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The Sudden Polarization Effect: MC–SCF Calculations on Planar and 90° Twisted Methylenecyclopropene

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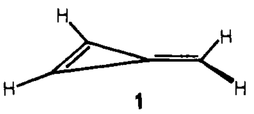
Abstract: Ab initio MC–SCF molecular orbitals are reported for electronic ground and excited states of planar and 90° twisted methylenecyclopropene within the framework of a four π-orbital FORS (full optimized reaction space) model. For planar methylenecyclopropene, individual state MC–SCF results include: ground state dipole moment, 1.33 D, and excitation energies, 3.32 eV ($^3B_2$), 4.71 eV ($^1B_2$), 4.87 eV ($^3A_1$), and 9.36 eV (2^1A_1). The SCF first ionization potential is 8.1 eV. Calculations for the 90° twisted species at a MNDO optimized geometry for the lowest diradical state ($^1D_1$) yield states having diradical (D) or pronounced zwitterionic (Z) character. Variational MC–SCF results are (excitation energy, dipole moment): $^1A_2$ ($^1D_1$) 0.0 eV, 0.67 D; $^3A_2$ ($^3D_1$) –0.06 eV, 0.65 D; $^3B_1$ ($^3D_2$) 0.53 eV, –0.96 D; 1^1A_1 ($^1Z_1$) 0.59 eV, 5.34 D; $^1B_1$ ($^1D_2$) 0.65 eV, –0.94 D. CI results for the second zwitterionic state 2^1A_1 ($^1Z_2$) are 7.58 eV and –5.83 D. These calculated properties, especially for the case of the twisted species, are highly sensitive to the method of calculation. CI calculations using ground state ($^1D_1$) orbitals led to significantly exaggerated dipole moments and state energies.

Following the pioneering work of Mulliken and co-workers,[2] it is now firmly established that alkene excited states have a potential surface minimum at a 90° twisted geometry.[3] Due to an avoided crossing, this minimum usually is poised above a ground state surface maximum and the "funnel" thus engendered provides a mechanism for both light-wasting reversion to starting alkene and cis–trans isomerization, following photoexcitation of alkenes.

One highly intriguing and still controversial development in this area is the recent prediction by Salem and co-workers that these twisted singlet excited states should have distinctly zwitterionic rather than biradical character.[4] Salem has termed this phenomenon "sudden polarization" because of its nearly instantaneous onset as a 90° twisted geometry is approached. These zwitterionic excited states have been suggested to play a key role in the photochemistry of vision;[5d] their general involvement in organic photochemical mechanisms has only begun to be recognized.[6]

Theoretical studies of twisted alkene excited states reported to date have been limited to linear polyenes and simple derivatives[4,5,7] yet, in principle, virtually *any* twisted π system should have strongly polarized singlet excited states.[8] It is thus crucial at this point that the principal features of this phenomenon be accurately characterized and understood. Fundamental questions include the degree of polarization, determination of which direction of polarization in an unsymmetrical system represents the lower energy state, and distribution of separated charge within the orthogonal molecular fragments. These often will have an important bearing on photochemical reactions.[6] The present work was undertaken as a step toward understanding these and other questions.

We present here results of ab initio MC–SCF calculations on the electronic ground and excited states of planar (**1**) and twisted (**2**) methylenecyclopropene. No intermediate structures are considered here, as we address primarily the extent of polarization in **2**, not the "suddenness" with which this polarization develops when **1** is converted to **2**.



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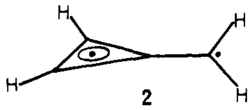

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As the archetypal nonalternant hydrocarbon, methylenecyclopropene is a molecule of considerable theoretical interest, despite its apparently transient existence.[9] In the present work, it provides a useful model for understanding critical features of the sudden polarization phenomenon. Species **2** derives from $\pi \rightarrow \pi^*$ excitation of **1**, followed by twisting about the exocyclic π bond. Previous semiempirical and ab initio SCF studies of **1** are primarily limited to its ground state[10] and we are aware of only one semiempirical investigation of twisted species **2**.[11]

The present study also reveals some of the difficulties inherent in theoretical treatments of highly polarized twisted alkene excited states. In particular, we had reservations about the ability of the commonly used[4,5c–f] ab initio SCF followed by 3 × 3 CI methods to correctly predict the properties of twisted excited states. Our results for twisted methylenecyclopropene (**2**) have implications concerning the computational effort required for reliable quantitative treatment of electronic states of any twisted alkene. We note, however, that *qualitatively*, the sudden polarization phenomenon can be reproduced by any type of molecular orbital calculation which includes electron repulsion.

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(1) (a) Iowa State University. (b) Iowa State University and Ames Laboratory, USDOE.

