Excited States and Optical Activity of Allenes. Allene, 1,3-Dimethylallene, and 1,2-Cyclononadiene

Arvi Rauk,*[1a] Alex F. Drake,[1b] and Stephen F. Mason[1b]

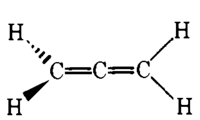
Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T3A 1N6, and the Department of Chemistry, King's College, University of London, London, England WC2R 2LS. *Received October 31, 1978*

Abstract: Ab initio molecular orbital and perturbative configuration interaction calculations are reported for allene (**1**). The vertical electronic transitions are found to be in the order $^1A_1 \rightarrow {}^1A_2$ $(\pi \rightarrow \pi^*)$ $<$ $^1A_1 \rightarrow {}^1B_2$ $(\pi \rightarrow \pi^*)$ $<$ $^1A_1 \rightarrow E$ $(\pi \rightarrow 3s)$ $<$ $^1A_1 \rightarrow {}^1B_2$ $(\pi \rightarrow \pi^*)$ $<$ $^1A_1 \rightarrow 2^1E, 2^1A_1, 2^1B_1, 2^1A_2$ $(\pi \rightarrow 3p)$ $<$ $^1A_1 \rightarrow 3^1A_1$ $(\pi \rightarrow \pi^*)$. The calculated excitation energies agree well with the band positions in the vacuum ultraviolet spectrum. The $^1B_2$ $(\pi \rightarrow \pi^*)$ state is found to have appreciable Rydberg character whereas the other $\pi \rightarrow \pi^*$ states are valence-like. Stereochemical arguments are presented in support of chirally distorted **1** as a model for 1,3-dimethylallene (**2**) and 1,2-cyclononadiene (**3**). In accordance with expectations based on the dynamic coupling theory, the optical activity of **2** is found to arise from asymmetry in the vibrational motion and the signs, temperature dependence, and solvent dependence of the CD spectrum can be rationalized by appropriate time-averaged distortions of the chromophore. In the same manner, the CD spectrum of **3** is explained by static distortions of the chromophore imposed by the constraints of the ring. In the spectrum of both (*R*)-(−)-**2** and (*R*)-(+)-**3**, the first band corresponds to $\pi \rightarrow \pi^*$ ($^1A_1 \rightarrow {}^1A_2$ of **1**) and the positively signed rotational strength arises as a consequence of a bend at the middle carbon of the cumulated π system. The optical activity of the second and third bands is expected to be a consequence of the splitting of the $\pi \rightarrow 3s$ transitions ($^1A_1 \rightarrow E$ of **1**) caused by a twist of one end of the chromophore relative to the other.

I. Introduction

As the parent of many textbook examples of chiral molecules which do not have asymmetric carbon atoms, allene (**1**) has been the subject of many attempts to elucidate its electronic structure. Calculations by semiempirical[2-6] and ab initio[7,8] methods are in agreement only on the order, $A_2 < B_1 < B_2$, for the singlet states which arise from $\pi \rightarrow \pi^*$ excitations. Of these, only the last, $^1B_2$, is accessible from the ground state by an electric dipole allowed transition which lies in the vacuum UV region of the spectrum.[9,10] Numerous transitions to Rydberg states have been identified experimentally[9-11] and analyzed theoretically,[12] but ambiguities in assignments abound.

The origin of the optical activity of allenes has been discussed many times.[6,13-16] Lowe[13] has proposed a sector rule based on Brewster's concept of helical distribution of group polarizabilities,[15,17] to predict the sign of rotation at the D lines of sodium. Lowe's rule correctly correlates the absolute configurations of many chiral allenes, including (*R*)-(−)-1,3-dimethylallene (**2**),[18,19] with their signs of optical rotation at the sodium D lines, but fails in a few cases, most notably in the case of (*R*)-(+)-cyclononadiene (**3**).[20] Crabbé et al.[16] have shown that a sector rule like Lowe's can be derived by a static coupling mechanism. Perturbation of the magnetic dipole allowed $^1A_1 \rightarrow {}^1A_2$ transition by partially screened nuclei of substituents allows admixture of the electric dipole allowed $^1A \rightarrow {}^1B_2$ transition and gives rise to a Cotton effect of the same sign as the rotation observed at the sodium D lines. The static coupling mechanism predicts that there should be an accompanying CD absorption of opposite sign at the site of the $^1A_1 \rightarrow {}^1B_2$ transition.



