Polarized Nonvertical Excited States: FORS MCSCF and CI Study of Torsion and Bending in Allene

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Abstract: Ab initio FORS (Full Optimized Reaction Space) MCSCF and CI calculations have been performed for low-lying electronic states of allene at planar geometries, and CI calculations have been performed along torsional and bending coordinates $(D_{2d} \rightarrow D_2 \rightarrow D_{2h} \rightarrow C_{2v} \rightarrow C_2 \rightarrow D_{2d})$. Excited-state minima which correlate with the 1^1B_1 state of allene are located at D_{2h} and C_{2v} geometries. These two nearly isoenergetic minima are strongly polarized, but in opposite directions. Polarization is not "sudden" along the C_2 coordinate, but develops gradually through bending and twisting motions. Potential involvement of these polarized states in allene photoreactions is discussed.

Introduction

The location and characteristics of minima on excited-state potential energy surfaces often are controlling features in photochemical reactions.[2] It is essential for photochemists to have a detailed understanding of the electronic nature and dynamics of molecules at these minima if mechanisms and reactivity are to be understood. For many organic molecules containing π bonds, the location of minima has long been accepted to occur at 90° twisting; however, it was only recently recognized that strong excited-state polarization, approaching zwitterionic character, will exist at this nonvertical geometry.[3] Salem termed this unusual phenomenon "sudden polarization"; however, it now seems, at least for ethylene, that the degree of suddenness depends critically on the reaction path.[3b] This polarization has been the subject of numerous theoretical studies[3-5] and its existence seems no longer controversial. Polarized nonvertical excited states have been suggested as intermediates in a variety of organic photoreactions,[3a,6] which include isomerizations, and addition of protic

solvents to π bonds, although definitive experimental evidence is difficult to obtain and interpret.

In the present work, undertaken as the beginning of a theoretical framework for the interpretation of allene photoreactions, we show that the polarization phenomenon extends to allenes, through investigation of twisted π bond minima[2c] on allene excited-state surfaces.[1c] Although their synthesis and ground-state chemistry have been well studied, surprisingly little is known about photoreactions of allene and higher cumulenes.[7,8] We believe the diversity of cumulene photochemistry will rival that of simple alkenes, and we are currently engaged in a detailed experimental study of cumulene photoreactions.[8] Simple π bond rotation in substituted allenes interconverts enantiomers, a process analogous to cis–trans isomerization in ethylene derivatives.

Allenes, like most alkenes, have long been believed to twist to planar geometries in their lowest singlet and triplet excited states.[9]

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Scheme I
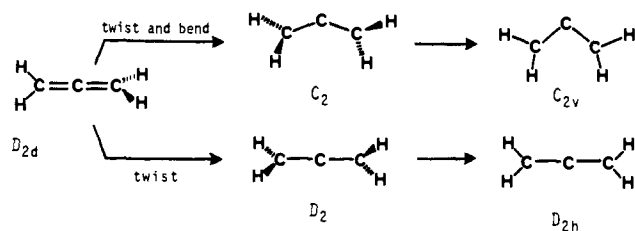
Obvious photochemical manifestations of this are the facile photoracemization and photoresolution of chiral allenes.[7b,c] As one example, we have observed that optically active 1,2-cyclo-nonadiene undergoes rapid racemization on direct irradiation, in addition to isomerization to a cyclopropene.[8a]
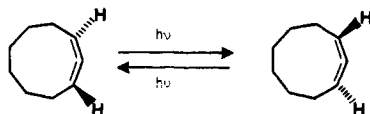
The first theoretical study in which the involvement of planar excited states in allene photochemistry was explicitly considered was an often overlooked but insightful paper by Borden.[9] Based on Pariser-Parr-Pople calculations, Borden concluded that excited-state twisting in both S_1 and T_1 should be facile and that the lowest singlet D_{2h} state is open shell (A_u), with two low-lying closed-shell excited states. This is precisely the situation required for "sudden polarization".[3]