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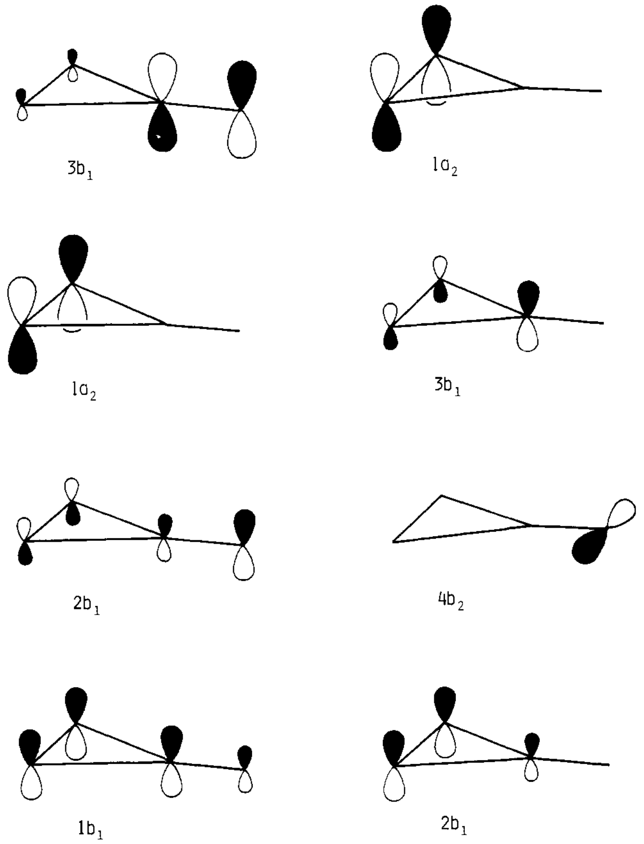


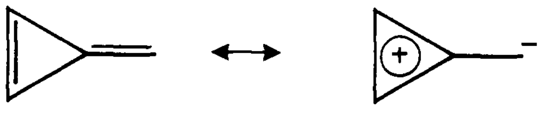
Figure 1. π molecular orbitals of planar and 90° twisted methylenecyclopropene.

Electronic Structure of Planar and 90° Twisted Methylenecyclopropene

Schematic π molecular orbitals of planar and twisted methylenecyclopropene are depicted in Figure 1. Low-lying electronic states arise from various occupations of these orbitals by four electrons. For the planar case, the lowest energy states are:

1^1A_1	$...(1b_1)^2(2b_1)_2$
$^1B_2$, $^3B_2$	$...(1b_1)^2(2b_1)^1(1a_2)^1$
2^1A_1, $^3A_1$	$...(1b_1)^2(2b_1)^1(3b_1)^1$

Here, ... represents the eight a_1 and four b_2 closed shells comprising the σ molecular framework. The ground state of **1** is expected to possess a significant dipole due to contribution from resonance structure **3**, while the B_2 excited states should have the opposite polarity.



1 **3**

Population of twisted methylenecyclopropene orbitals gives rise to low-lying states having either pronounced diradical (D) or zwitterionic (Z) character. The lowest energy possibilities are:

$^1A_2$, $^3A_2$	$...(2b_1)^2(4b_2)^1(3b_1)^1$	$(^1D_1, {}^3D_1)$
$^1B_1$, $^3B_1$	$...(2b_1)^2(4b_2)^1(1a_2)^1$	$(^1D_2, {}^3D_2)$
1^1A_1	$...(2b_1)^2(4b_2)^2$	$(^1Z_1)$
2^1A_1	$...(2b_1)^2(3b_1)^2$	$(^1Z_2)$

In this case, ... represents the eight a_1, three b_2, and one b_1 orbitals of the σ skeleton.

Table 1. Energies of Electronic States of Planar Methylenecyclopropene

state	dominant configuration	no. of config[a]	FORS MC-SCF energy	CI energy[b,c]
1^1A_1	$...(1b_1)^2(2b_1)^2$	12	−153.60553 (0.0)	−153.60553 (0.0)
$^3B_2$	$...(1b_1)^2(2b_1)^1(1a_2)^1$	9	−153.48349 (3.32)	−153.45483 (4.10)
$^1B_2$	$...(1b_1)^2(2b_2)^1(1a_2)^1$	8	−153.43247 (4.71)	−153.37590 (6.24)
$^3A_1$	$...(1b_1)^2(2b_1)^1(3b_1)^1$	6	−153.42652 (4.87)	−153.39749 (5.66)
2^1A_1	$...(1b_1)^2(2b_1)^1(3b_1)^1$	12	−153.26168 (9.36)	−153.18222 (11.52)

[a] Number of configurations used in FORS MC-SCF calculations or CI calculations. [b] Total energies given in hartrees and in parentheses, relative energies in eV. [c] CI results are based on orbitals MC-SCF optimized for the 1^1A_1 ground state.