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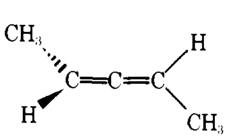
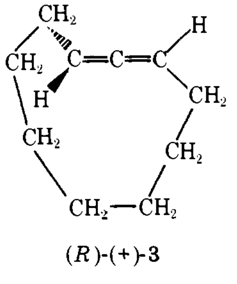


(*R*)-(−)-**2**



(*R*)-(+)-**3**

Crabbé et al.[16] have shown that application of the coupled oscillator model of Hohn and Weigang[21] leads to the correct prediction for **3**. In this dynamic coupling model, the magnetic moment of the $^1A_1 \rightarrow {}^1A_2$ transition couples with transient electric dipoles induced in the substituents by the radiation field to produce optical activity. The coupling is governed by the coulombic potential between the induced electric dipole in the substituent and the leading electric multipole of the $^1A_1 \rightarrow {}^1A_2$ transition of the allenic chromophore, the latter being an octopole. An interesting consequence of the dynamic coupling model is that the $^1A_1 \rightarrow {}^1A_2$ transition of **2** exhibits circular dichroism largely by virtue of the fact that vibrational motions move the axially symmetrical methyl groups out of the nodal surfaces of the $^1A_1 \rightarrow {}^1A_2$ transition octopole.

We present below a rigorous analysis of the lower singlet electronic states of allene and propose an explanation for the circular dichroism (CD) spectra of **2** and **3** which largely corroborates predictions based on the dynamic coupling model and invokes an important role for the Rydberg $\pi \rightarrow 3s$ transition.

II. Theory

The theoretical method employed in the present study has been described in detail elsewhere.[22] Only a brief resumé is given below. Partially correlated wave functions for the ground and excited states of the molecular system are determined to first order by Rayleigh-Schrödinger perturbation theory.

$$\Psi_n = \Psi_n{}^0 - \sum_j \lambda_{jn}\Phi_j{}^0 \qquad (1)$$

where

$$\lambda_{jn} = \frac{\langle \Psi_n{}^0|H|\Phi_j{}^0\rangle}{\langle \Phi_j{}^0|H|\Phi_j{}^0\rangle - \langle \Psi_n{}^0|H|\Psi_n{}^0\rangle} \qquad (2)$$

Here, H is the exact electronic Hamiltonian operator, $\Phi_j{}^0$ is a spin-adapted (singlet) configuration constructed from one or more electron replacements in the Hartree-Fock SCF de-

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Table I. Excitation Energies, Oscillator Strengths, and Optical Rotatory Strengths for Allene in the D_{2d} Geometry