For thermal isomerizations, the intermediacy of planar geometries has been the subject of a number of ab initio[10,11a-h] and semiempirical[11i] theoretical studies, which have led to a wide range (48-82 kcal/mol) of predicted values for the barrier of rotation in allene. In many of these studies, energies of the lowest lying D_{2h} states, ^1A_u, ^3A_u, $1\,^1A_g$, and $2\,^1A_g$, were calculated; however, the major point of interest was the ground-state rotational barrier. In the most definitive study, Pople et al. have shown that this ground-state barrier should occur at a bent (C_{2v}) geometry,[11g] and an open-shell ^1A_u state. More recently, Krogh-Jespersen has recalculated this barrier using split valence basis set geometry optimization and with inclusion of correlation energy.[11h] A value of ca. 50 kcal/mol is predicted in both studies, which is in good agreement with estimates from experimental work of Roth and co-workers.[12]

Electronic Structure of D_{2d}, D_{2h}, and C_{2v} Allene

The two most symmetrical pathways (Scheme I) toward planarity in allene are a simple torsion about the C-C-C axis (D_2 symmetry maintained) and a combination of conrotatory twisting and C-C-C bending (C_2 maintained). Subsequent in-plane bending interconverts D_{2h} and C_{2v} structures. Lower symmetry paths toward planarity are possible, as are other distinctly different reaction coordinates leading to allene photoproducts; these will not be explicitly considered here.

Figure 1 shows the correlation of allene π molecular orbitals along these D_2 and C_2 twisting and bending coordinates. Orbital energies are from RHF calculations on the lowest closed-shell state. The 2e and 3e orthogonal π MO's of allene are split in D_2 and C_2, such that the highest occupied and lowest vacant orbitals remain of like symmetry (b_2 or a). This ensures a totally symmetric lowest excited state along most of the D_2 or C_2 coordinates.

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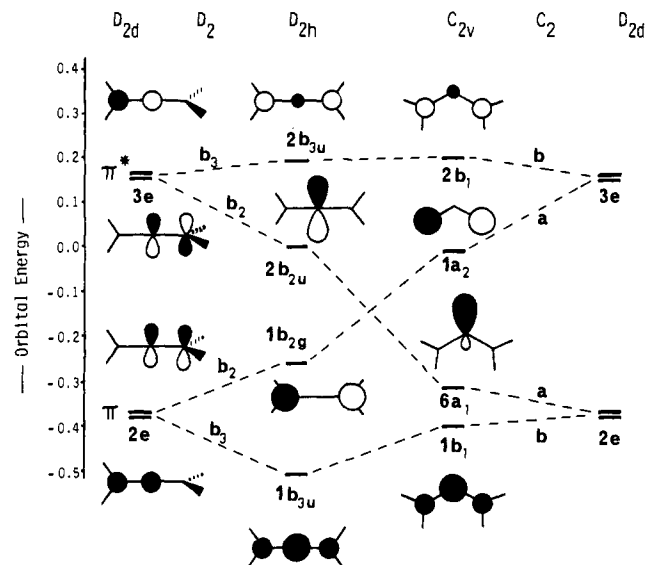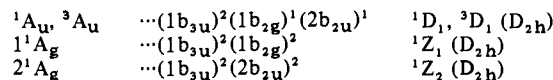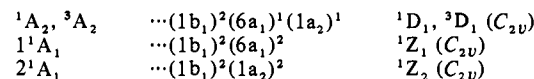

Figure 1. Orbital correlation for twisting and bending in allene.

Population of orbitals at planar geometries gives rise to low-lying states which have either pronounced diradical (D) or zwitterionic (Z) character. For D_{2h} these are:

$$^1A_u, \,^3A_u \quad \cdots(1b_{3u})^2(1b_{2g})^1(2b_{2u})^1 \quad ^1D_1, \,^3D_1 \,(D_{2h})$$
$$1\,^1A_g \quad \cdots(1b_{3u})^2(1b_{2g})^2 \quad ^1Z_1 \,(D_{2h})$$
$$2\,^1A_g \quad \cdots(1b_{3u})^2(2b_{2u})^2 \quad ^1Z_2 \,(D_{2h})$$

Here, . . . represents the four a_g, one b_{3g}, one b_{2u}, and three b_{1u} closed shells comprising the σ molecular framework. For C_{2v}:

$$^1A_2, \,^3A_2 \quad \cdots(1b_1)^2(6a_1)^1(1a_2)^1 \quad ^1D_1, \,^3D_1 \,(C_{2v})$$
$$1\,^1A_1 \quad \cdots(1b_1)^2(6a_1)^2 \quad ^1Z_1 \,(C_{2v})$$
$$2\,^1A_1 \quad \cdots(1b_1)^2(1a_2)^2 \quad ^1Z_2 \,(C_{2v})$$

In this case, . . . represents five a_1 and four b_2 closed shells of the σ skeleton.