The two D configurations involve single occupation of the exocyclic inplane p orbital ($4b_2$), whereas the Z_1 and Z_2 configurations place 2 and 0 electrons, respectively, in this orbital. Thus the two D states are anticipated to have only moderate dipole moments while Z_1 and Z_2 should have large moments, these being in opposite directions.

The relative energies of the Z_1 and D states depend on the magnitude of the pairing energy required to form the zwitterion $(4b_2)^2$ compared to the promotion energy required to form the diradicals $(4b_2)^1(3b_1)^1$ or $(4b_2)^1(1a_2)^1$. It is relatively straightforward to predict that $^1D_1$ will be the lowest energy singlet state, however $^1D_2$ and $^1Z_1$ are expected to be quite close, while $^1Z_2$ should lie well above these three.

Computational Methods

Initially, we note that for both planar and twisted forms of methylenecyclopropene, all states but the highest considered possess a unique symmetry designation. For this reason, strong configuration interaction is not expected for any of these states; their wave functions consequently must be dominated by the SCF configurations described above. This simple situation does not always exist for twisted alkenes, particularly when the two p orbitals of the broken double bond are related by a symmetry operation of the molecular point group.[7c-f] As recently noted by Michl,[12] the proper minimal treatment at such twisted "biradicaloid" geometries should be MC-SCF (multiconfiguration SCF) calculation.

Despite the apparent adequacy of an SCF description of low-lying states of **1** and **2**, important differences in correlation energies exist among these states due to differing occupation of π system orbitals. In addition, the expected large changes in electronic charge distribution, especially significant for twisted molecule **2**, make it unlikely that any simple set of orbitals can quantitatively describe all the states of either species, in the absence of very extensive configuration interaction. These two problems—correlation effects and orbital reoptimization—dictate the necessity of separate MC-SCF optimization for each state of planar and twisted methylenecyclopropene.

MC-SCF calculations were carried out within the framework of the Full Optimized Reaction Space (FORS) model of Ruedenberg.[13,14] Briefly, the FORS wave function consists of all configurations of a given electronic symmetry type which can be constructed through distribution of the higher energy electrons within an appropriate orbital subspace, while keeping lower lying

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Table II. Charge Distribution in Planar Methylenecyclopropene[a]

state	dipole moment[b]	Mulliken populations[c]				
		C_1	C_2	C_3, C_4	H_1, H_2	H_3, H_4
1^1A_1	1.33	6.54	5.93	6.18	0.82	0.77
$^3B_2$	−0.66	6.49	5.97	6.22	0.79	0.76
	(−0.60)	(6.40)	(5.90)	(6.26)	(0.82)	(0.77)
$^1B_2$	−1.69	6.50	5.92	6.25	0.77	0.77
	(−1.87)	(6.36)	(5.79)	(6.34)	(0.82)	(0.77)
$^3A_1$	0.67	6.53	5.99	6.17	0.80	0.77
	(0.53)	(6.43)	(6.04)	(6.18)	(0.82)	(0.77)
2^1A_1	4.98	6.84	5.86	6.10	0.81	0.74
	(4.67)	(6.76)	(6.04)	(6.02)	(0.82)	(0.77)

[a] For each state, the first entry is the MC-SCF result optimized for that state, and the second entry, where given, is a CI result, using orbitals optimized for the 1^1A_1 ground state. [b] In Debye, positive sign implies  polarity. [c] Numbering scheme for atoms is shown in Figure 2.

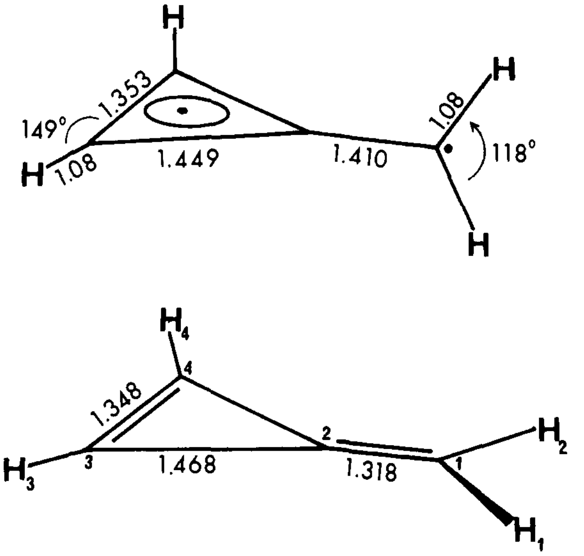

Figure 2. MNDO optimized geometries for planar and twisted methylenecyclopropene; bond lengths in ångstroms.

orbitals doubly occupied and subjecting all occupied orbitals to MC-SCF optimization. The FORS model and its various applications have been described elsewhere[13,14] and we turn directly to the FORS description of **1** and **2**.