state	excitation energy, eV		oscillator strength	rotatory strength		transition moments[e]	
	exptl	calcd[a]	f	$[R]^{\mathrm{r}}$	$[R]^{\nabla}\cdot\Delta E$	$\langle\Psi_0\|\mathbf{r}\|\Psi_n\rangle$	$\langle\Psi_n\|\mathbf{m}\|\Psi_0\rangle$
$1A_2$ (2e → ne; $\pi \rightarrow \pi^*$)		6.49					1.0334
$1B_1$ (2e → ne; $\pi \rightarrow \pi^*$)	6.72[b]	6.84					
1E (2e → na_1; $\pi \rightarrow$ 3s)	6.72[b], 7.16[c,d]	7.21 (7.04)	0.0819	±68.5	±17.71	0.4873	−0.5532
$1B_2$ (2e → ne; $\pi \rightarrow \pi^*$)	7.3[b,c]	7.88 (6.74)	0.3341			−1.4219	
2E ($\pi \rightarrow 3pb_2$)	8.03[c]	8.13 (8.87)	0.0088	±9.9	±3.23	−0.1430	−0.2727
$2A_1$; $2B_1$ ($\pi \rightarrow$ 3pe)	8.15[c]	8.15–8.25					
$2A_2$ ($\pi \rightarrow$ 3pe)	8.20[b]	8.25					0.2574
$3A_1$ (2e → ne; $\pi \rightarrow \pi^*$)		8.56					
3E ($\pi \rightarrow 3da_1$)	8.37[c]	8.72 (8.74)	0.0388	±17.0	±5.45	0.3009	−0.2222
$2B_2$ ($\pi \rightarrow$ 3pe)	8.58[b]	8.86 (8.10)	0.0930			0.6846	
4E; 5E; $3B_1$; $3A_2$; $4A_1$ ($\pi \rightarrow$ 3d)		8.91–8.95	0.0066	±5.0	±0.74	−0.1300[f,g]	0.1514[f-h]
6E ($\pi \rightarrow$ 4s)	8.58[b,c]	9.01 (10.21)	0.0052	±6.1	±2.30	0.1014	−0.2379
$3B_2$ ($\pi \rightarrow$ 3de)	8.78[b]	9.07 (8.03)	0.5351			1.6496	

[a] The numbers in parentheses were obtained by the ratio $\langle\Psi_0|\nabla|\Psi_n\rangle/\langle\Psi_n|\mathbf{r}|\Psi_0\rangle$. [b] Reference *g*. [c] Reference *h*. [d] See text for discussion. [e] In atomic units. $A_1 \rightarrow A_2$ and ${}^1A_1 \rightarrow {}^1B_2$ transitions are polarized parallel to the C–C–C bond; $A_1 \rightarrow E$ transitions are polarized perpendicular to the C–C–C bond (only one component given). [f] $1A_1 \rightarrow 4E$. [g] $\langle A_1|r|5E\rangle = -0.1100$, $\langle 5E|\mathbf{m}|1A_1\rangle = -0.1192$. [h] $\langle 3A_2|m_x|1A_1\rangle = 0.0555$.

terminant, Φ_{HF}, of occupied orbitals by virtual orbitals, and $\Psi_n{}^0$ is in general a linear combination of quasi-degenerate $\Phi_l{}^0(l \neq j)$ obtained by diagonalizing a small block of the complete Hamiltonian matrix after regrouping. The function $\Psi_n{}^0$ constitutes the "zero-order" part of the wave function and the set $\Phi_j{}^0$ the "first-order" correction.[22] It is assumed that doubly or more highly excited configurations do not contribute to $\Psi_n{}^0$. For the ground state ($\Psi_0{}^0 \equiv \Phi_{HF}$), the first-order corrections, $\Phi_j{}^0$, are derived from the space of all doubly excited configurations, excluding excitations from the core 1s orbitals or to the three most highly antibonding orbitals. A consequence of the above assumption is that doubly or more highly excited configurations may be omitted from the excited-state description as they do not contribute to first order to values of transition moments over operators such as the electric dipole moment operator $\boldsymbol{\mu}$, the magnetic dipole moment operator $\mathbf{m}$, and the gradient operator ∇, which consist of a sum of the corresponding one-electron operators. In atomic units

$$\boldsymbol{\mu} = \sum_j \mathbf{r}_j \qquad (3)$$

$$\mathbf{m} = \sum_j \frac{\mathbf{r}_j \times \nabla_j}{i} \qquad (4)$$

$$\nabla = \sum_j \nabla_j \qquad (5)$$

From the commutator relationship between the position, momentum, and Hamiltonian operators may be derived the relationship

$$\langle\Psi_0|\boldsymbol{\mu}|\Psi_n\rangle = \frac{1}{(E_n - E_0)}\langle\Psi_0|\nabla|\Psi_n\rangle \qquad (6)$$

Which is true for exact electronic wave functions. The agreement between the excitation energy obtained from eq 6 and that obtained by the perturbative CI procedure[22] provides an independent check of the quality of the wave functions.