It is readily predicted that the open-shell states (A_u or A_2 symmetry) will be nonpolar, while the four closed-shell states (A_g or A_1 symmetry) will be strongly polarized in specific planes, as represented by structures 1-4 (in-plane orbital occupation shown).
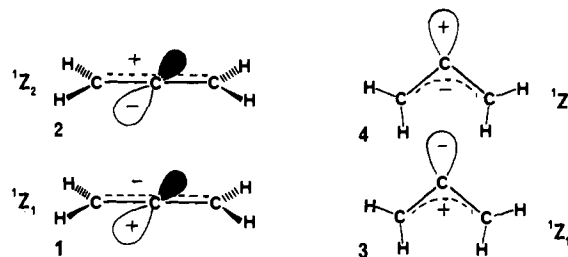
The central portion of Figure 1 corresponds to in-plane bending ($D_{2h} - C_{2v}$). This results in an orbital crossing, which, as we show below, defines an avoided state crossing and the existence of two excited-state minima of distinctly different character (i.e., 1 and 3). This double minimum is one of the central and most interesting features of allene excited-state potential surfaces.

Theoretical Methods

Two complementary approaches to excited-state calculations were used in this study: MCSCF calculation at D_{2h} and C_{2v} geometries, and limited CI calculations for a much larger number of points along twisting and bending potential surfaces. The MCSCF calculations rigorously establish the order and character of valence states, while the CI calculations are more expeditious for examining a large number of geometries and states. In general, MCSCF and CI results agree well.

As in our previous study on sudden polarization in twisted methylenecyclopropene,[4] we have employed the FORS MCSCF

Table I. Energies of Allene Electronic States

geometry	state	FORS MCSCF energy (hartrees)	CI energy	CI rel energy (eV)[b]
D_{2d}	1^1A_1		-115.869 65	0.0
	1^1A_2		-115.615 28	6.92 (6.49)[a]
	1^1B_1		-115.595 99	7.45 (6.84)[a]
	1^1E		-115.591 68	7.56 (7.21)[a]
D_{2h}	1^1A_u ($^1D_1$)	-115.797 28	-115.776 43	2.54
(geometry I)	1^1A_g ($^1Z_1$)	-115.747 19	-115.717 30	4.16
	2^1A_g ($^1Z_2$)	-115.656 77	-115.635 28	6.38
	1^1B_{1g}		-115.598 15	7.39
	1^1B_{2g}		-115.569 89	8.16
	1^1B_{2u}		-115.562 07	8.37
C_{2v}	1^1A_2 ($^1D_1$)	-115.774 13	-115.748 44	3.30
(102.8°)	1^1A_1 ($^1Z_1$)	-115.740 50	-115.720 48	4.06
(geometry II)	1^1B_1		-115.561 52	8.38
	2^1A_1 ($^1Z_2$)	-115.539 61	-115.543 03	8.89
	1^1B_2		-115.523 12	9.43
	2^1B_1		-115.517 70	9.58
C_{2v}	1^1A_2 ($^1D_1$)	-115.821 43		
(135.4°)	1^1A_1 ($^1Z_1$)	-115.716 64		
(geometry III)	2^1A_1 ($^1Z_2$)	-115.678 53		

[a] Excitation energies from ref 21. [b] All relative to the allene ground state with comparable basis and CI.

(full optimized reaction space multiconfiguration self-consistent field) method of Ruedenberg.[13] This beautifully simple ab initio method allows for recovery of a significant fraction of the correlation energy since the dominant correlating orbitals and configurations are included.

The atomic basis used in MCSCF calculations consisted of a (10s/5p) basis of even-tempered Gaussian primitives Raffenetti contracted to a (3s/2p) basis on carbon, and a (4s) basis of Gaussian primitives scaled by 1.2 and Raffenetti contracted to a (2s) basis on hydrogen.[14] MCSCF computations were performed using the ALIS system for quantum chemical calculations.[15]

In the FORS wave function for each planar allene state, inner shell and σ framework orbitals are held to double occupancy, while the remaining four electrons are distributed in all possible ways among the four π-type orbitals shown in Figure 1. This leads to eight space-spin configurations for the zwitterionic states, and four configurations of like symmetry for the diradical at each geometry. The small number of configurations permits optimization for each state separately in an MCSCF calculation. The σ skeleton can then readjust to the varying π-electron distributions; thus, the FORS MCSCF calculations may be expected to yield reliable estimates for electronic distributions and excitation energies of valence states.

