$ state of cyclopropenylidene (**12**) shows that this species has a localized C_1C_3 double bond, one odd σ-electron on C_1 and one π-electron on C_2. Consequently, from the π-electron system point of view, the situation is equivalent to that depicted for **11**. At this point it is worth noticing that some years ago Baird reported[54] that the optimum energy structure for **11**, calculated with the ROHF method using a STO-3G basis set,[55] is of the "ethylenic" type with one CC double bond of length 1.30 Å, two CC single bonds of length 1.47 Å, and the hydrogen atom bonded to the radical center (C_2) bent 47° out of the CCC plane. The same author suggested that the C_{2v} structure of the $^2B_1$ state of **11** undergoes distorsion toward nonplanarity at the radical center because of the relief of strain accompanying the relaxation of the C_2CH bond out of the ring plane. Later ab initio calculations by Poppinger et al.[56] with the split-valence 4-31G basis set[57] confirmed that at the SCF level the preferred equilibrium geometry of **11** is essentially that found by Baird.[54] Summarizing the above discussion, we conclude that *the ultimate cause of the unexpected SCF/3-21G result concerning the highly unsymmetrical equilibrium geometry predicted for the lowest triplet state of cyclopropenylidene is the Hartree–Fock instability shown by the ROHF solution of the* $^3A_2$ *state.* It has been recently shown[58] that an appropriate MCSCF wave function averts the symmetry breaking phenomenon in analogous molecular geometry calculations. It is likely, therefore, that such a model should predict for the $^3A_2$ state of **1** a C_{2v} structure that might be the true equilibrium geometry of the lowest triplet state of this species, in agreement with the MNDO results. The question naturally arises as to why MNDO-HE predicts the $^3A_2$ state to be a true potential energy minimum, despite the fact that this method is based on a single-configuration SCF formalism. The explanation lies on the fact that HE method *does* successfully predict a C_{2v} structure for **10**, at either the semiempirical[52] or ab initio[59] level of theory. This interesting result is ascribed to the pseudo-closed-shell character of the HE wave function. This topic will be discussed in detail elsewhere.[59]

The singlet open-shell diradical $^1A_2$ (**3**) is predicted to be the first excited singlet state of **1**. As expected, the optimized structure of this electronic state is nearly identical with that found for $^3A_2$ and shows, as compared with that calculated for the ground-state singlet, a substantial increase of the $C_3C_1C_2$ bond angle and a shortening of the C_1C_2 bond distance. The increase in the bond angle is easily understood taking into account that the transformation of the 1^1A_1 state to the $^1A_2$ state involves the promotion of an electron from the $6a_1$ orbital, which favors small $C_3C_1C_2$ angles, to the C_2C_3 antibonding orbital $1a_2$. Although our best ab initio estimated value of the 1^1A_1–$^1A_2$ energy gap (70.1 kcal/mol) again is about twice as big as the value (33.4 kcal/mol)

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predicted by MNDO, it is remarkable that the $^1A_2$–$^3A_2$ energy difference estimated at the CISD/6-31G* level (3.7 kcal/mol) is in reasonable agreement with the MNDO value (5.2 kcal/mol). As found for the $^3A_2$ state, the harmonic vibrational analysis proved that while the MNDO-optimized structure calculated for the $^1A_2$ state is a true potential energy minimum, the structure computed with the 3-21G basis set has three imaginary frequencies, which again correspond to normal modes of b_2, a_2, and b_1 symmetries. Additional calculations, analogous to those mentioned above for the $^3A_2$ state, proved that the SCF wave function of the $^1A_2$ state is also subject to Hartree–Fock instability. As a consequence, the SCF/3-21G equilibrium geometry calculated for the lowest open-shell singlet state of **1** was found to be a highly unsymmetrical (C_1) structure, which closely resembles the structure shown in Figure 3b, lying 8.3 kcal/mol lower in energy than the C_{2v} geometry. Therefore, it is likely that an appropriate MCSCF treatment should predict a C_{2v} structure for the equilibrium geometry of the lowest open-shell singlet state of **1**, in accordance with MNDO results.