In the FORS wave function for each of the states of planar and twisted methylenecyclopropene, inner-shell and σ framework orbitals are held to double occupancy. The remaining four electrons are distributed within the four π-type orbitals shown in Figure 1. This leads to a dozen or less space-spin configurations for each state; the exact numbers are given in Tables I and III. This π-orbital FORS clearly should be capable of satisfactorily describing breakage of the exocyclic π bond on twisting. Additionally, these configurations include the important near-degeneracy correlations associated with the various $\pi \rightarrow \pi^*$ double excitations. Because of inclusion of these correlation effects, and because separate optimization for each state allows the σ skeleton to readjust to varying π-electron distributions, our FORS MC-SCF calculations may be expected to yield reliable estimates of electronic excitation energies.

In addition to these fully optimized MC-SCF calculations, we also have performed SCF and SCF-CI calculations in some instances. Our CI calculations include the identical set of configurations used in the FORS MC-SCF computation but use orbitals MC-SCF optimized for the ground state to construct each excited state. These full CI calculations in a four-orbital space are entirely analogous to the 3 × 3 CI within a two-orbital space often used to treat twisted alkenes.[4] Thus comparison of our MC-SCF and SCF-CI results permits accurate assessment of the quantitative reliability of the 3 × 3 CI technique. SCF calculations (without CI) also were performed on twisted states; these provide an estimate of the relative effects of SCF orbital optimization and configuration interaction in determining properties of these states.

The atomic basis used in these calculations was of double-ζ quality. Specifically, it consisted of a 8s/4p set of even-tempered Gaussian primitives generally contracted to 3s/2p on carbon and a 4s set of even-tempered Gaussian primitives scaled by 1.2 and generally contracted to 2s on hydrogen.[15] All computations except geometry optimization were performed by using the ALIS system for quantum-chemical calculations.[16]

Molecular Geometries

Experimental geometries for **1** and **2** are unavailable and it did not prove feasible to optimize these at the MC-SCF level. For internal self-consistency, we have thus chosen to use geometries for both **1** and **2**, optimized using the semiempirical MNDO method.[17] In these calculations, C-H bond lengths and angles were kept fixed at reasonable values and all C-C distances were optimized. Optimized geometries are shown in Figure 2; for planar structure **1**, these are consistent with results of previous calculations.[10] For twisted species **2**, our calculations used the half-electron open-shell method,[17] with geometry optimization of the lowest diradical ($^1D_1$; $^1A_1$) state. Dewar and Kohn have previously reported a MINDO/2 optimized geometry for **2**; however, it is clear from their description that this calculation was for the $^1Z_1$ state.[11] This is almost certainly a computational error since $^1D_1$ is formally treated by the MINDO/2 program as an excited state in terms of orbital occupation. Due to this programming artifact, specification of a ground-state configuration as input to the calculation would produce the excited state $^1Z_1$.

Our calculations thus represent the ground and *vertical* excited states of twisted methylenecyclopropene, with the optimized geometry for **2** representing a ground state potential surface saddle point. Each of the twisted form upper states should have its own energy minimized geometry, which may differ significantly from these vertical states. Most importantly, $^1Z_1$ should be stabilized by shortening the exocyclic bond—thus minimizing charge separation—and by pyramidalization at the methylene carbon.[5c,e,f,7b-f] Indeed, at geometries not considered here, and in polar media, $^1Z_1$ may lie below $^1D_1$ in view of their small separation.

Results of Calculations

Planar Methylenecyclopropene (1). FORS MC-SCF total energies and excitation energies for the various electronic states of **1** are given in Table I. With the exception of the $^1B_2$ and $^3A_1$ states, the order of these is unambiguously established.

Non-CI SCF calculations were performed only for the ground state of **1**, with a resultant total SCF energy of −153.55205 hartrees and a Koopmans' theorem first ionization potential of 8.1 eV. The calculated SCF dipole moment is 1.98 D, in good agreement with previously reported ab initio SCF values of 2.08[10a] and 2.25 D.[10d] The corresponding MNDO value was 1.21 D.

Gross Mulliken populations and dipole moments for each of the FORS MC-SCF planar states are given in Table II. Assuming an average carbon population of ca. 6.2 electrons, it is clear that appreciable polarization exists for both ground and excited states.