CI calculations were performed using a modified version of GAMESS,[16] which utilizes the graphical unitary group approach of Brooks and Schaefer.[17] For carbon, the Dunning–Hay contraction (3s, 2p)[18] of Huzinaga's (9s, 5p) basis[19] was augmented with a single Rydberg 3s function ($\alpha = 0.023$),[18] while for hydrogen, a comparable (4s/2s) basis was employed.[18] The RHF energy of allene with this basis at its experimental geometry[20] is -115.829 59 hartrees. Because of the manner in which integrals are calculated, it is not feasible to use a comparable even-tempered basis[14] with GAMESS.

At all geometries, the singlet CI space included single and double excitations from the six highest occupied MO's to the lowest eight virtuals; this yields a total of 1225 configurations of all symmetries. Care was taken that the virtuals included important π^* correlating orbitals. At all points except allene, the triplet ROHF MO's were used as a basis for CI. As has been shown previously, these should not introduce an unbalanced description of close-lying states.[5h] For allene, RHF orbitals were used because of the biconfigurational nature of the lowest D_{2d} triplet states.

This double-ζ (DZ) + Rydberg basis and relatively small CI should yield the correct order and correlation of low-lying states, although absolute excitation energies will be too high. It seems unlikely to us that extensive geometry optimization or use of a higher quality basis and larger CI would substantively change the correlations and conclusions described below.

Results of Calculations: Effects of Torsion and Bending on Allene Excited States

Energies and excitation energies calculated for allene low-lying states at its experimental geometry,[20] using the basis and CI space described above, are given in Table I. The excited-state ordering ($^1A_2 < {}^1B_1 < 1^1E$) for D_{2d} symmetry agrees with the results of previous calculations,[21] although excitation energies are higher owing to the smaller CI. The two lowest excited states are predicted to be valence ($\pi \rightarrow \pi^*$) but both correspond to optically forbidden transitions in D_{2d}. These result from in-phase and out-of-phase combinations of the $2e_x \rightarrow 3e_y$ and $2e_y \rightarrow 3e_x$ excitations. Slightly higher in energy are the degenerate 1^1E states, which are predominantly Rydberg ($\pi \rightarrow$ 3s). Extensive CI calculations with a large basis set might change the valence-Rydberg state ordering, but this would not affect the correlations shown below.

There are two previous ab initio studies of allene excited states,[1b,21] in addition to a number of semiempirical calculations.[22] Schaad, Burnelle, and Dressler[1b] drew correlations between D_{2d} and D_{2h} singlet and triplet states, based on CI calculations with a small valence basis, but predicted that 1^1A_u (D_{2h}) and 1^1A_g would be nearly isoenergetic. In a study of allene optical activity, Rauk, Drake, and Mason used a DZ + d + Rydberg basis and large CI for limited (10°) bending and twisting in allene excited states.[21] Twisting by 10° splits the degeneracy of the Jahn–Teller unstable 1^1E states ($\pi \rightarrow$ 3s) and was predicted to stabilize both $^1A_2$ and $^1B_1$.