As seen in Table I, MNDO predicts the triplet $^3B_1$ (**4**) to be the third excited state above the ground state. Regarding the relative energy ordering of triplet states $^3A_2$ and $^3B_1$, it is interesting to note that while MNDO predicts $^3A_2$ to lie 6.8 kcal/mol below $^3B_1$, the ab initio calculations at the SCF level predict the latter state to be lower in energy by 4.8–7.5 kcal/mol, depending on the basis set. However, at the highest level of theory, namely CISD/6-31G*, the A_2 triplet is found to lie 3.5 kcal/mol below the B_1, in qualitative agreement with MNDO results. As regards the energy separation between the ground-state singlet and the $^3B_1$ excited state, the value (69.9 kcal/mol) estimated at the CISD/6-31G* level of theory again is found to be about twice as big as the MNDO predicted energy gap (35.0 kcal/mol) but is in excellent agreement with the value calculated (70.3 kcal/mol) by Schaefer and co-workers[18] at the CISD/DZ+P level. The latter finding supports again the assumed additivity of the d-polarization functions and electron correlation effects on the relative energies of the electronic states of **1**. The practical implications of this conclusion can be of paramount importance in the calculation of the low-lying electronic states of larger cycloalkenylidenes. Regarding the force constant analysis of the MNDO- and 3-21G-calculated molecular geometries for the $^3B_1$ state, both methods showed these structures to be genuine potential energy minima, in accordance with Schaefer's harmonic vibrational analysis of this state.

The second excited singlet in Tables I and IV is the open-shell singlet $^1B_1$ (**4**). The geometrical differences between the MNDO- and 3-21G-optimized structures for this state are somewhat larger than in the case of the open-shell singlet of A_2 symmetry. On the other hand, both the MNDO- and 3-21G-optimized geometries of the B_1 singlet more nearly resemble that of the ground-state singlet than that of the lower energy singlet A_2. The similarity between the $C_3C_1C_2$ bond angles calculated for the 1^1A_1 and $^1B_1$ states can be attributed to a near compensation of two opossite effects. Thus, while the leakage of an electron from the $6a_1$ orbital favors an increase of the above bond angle, the occupation of the C_2C_3 bonding $1b_2$ orbital leads to a similar decrease of that angle. As seen in Tables I and II, while the optimized geometries obtained for the $^3B_1$ and $^1B_1$ states are very similar, their energy separation is calculated (e.g., 31.1 and 58.3 kcal/mol at the MNDO and SCF/6-31G* levels, respectively) to be quite large. This result is in sharp contrast with that found for the singlet and triplet states of A_2 symmetry (e.g., 5.2 and 5.3 kcal/mol at the aforementioned levels). Such a difference is easily understood by examining the different spatial localization of the singly occupied orbitals involved in electronic configurations **3** and **4** (Figure 2) and noting that the exchange integral causing the singlet–triplet energy splitting is expected to be larger for the orbital pair $6a_1$–$2b_1$ than for the pair $6a_1$–$1a_2$. The force constant matrix analysis proved the MNDO- and 3-21G-optimized structures of the $^1B_1$ state to be true equilibrium geometries.

The open-shell singlet $^1B_2$ (**7**) is predicted to be the fifth excited state of **1** at all different levels of theory considered. Interestingly, while the structure of this state could be optimized within the C_{2v} point group symmetry, geometry optimization of the counterpart triplet $^3B_2$ invariably leads to linear geometries corresponding to breaking of the C_2C_3 bond. It is worth noting that the optimized $C_3C_1C_2$ bond angle of the $^1B_2$ state is the largest one of all the structures calculated for the low-lying electronic states of **1** listed in Table I. This result suggests that single occupation of the C_2C_3 antibonding $1a_2$ orbital and electron vacancy of the $6a_1$ orbital confers to this linkage the highest antibonding character that can be held within a cyclopropenylidene-like structure. Further increase of the antibonding character of the C_2C_3 bond (as in **6**, where the $1a_2$ orbital is doubly occupied) leads to its breaking, most likely yielding the diradical allenic structure **8**. The discrepancies between the ab initio and MNDO calculated geometries are more accentuated for the $^1B_2$ state than for the excited states of lower energy, and the 1^1A_1–$^1B_2$ energy separation estimated at the CISD/6-31G* level (198.1 kcal/mol) is substantially larger than the MNDO value (125.3 kcal/mol). The harmonic vibrational analysis proved that while the MNDO-optimized structure calculated for the $^1B_2$ state is a true potential energy minimum, the structure computed with the 3-21G basis set has three imaginary frequencies corresponding to normal modes of b_2, a_2, and b_1 symmetries. Since this result is analogous to that found for the $^1A_2$ and $^3A_2$ states, we presume that the SCF wave function of the $^1B_2$ state also suffers from the same Hartree–Fock instability problem aforementioned.