Inclusion of $\pi \rightarrow \pi^*$ excitations in MC-SCF calculation reduces the predicted dipole moment by ca. 33% to 1.33 D. No experimental value for this dipole moment is yet available for com-

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Table III. Energies of Electronic States of Twisted Methylenecyclopropene

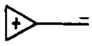
state	dominant config	no. of config[a]	FORS MC-SCF energy	SCF[b] energy	CI energy[b,c]	
					$^1D_1$ orbitals	$^1D_2$ orbitals
$^3A_2$ ($^3D_1$)	... $(2b_1)^2(3b_1)^1(4b_2)^1$	4	−153.49013 (−0.06)	−153.46075 (0.06)	−153.49010 (−0.05)	−153.45335 (0.29)
$^1A_2$ ($^1D_1$)	... $(2b_1)^2(3b_1)^1(4b_2)^1$	4	−153.48810 (0.0)	−153.45870 (0.0)	−153.48810 (0.0)	−153.45151 (0.34)
$^3B_1$ ($^3D_2$)	... $(2b_1)^1(1a_2)^1(4b_2)^1$	5	−153.46849 (0.53)	−153.43360 (0.68)	−153.43483 (1.45)	−153.46770 (−0.10)
1^1A_1 ($^1Z_1$)	... $(2b_1)^2(4b_2)^2$	8	−153.46656 (0.59)	−153.44084 (0.49)	−153.37761 (3.01)	−153.35976 (2.84)
$^1B_1$ ($^1D_2$)	... $(2b_1)^2(1a_2)^1(4b_2)^1$	4	−153.46414 (0.65)	−153.42980 (0.79)	−153.42992 (1.58)	−153.46414 (0.0)
2^1A_1 ($^1Z_2$)	... $(2b_1)^2(3b_1)^2$	8			−153.20936 (7.58)	−153.13516 (8.95)

[a] The number of configurations used in the FORS MC-SCF or CI calculations. [b] Total energies in hartrees and, in parentheses, relative energies in eV. [c] CI results are based on orbitals MC-SCF optimized for the $^1D_1$ or $^1D_2$ state, as indicated.

Table IV. Charge Distribution in Twisted Methylenecyclopropene[a]

state	dipole moment[b]	Mulliken populations[c]				
		C_1	C_2	C_3, C_4	H_5, H_6	H_7, H_8
$^3A_2$ ($^3D_1$)	0.65	6.40	6.05	6.18	0.82	0.77
	(0.67)	(6.41)	(6.04)	(6.18)	(0.82)	(0.77)
$^1A_2$ ($^1D_1$)	0.67	6.41	6.04	6.18	0.82	0.77
$^3B_1$ ($^3D_2$)	−0.96	6.45	6.00	6.23	0.78	0.76
	(−0.87)	(6.41)	(5.85)	(6.29)	(0.81)	(0.77)
1^1A_1 ($^1Z_1$)	5.34	6.84	5.76	6.15	0.81	0.74
	(8.29)	(7.36)	(5.36)	(6.06)	(0.80)	(0.77)
$^1B_1$ ($^1D_2$)	−0.94	6.46	5.99	6.24	0.78	0.76
	(−0.87)	6.41)	(5.85)	(6.29)	(0.81)	(0.77)
2^1A_1 ($^1Z_2$)						
	(−5.83)	(5.45)	(6.90)	(6.21)	(0.84)	(0.77)

[a] For each state, the first entry is the MC-SCF result optimized for that state, and the second entry, where given, is a CI result based upon orbitals optimized for the lowest singlet $^1A_2$ state.

[b] In Debye, positive sign implies . [c] The numbering scheme for atoms is shown in Figure 2.

parison; however, our calculated value should be fairly accurate, depending to a large measure on the reliability of our chosen geometry. Although reduced from previous estimates, this still is an appreciable moment for a hydrocarbon. Interestingly, the lowest B_2 singlet and triplet excited states display opposite polarity to that of the ground state, due to promotion of an electron into the $1a_2$ orbital, entirely localized on the three-membered ring.

Interestingly, the $^3A_1$ and 2^1A_1 states, although formally derived from the same configuration, show widely disparate charge distributions and a 4.5 eV separation. The triplet is a valence state whereas the $3b_1$ HOMO of the singlet displays a tendency toward spatial diffuseness. Our basis set does not contain Rydberg functions; presumably their inclusion would allow the 2^1A_1 state to acquire more Rydberg character, thus decreasing its energy and dipole moment.

90° Twisted Methylenecyclopropene (2). FORS MC-SCF total energies and excitation energies for **2** are given in the first column of energies in Table III. Interestingly, the first five states of this twisted species are calculated to lie in a 0.7 eV range, as compared to the ca. 9 eV range in the planar case. Corresponding singlet and triplet states of **2** are closely paired, as the orthogonality of singly occupied orbitals causes the exchange integral responsible for the singlet–triplet splitting to be quite small.

Our calculations establish $^1D_1$ as the lowest singlet state of twisted methylenecyclopropene at the geometry calculated. Vertically above this lie a strongly polarized excited singlet ($^1Z_1$) at 0.59 eV and, only marginally higher, a second diradical ($^1D_2$) at 0.65 eV. Significantly higher (>7 eV) is a second zwitterionic state ($^1Z_2$) of opposite polarity to the first. We have not performed MC–SCF optimization for $^1Z_2$ due to its high energy; however, CI results for this state, using $^1D_1$ orbitals, are listed in Tables III and IV.