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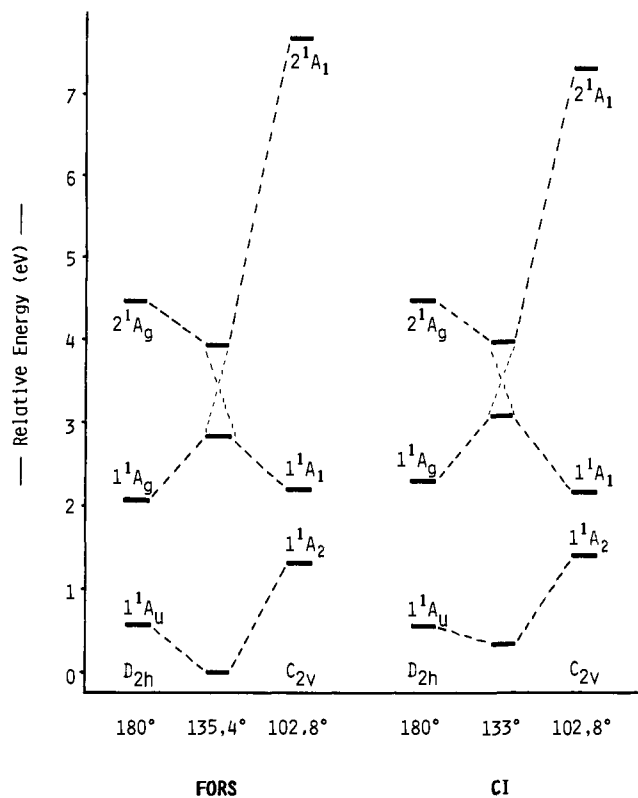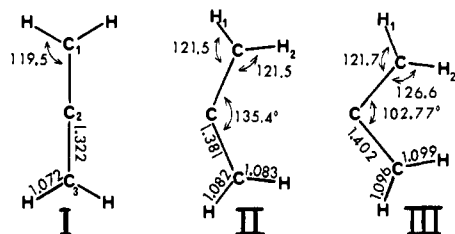
Figure 2. Comparison of MCSCF and CI results (1^1A_u energy used for alignment).

Figure 3. Potential surfaces for twisting and bending in allene.

Table II. Charge Distribution in Planar Allene States[a]

			Mulliken populations (MC-SCF)			
	state		C_1	C_2	H_1	H_2
D_{2h}	^1A_u ($^1D_1$)	σ	5.390	4.880	0.84	
		π	1.010	0.980		
	1^1A_g ($^1Z_1$)	σ	5.285	4.336	0.77	
		π	1.405	1.184		
	2^1A_g ($^1Z_2$)	σ	5.511	5.464	0.87	
		π	0.689	0.666		
C_{2v}	1^1A_2 ($^1D_1$)	σ	5.370	4.889	0.85	0.83
		π	1.020	0.961		
	1^1A_1 ($^1Z_1$)	σ	5.549	5.451	0.83	0.88
		π	0.761	0.499		
	2^1A_1 ($^1Z_2$)	σ	5.183	4.449	0.83	0.78
		π	1.337	1.291		

[a] At geometries I and III shown in the text.

Points on the allene $D_{2h} \rightarrow C_{2v}$ potential surface have previously been calculated by Pople et al. in a study of allene thermal isomerization.[11g] The rotational barrier corresponds to the C_{2v} open-shell state ($^1A_2$); however, to verify that these were of higher energy, calculations were performed for D_{2h} and C_{2v} closed-shell states, and minima at C_1–C_2–C_3 internal angles of 180 and 102.8° were observed.[11g] To establish that these are true minima, we performed gradient SCF optimizations (STO-3G basis) with no restriction on symmetry or planarity; the resultant geometries (I and III shown below) are planar and virtually unchanged from those reported by Pople.[11g]

Next, FORS MCSCF calculations[13] were performed for the lowest singlet open-shell (^1A_u or $^1A_2$) and lowest closed-shell (^1A_g or $^1A_1$) states at the two minima (180 and 102.8° bending) and an intermediate point (135.4° bending; geometry II), which corresponds to the predicted $^1A_2$ barrier.[11g] State energies are listed in Table I. Each energy is the result of individual FORS optimization for that particular state. The order and nature of the states are in excellent agreement with qualitative predictions and the results of previous calculations. Relative state energies for geometries I–III are shown on the left side of Figure 2.