Finally, the doubly excited closed-shell singlet 2^1A_1 (**5**) is predicted to be the sixth excited state of **1**. As found for the ground state, the 3-21G-optimized structures calculated at the SCF and TCSCF levels of theory for this excited state are nearly identical. This result is a consequence of the large value (0.993) obtained for the c_2 coefficient in the TCSCF wave function **1**. It is remarkable that the $C_3C_1C_2$ bond angle (52.8°) is only 0.6° wider than that calculated for the $^1B_1$ state. This result clearly indicates that the leakage of a second electron from the $6a_1$ orbital does not lead to a significant increase of the above bond angle. It is to be noted that the 3-21G-optimized structure differs appreciably from that predicted by MNDO. In agreement with the assumed antiaromatic nature of this state, the 3-21G-calculated geometry displays alternating (long–short) C_1C_2 and C_2C_3 bond distances whereas the MNDO-calculated CC bond lengths are nearly identical, indicating that the four π-electrons are fully delocalized on the three carbon atoms. Moreover, the 1^1A_1–2^1A_1 energy separation estimated at CISD/6-31G* level (235.7 kcal/mol) is substantially greater than the MNDO value (144.0 kcal/mol). These results suggest that MNDO grossly underestimates the antiaromatic destabilization due to the delocalized four π-electrons. While the MNDO-optimized structure could not be characterized as a stable equilibrium geometry due to the nonconvergence to self-consistency problems arisen in the calculation of the Hessian, the harmonic vibrational analysis of the TCSCF/3-21G-optimized structure for the 2^1A_1 state showed an imaginary frequency corresponding to a normal mode of b_2 symmetry. This normal mode breaks the C_{2v} molecular symmetry and leads to CCC linear geometry with a short and a long CC bond length. It appears, therefore, that due to its intrinsic antiaromatic character the 2^1A_1 state (**5**) does not have any equilibrium geometry possessing a cyclic arrangement of the three carbon atoms.

Charge Distributions. As expected the charge distribution changes significantly along the seven low-lying electronic states of **1** described above. The atomic net charges, determined from the Mulliken population analysis,[60] 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-calculated values.

In general, the calculated 6-31G* atomic net charges qualitatively agree fairly well with the MNDO values. As expected on the basis of the appreciable differences noted for the corresponding optimized geometries, the largest discrepancies between

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Table V. Mulliken Atomic Net Charges and Dipole Moments (Debyes) for Several Electronic States of Cyclopropenylidene at the SCF/6-31G* Level of Theory[a-c]

state	C_1	C_2	μ
1^1A_1[d]	−0.047 (+0.052)	−0.201 (−0.156)	3.07 (2.71)
$^3A_2$	+0.055 (+0.124)	−0.274 (−0.206)	1.02 (1.11)
$^1A_2$	+0.070 (+0.124)	−0.276 (−0.206)	0.60 (1.06)
$^3B_1$	−0.069 (−0.216)	−0.186 (−0.018)	1.42 (2.58)
$^1B_1$	−0.176 (−0.224)	−0.148 (−0.015)	2.64 (2.65)
$^1B_2$	+0.036 (−0.071)	−0.300 (−0.111)	1.57 (1.30)
2^1A_1[d]	−0.343 (−0.397)	−0.074 (+0.074)	2.13 (2.11)

[a] See footnote *a* in Table IV. [b] Atom numbering as in **1**. [c] The quantities in parentheses are the MNDO-calculated values. [d] Based on the TCSCF wave function.

the 6-31G* and MNDO charge distributions are found for the higher excited states.