Table IV lists Mulliken populations and dipole moments for low-lying electronic states of **2**. The singlet and triplet diradical states have dipole moments moderately reduced from the planar ground state, while polarization of the two zwitterionic states ($^1Z_1$ and $^1Z_2$) is quite pronounced. The large predicted dipole moment for $^1Z_1$, 5.34 D, is due to transfer of ca. 0.4 electron to the methylene carbon (C_1), over and above the ca. 0.2 electron transferred in $^1D_1$. This produces a formal charge of −0.84 on the methylene carbon, with a resultant large dipole. Thus, for the twisted species **2**, electronic excitation strongly enhances polarization, rather than leading to the reversal noted above for **1**. In simple valence-bond terms, the various states of **2** are best represented as below.

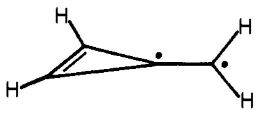
Resonance stabilization of the cyclopropenyl cation might be expected to cause the resultant three-ring charge deficiency in $^1Z_1$ to be delocalized throughout the ring. In actual fact, ca. 75% (0.3 electron) of the transferred charge is contributed by the quaternary carbon (C_2), with minimal contribution (0.05 electron each) from the other ring carbons. We conclude from this that minimization of charge separation is a more effective means of zwitterion stabilization than charge delocalization. This same phenomenon has been noted in several other related cases[7a,b] and presumably is quite general.

For $^1Z_2$, our CI calculations, using $^1D_1$ orbitals, are less reliable, but should nonetheless provide a qualitative picture of its charge

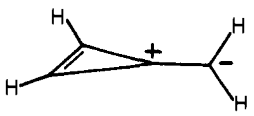
Table V. Detailed Population Analysis of the $^1Z_1$ Twisted State[a]

		C_1	C_2	C_3, C_4	H_1, H_2	H_3, H_4
σ population		5.22	5.23	5.24	0.81	0.73
		(5.47)	(4.96)	(5.21)	(0.79)	(0.77)
π population		1.62	0.53	0.91	0.00	0.01
		(1.89)	(0.40)	(0.85)	(0.01)	(0.00)
total population		6.84	5.76	6.15	0.81	0.74
		(7.36)	(5.36)	(6.06)	(0.80)	(0.77)
population gain following MC-SCF optimization	σ:	−0.25	0.27	0.03	0.02	−0.04
	π:	−0.27	0.13	0.06	−0.01	0.01
	total:	−0.52	0.40	0.09	0.01	−0.03

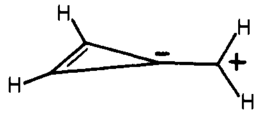
[a] Mulliken populations for the MC-SCF and CI ($^1D_1$ orbitals) wave functions. CI results are in parentheses.



$^1D_1$, $^3D_1$, $^1D_2$, $^3D_2$



$^1Z_1$



$^1Z_2$

distribution. Here, the methylene carbon loses ca. 0.9 electron from its population of 6.4 in $^1D_1$, with a corresponding gain of 0.9 electron at the quaternary carbon, again relative to $^1D_1$. As we show below, a major error in the use of limited CI rather than MC–SCF functions is an overestimate of charge transfer. Nevertheless, even with optimization, this state still would have a large negative dipole moment. Because of minimization of charge separation and the antiaromaticity of the cyclopropenyl anion, the transferred charge is almost entirely localized on C_2.

Rotational Barrier in Methylenecyclopropene. Our calculations afford three distinct estimates of the exocyclic π-bond rotational barrier in methylenecyclopropene: MNDO, 31.7 kcal/mol; SCF, 57.3; FORS MC–SCF, 72.4. SCF estimates of bond energies are unreliable and our MC–SCF value clearly is much too high. The greater percentage of π correlation energy recovered by four out-of-plane π orbitals in **1**, as opposed to three out-of-plane and one in-plane orbitals in **2**, and the neglect of left–right correlation in the exocyclic C–C σ bond, this being greater for the longer bond of **2**, contribute to a FORS MC–SCF overestimation of the rotational barrier. In addition, these are not MC–SCF optimized geometries and we suspect that such optimization would lower the energy of twisted **2** more than planar **1**. The MNDO calculation, with its extensive semiempirical parameterization, probably affords the best estimate of this rotational barrier, although no experimental support exists for this assumption. In view of their abovementioned probable computational error, it is surprising that our 31.7 kcal/mol value is so close to the 30.6 figure reported by Dewar and Kohn.[11]

Despite this misalignment of relative energy scales which leads to an apparent overestimate of the rotational barrier, our FORS MC–SCF procedure should provide reliable values for excitation energies. For illustrative purposes, we combine the MNDO rotational barrier with MC–SCF excitation energies, arriving at the schematic state correlation diagram shown in Figure 3.