To establish the correlation of states, CI calculations were then performed at a total of 15 regularly spaced points along reaction coordinates shown in Scheme I. Results are summarized in Figure 3 and energies at SCF minima are given in Table I. Geometries were either SCF optimized for the lowest closed-shell state ($D_{2h} \rightarrow C_{2v}$ portion) or extrapolated from D_{2d} to the minimum. The calculations show only a small portion of the multidimensional surfaces; nevertheless, the straightforward twisting and bending
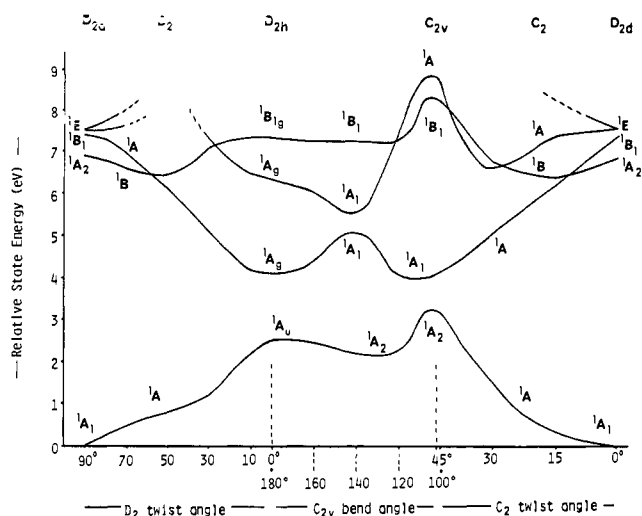
reaction pathways shown seem intuitively reasonable. CI calculations support the contention that geometries I and III are true excited-state minima. In-plane bending or symmetrical (D_2 or C_2) twisting motions raise the energy of S_1 ($^1Z_1$) relative to either planar minimum.

As a comparison of FORS MCSCF and CI techniques, results for comparable geometries and states in D_{2h} and C_{2v} are contrasted in Figure 2. Although absolute energies will differ because of the slight difference in basis sets, relative ordering and energies do provide for direct comparison. Natural orbital occupational numbers for two methods were quite similar, with the greatest difference observed for 2^1A_1 (102.8°); this has significant Rydberg character and is lowered by the addition of diffuse orbitals to the CI basis set. The overall good agreement provides confidence in the adequacy of our small CI.

As previously noted by Rauk and co-workers, both the $^1A_2$ and $^1B_1$ valence excited states of allene are lowered by twisting and bending.[21] We observe that the $^1B_1$ state becomes ^1A, is continuously stabilized, and correlates with the ^1A_g (D_{2h}) or $^1A_1$ (C_{2v}) minima. This can be understood from the orbital correlation diagram shown in Figure 1. The degenerate 2e and 3e orbitals of allene split in D_2 or C_2 such that the highest occupied and lowest unoccupied MO's are of like symmetry. This results in states corresponding to ground, single, or double excitation being of like symmetry (^1A). The orbital crossing at the center of Figure 1 clearly is the origin of the avoided state crossing which occurs at 140° bending, and the existence of separate D_{2h} and C_{2v} minima. Thus, some correlations for low-lying states shown in Figure 3 are interpretable in terms of MO behavior.

The $^1A_2$ state of allene is initially stabilized within the limited deformation examined by Rauk,[21] but ultimately correlates with

Table III. Dipole Moments

		dipole moments (D)		
	state	SCF	MCSCF	CI
C_{2v} (102.8°)	$^1A_2$ ($^1D_1$)	0.75	0.72	
	1^1A_1 ($^1Z_1$)	4.01	3.39	3.78
	2^1A_1 ($^1Z_2$)	−1.11	−0.71	
C_{2v} (133°)	1^1A_1 ($^1Z_1$)			3.086
C_{2v} (142°)	1^1A_1 ($^1Z_1$)			0.322
C_2 (102.8° bend)	1^1A_1 ($^1Z_1$)			3.01^a

^{a} 20° out-of-plane twist for all hydrogens.

an upper excited state of ^1B symmetry. From CI calculations, this state is found to be a complex mixture of Rydberg and valence excitations.

Based on these correlations, singlet photoisomerization of allene should proceed through initial population of the $^1A_2$ valence state, either directly or through internal conversion from upper excited states. Rotation or rotation-bending motions permit crossing to a ^1A state (D_2 or C_2), which correlates with linear or bent planar minima. Nonadiabatic coupling will result in crossing to the allene ground state. Since the minima in S_1 and the closest approach of S_0 and S_1 apparently occur at planar geometries, racemization should be efficient. It is significant that neither our calculations nor those of Rauk[21] predict any barrier to rotation in vertically excited allene.