Regarding the ground-state singlet, at variance with the MNDO results, which predict a small *positive* net charge at the carbene center, the 6-31G* calculation gives a *negative* net charge on this atom. However, this negative charge is found to be less significant than has been considered in previous theoretical studies. Thus, earlier EHT[5] and INDO[8] calculations have predicted a substantial negative net charge at the divalent carbon that has been taken as a theoretical rationalization of the nucleophilic character attributed to **1** on the basis of the nucleophilic behavior shown by its diphenyl derivative.[61] According to both MNDO and 6-31G* results, the largest electron charge deficiency at the carbene center corresponds to the singlet and triplet excited states of A_2 symmetry, but the 6-31G*-calculated net positive charges on this atom are substantially smaller than the values predicted by MNDO. On the other hand, the singlet and triplet excited states of B_1 symmetry show a net negative charge on the carbene center that is notably smaller than the MNDO-calculated value. In regards to the doubly excited open-shell singlet $^1B_2$, the 6-31G* calculation gives a small positive net charge at the carbene center and a substantial negative net charge at the C_2 atom whereas MNDO predicts an essentially identical negative net charge for the three carbon atoms. Finally, both methods agree in predicting the doubly excited closed-shell singlet 2^1A_1 as the electronic state possessing the largest net negative charge at the carbene center.

A comparison between the MNDO- and 6-31G*-calculated dipole moments reveals that, except for the $^1A_2$ and $^3B_1$ states, both methods give similar values. Curiously, the dipole moment calculated with the 6-31G* basis set for ground-state singlet (3.07 D) is greater than the MNDO value (2.71 D) but still is too small compared with the value (3.32 D) calculated with a DZ+P basis set with the same TCSCF description.[18] This discrepancy between the TCSCF/6-31G*- and TCSCF/DZ+P-calculated dipole moments for the 1^1A_1 state is striking, inasmuch as the value calculated at the single-configuration SCF level with the 6-31G* basis set comes out to be 3.33 D, which is essentially identical with the TCSCF/DZ+P predicted value.

Regarding the $^3B_1$ state, for which MNDO predicts a dipole moment that is about a 80% larger than the value calculated with the 6-31G* basis set, it is to be noted that for such a state the MNDO method grossly overstimates the excess of electron charge at the carbene center, as compared with the 6-31G*-calculated charge distribution.

V. Conclusions

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

First, in agreement with earlier theoretical calculations and experimental findings, the electronic ground state is predicted to be a closed-shell singlet $^1A_1$. The MNDO atomic net charge at the carbene center does not support the assumed strong nucleophilic character of singlet cyclopropenylidene; in addition, the present ab initio results suggest only a weak nucleophilic character for this species.

Second, the first excited state is predicted to be the $^3A_2$ triplet rather than the $^3B_1$ triplet, which correlates with the lowest triplet state of methylene. This excited state may be considered to arise formally through excitation of one electron from the lone-pair σ-orbital of the carbene center to the π^*-orbital of the ethylene moiety of the molecule. Both MNDO and ab initio results predict a positive atomic net charge at the carbene center of this excited state, as well as for the singlet open-shell diradical state $^1A_2$ arising from the same electronic configuration. Consequently, it appears that these excited states might exhibit an electrophilic character. On the basis of the three imaginary frequencies shown by the geometrical structure calculated at the SCF level of theory for the $^3A_2$ state, the potential existence of such a state has been discarded in a recent ab initio study. The present ab initio calculations suggest that the SCF wave functions of both open-shell states of A_2 symmetry are subject to Hartree–Fock instability. Although our study is by no means the "final word" on the question of the possible existence of the $^3A_2$ state, we believe that an appropriate MCSCF description should predict a true C_{2v} equilibrium geometry for this state.

Third, all of the calculated excited states, including the $^3A_2$ and $^1A_2$, are predicted to lie very high in energy above the ground-state singlet. Consequently, it is very unlikely that these excited electronic states may play any significant role in the chemistry of (singlet) cyclopropenylidene.

As a bonus, the present study shows 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 cyclopropenylidene, 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 these excited states relative to that of the ground-state singlet. 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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