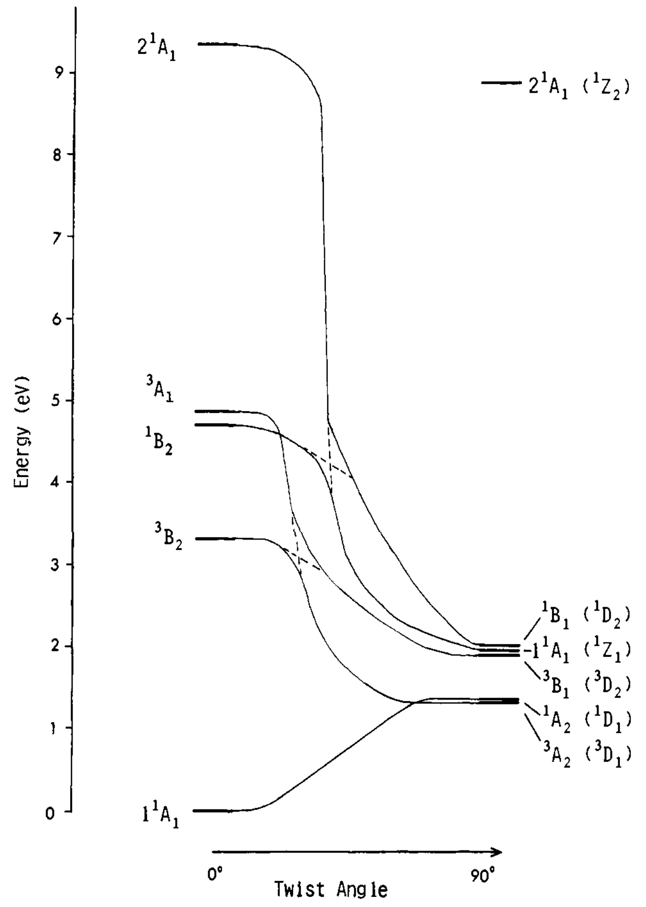


Figure 3. Schematic state correlation diagram for exocyclic π bond twisting in methylenecyclopropene.

Comparison of Calculational Methods. In this section, we analyze the ability of different types of calculation to predict the properties of planar and, more critically, 90° twisted alkene excited states. To this end, three types of calculation were performed: (a) fully optimized MC–SCF calculation for individual states, results of which were described above; (b) limited CI calculation, using orbitals optimized for a single state; and (c) SCF calculation (no CI included).

For planar methylenecyclopropene, CI results, using ground state orbitals, are summarized in Tables I and II. CI excitation energies clearly are overestimates; however, state ordering and charge distributions generally agree quite well with MC–SCF results. The only significant variation between the two lies in ordering of the $^1B_2$ and $^3A_1$ states. Overall, limited CI calculations yield a qualitatively correct picture of the planar molecule's excited states.

Dramatically different results obtain for twisted configuration **2**. In this case, we have performed CI calculations based on both sets of diradical orbitals, with resultant energies given in Table III. The two state orderings from these calculations are in poor agreement with each other and with results of independent MC–SCF optimizations. Quite strikingly, use of $^1D_2$ orbitals even fails to predict $^1D_1$ as the ground state. A more serious failing in the context of "suddenly polarized" excited states is the prediction using either set of orbitals that $^1Z_1$, the lowest zwitterionic state, is 2.5–3 eV above $^1D_1$; separate MC–SCF optimization shows $^1Z_1$ to be nearly degenerate with $^1D_2$ at ca. 0.6 eV.

This CI calculation overestimate of $^1Z_1$ excitation energy relative to MC–SCF optimization clearly is due to misrepresentation of charge distribution and exaggeration of charge separation across the twisted bond. This is supported by comparison of Mulliken populations for the two types of calculation, summarized in Table IV. Compared to the ground ($^1D_1$) state, the CI wave function transfers 0.95 electron to the methylene carbon, while the more correct MC–SCF wave function shows the actual shift to be only 0.43 electron. In addition the CI wave function for $^1Z_1$ shows greater delocalization of positive charge with 0.68 electron being donated by the quaternary carbon (C_2) and 0.12 electron each by the other ring carbons (C_3, C_4). By comparison, the MC–SCF charge shifts for $^1Z_1$ is 0.38 electron from C_2 and 0.03 electron each from C_3 and C_4.

This exaggeration by the CI wave function of charge separation about the twisted bond, and failure to localize this charge near the twisted bond, has the obvious consequence of dramatically raising the energy of the zwitterionic state, as well as inflating its calculated dipole moment. Recent literature suggests this to be quite general,[7a,b] hence the enormous dipole moments calculated in some cases[5d,e] by using 3 × 3 CI methods are probably gross overestimates.