Ground-state allene π bond rotation should proceed through the $^1A_2$ state at the lowest point between D_{2h} and C_{2v}. Our calculations suggest a saddle point at ca. 130° bending and a barrier of 51.2 kcal/mol, in very good agreement with previous results.[11g,h,12]

Polarization in Planar Allene Excited States

Polarization in S_1 at planar geometries is well described by the simple zwitterionic structures **1** and **3**, since these configurations dominate the CI or MCSCF wave functions (CI coefficients > 0.97). This is reflected in FORS and CI occupation numbers, Mulliken populations (Table II; σ and π components shown), and dipole moments (Table III). Inspection of Table II shows that the $^1D_1$ states have balanced σ and π electron distributions, while the ^1Z states are strongly polarized. The localization of central carbon polarization in orthogonal σ and π molecular orbitals is fundamentally different from a twisted π bond (e.g., ethylene) in which positive or negative character is associated with different carbons. Additionally, this σ/π polarization permits significant minimization of effective charge separation through weightings of the $1b_{3u}$ (D_{2h}) and $1b_1$ (C_{2v}) orbital coefficients, which can partly compensate for central carbon charge deficiency or excess. The 3.39-D MCSCF dipole moment (Table III) calculated for the lowest C_{2v} 1^1A_1 state is quite substantial for a C_3 hydrocarbon. MCSCF dipole moments are probably more accurate than the CI or SCF values, because of the greater optimization of the wave function charge distribution. Because of its substantial Rydberg character, $^1Z_2$ (C_{2v}) is not well represented by the simple valence representation **4**. For other states, the close congruence of MCSCF and CI relative energies and occupation numbers is consistent with their dominant valence nature.

One important conclusion is that polarization in allene due to π bond rotation does *not* appear to occur "suddenly"[3] as the molecule approaches planarity. As one illustration, the 3.78-D CI dipole in $^1Z_1$ at 102.8° bending is diminished only 20% by a 20° C_2 twist of all four hydrogens; thus *orthogonality is not a requisite for polarization*. A novel (but artificial) sudden polarization can be achieved, however, through twisting and bending toward the maximum in the $^1Z_1$ surface at ca. 140° bending.[23] Here, the dipole moment abruptly changes (3.09 to 0.322) owing

(23) We are grateful to a referee for suggesting this possibility.

to the change in configurational character engendered by the orbital crossing. Although this point is accessible from allene vertical excited states, we have no basis to suppose that a significant fraction of molecules will choose this pathway. The minimum in the upper zwitterionic state probably is inaccessible from allene S_1, since this correlates with upper excited states (Figure 3) of D_{2d} allene. It is also conceivable that D_{2h} and C_{2v} interconversion might occur through in-plane vibration, for which the true barrier may be smaller than the >1 eV suggested by our calculations.

Conclusion

Previous theoretical investigations of C_3H_4 potential surfaces have explored the ground-state inversion barrier in allene,[11] thermal and photochemical opening of cyclopropene to a vinyl carbene,[24] and the cyclopropylidene to allene conversion.[25] We have presented here an ab initio study of the location and electronic nature of strongly polarized excited state minima or "funnels" on allene potential surfaces, which can be reached through π bond twisting. For singlet allene, two planar minima exist, and we believe that either should be accessible to allene vertical (D_{2d}) excited states. As in ethylene derivatives, this π bond rotation provides a simple mechanism for interconversion of stereoisomers which, in allene, are enantiomers. Racemization from both singlet and triplet states of allene has been observed experimentally.[7]

Other allene photoreactions may also involve polarized singlet states. We have observed that phenylallenes undergo facile non-acid-catalyzed addition of alcohols, with formation of allylic
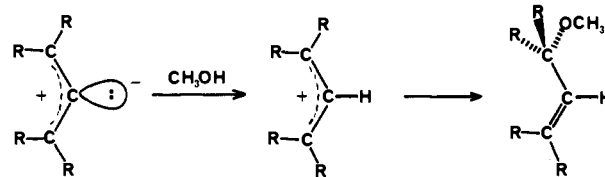
methyl ethers,[8b] and we have suggested a possible mechanism which involves central carbon protonation of a zwitterionic C_{2v} excited state to give an allyl cation. Yates has observed similar reactions in acidic media.[7h] Electronically, this protonation should be an adiabatic process, directly yielding a ground-state allyl cation. Because of the positive charge stabilization afforded by substituents, it may be that the C_{2v} minimum would be favored in highly substituted allenes.

Somewhat paradoxically, zwitterionic planar species have been proposed for the structure of small-ring allenes such as 1,2-cyclohexadiene,[26] in which the allene is constrained to near-planarity. However, as we have shown theoretically,[27] and as supported by experiment,[28] this molecule has a chiral equilibrium structure. The zwitterions are excited states and should not be involved in ground-state reactions.

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