The redistribution of charge in $^1Z_1$ accomplished by MC–SCF optimization merits further consideration. As noted above, proper MC–SCF calculation reduces this by 55% (0.95 to 0.43 electron) relative to the CI result with $^1D_1$ orbitals. Detailed analysis of this reduction is shown in Table V, where total atomic populations are divided into contributions from σ and π orbitals. In contrast to results of Malrieu,[7b] the 0.52-electron reduction in methylene carbon population is not due solely to σ-electron reorganization. Rather, the reduction in charge shift is divided evenly between σ and π orbitals.

It is clear that most of the inaccuracy of the limited CI representation of $^1Z_1$ is due to use of unoptimized orbitals. To examine the importance of this problem, and since each of the five lowest states of **2** is represented by a single dominant SCF configuration, we have also performed non-CI SCF calculations on each state, with the results given in Table III. Not surprisingly, these calculations predict essentially the same state ordering as the fully optimized MC-SCF treatment and all five states lie in a narrow range of 0.85 eV. Thus separate SCF calculations provide a reasonably good description of both diradical and zwitterionic states, their only failing being neglect of π-electron correlation in the cyclopropenyl ring. It is not feasible to include this correlation by following the SCF calculation on each state with the small CI calculations used here, as the SCF calculations on the zwitterionic or diradical states optimize only two or three, respectively, of the orbitals required for the four-orbital full-CI calculations used here.

Conclusions

Our calculations on 90° twisted methylenecyclopropene, just as those of Salem,[4,5c–e] Bonacic-Koutecky,[5f,7e,f] Schaefer,[7d] Malrieu,[7a–c] and others on related hydrocarbons, clearly reveal this short-lived species to have significantly polarized singlet excited states. We see no reason to doubt the existence of such states, although it is in general difficult to unambiguously prove their involvement in organic photoreactions. In the present case, very little methylenecyclopropene photochemistry has been reported,[18] thus there presently exists no correlation of our results with experiment. We believe it of general significance, however, that the degree of polarization is significantly less than a fully developed zwitterion and these states are better regarded as strongly polarized rather than truly zwitterionic.

For twisted methylenecyclopropene, it is straightforward to understand the preferred direction of polarization; this simply derives from the wide disparity in energies of the two molecular fragments, with preferred $^1Z_1$ double occupancy of the lower energy fragment. In this case, the $^1Z_1$–$^1Z_2$ spacing (>5 eV) is significantly larger than the values (<0.7 eV) typically predicted for linear polyenes.[4,5,7] A priori prediction of the lower energy zwitterion is of obvious chemical importance.

Our research provides clear illustration of the necessity of separate orbital optimization for each state of twisted alkene, either at the SCF level or, preferably, via MC-SCF calculation whenever the twisted states are not properly described within the Hartree-Fock formalism. Limited CI calculations with all states sharing a common set of orbitals overestimate the excitation energy to zwitterionic states, exaggerate charge separation across the twisted bond, and fail to concentrate charge on the two atoms comprising this bond. Similar conclusions have been reached independently by other research groups through calculations on linear polyenes.[7a,b]

An obvious alternative to our FORS MC-SCF procedure is large scale configuration interaction. Several such studies of pyramidalized ethylene recently have been reported. Brooks and Schaefer[7d] based their CI study on orbitals from a two-configuration MC-SCF calculation. They found it necessary to place a constraint on the coefficients of these two configurations in order to obtain orbitals which gave physically reasonable dipole moments for their CI wave function. Bonacic-Koutecky and co-workers performed very large CI calculations,[7e,f] using either SCF orbitals from the triplet diradical state or natural orbitals from preliminary CI calculations on the two zwitterionic states. Not surprisingly, they find calculated dipole moments to be quite sensitive to this orbital choice.

In summary, the quantitative treatment of twisted alkene excited states obviously is an intricate problem, with results highly dependent on the orbital basis chosen. This research and the results of others demonstrate that when only a few configurations are used to represent each state, orbital optimization is strictly necessary to obtain reasonable values for dipole moments and excitation energies. The few extensive CI studies reported indicate that preliminary MC-SCF optimization of valence shell orbitals is likely to be highly effective in reducing both the number of and degree of excitation of configurations required to obtain accurate results. Whatever theoretical approach is taken in the treatment of these highly polarizable twisted alkene states should include careful consideration of the sensitivity of calculated properties to the orbital basis chosen.

We are continuing to pursue both theoretical and experimental aspects of the sudden polarization phenomenon.[19]

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(18) Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1979**, *57*, 1–109.

(19) Preliminary calculations on 90° twisted fulvene show this to be another case in which two low-lying excited states exist, one zwitterionic with the negative polarity in the five-membered ring ($^1Z_1$) and the second diradical ($^1D_2$). In this case it appears that $^1D_2$ may be of lower energy than $^1Z_1$.