A vertical electronic transition between the ground state, Ψ_0, and excited state, ψ_n, is characterized by the oscillator strength, f_{on}, and optical rotatory strength, $[R_{on}]^{\mathrm{r}}$, which (the latter in atomic units) are given by

$$f_{on} = \frac{2}{3}\langle\Psi_0|\nabla|\Psi_n\rangle\langle\Psi_n|\boldsymbol{\mu}|\Psi_0\rangle \qquad (7)$$

$$[R_{on}]^{\mathrm{r}} = -i\langle\Psi_0|\boldsymbol{\mu}|\Psi_n\rangle\langle\Psi_n|\mathbf{m}|\Psi_0\rangle \qquad (8)$$

The origin dependence of $[R_{on}]^{\mathrm{r}}$ may be removed by substitution of eq 6 into eq 8. The resulting expression, described as $[R]^{\nabla}\cdot\Delta E$ in Table I, is

$$[R_{on}]^{\nabla}\cdot\Delta E = -i\langle\Psi_0|\nabla|\Psi_n\rangle\langle\Psi_n|\mathbf{m}|\Psi_0\rangle \qquad (9)$$

III. Method

All Hartree-Fock SCF calculations on the allenes were performed using the POLYATOM system of programs.[23] The double ζ [9s5p/4s → 4s2p/2s] basis of Dunning[24] was augmented by a single diffuse s ($\alpha_s = 0.015$) and a single set of diffuse p ($\alpha_p = 0.011$) functions on each carbon atom as well as a full set of d-type Gaussian functions ($\alpha_d = 0.0118$) on the middle carbon atom. It is expected that such a basis will allow an adequate description of the lower excited singlet valence and Rydberg states of the allenic chromophore.

For the purpose of defining zero- and first-order contributions to the wave functions[22] as discussed in the previous section, a criterion of $\lambda = 0.025$ was adopted. All configurations for which the coefficient λ_{jn} (eq 2) is greater than 0.025 are included in $\Psi_n{}^0$. This choice of λ leads to dimensions of the order of 100 for the zero-order part of the Hamiltonian matrix[22] in the present case.

No geometry optimizations on the ground-state structures were performed. The equilibrium ground-state geometry of allene was taken from the electron diffraction measurements of Maki and Toth[25] (C-C = 1.308 Å, C-H = 1.087 Å, HCH = 118.2°). Two deformations from D_{2d} symmetry were examined, namely, a *bend* of the C-C-C skeleton through 10° in such a way as to reduce the symmetry to C_2 and a *twist* of one end relative to the other through 10°, again preserving C_2 symmetry (D_2, if no bend). All other parameters were kept fixed at the values used for the equilibrium D_{2d} geometry.

IV. Experimental Section

(*S*)-(+)-1,3-Dimethylallene ($[\alpha]^{23}{}_{\mathrm{D}}$ +21.0°, ether) and (*R*)-(+)-1,2-cyclononadiene ($[\alpha]^{23}{}_{\mathrm{D}}$ +138.0°, 3-methylpentane) were kindly supplied by Professor P. Crabbé. Absorption spectra were measured with a Cary 17, CD spectra with a Jouan CD 185, and optical rotations with a Perkin-Elmer 141. The CD spectra obtained from (*S*)-(+)-1,3-dimethylallene, shown in Figure 2, have been inverted to correspond to those of (*R*)-(−)-1,3-dimethylallene in order to facilitate the discussion.

V. Results and Discussion

Allene Ground State. The energy of the ground state of allene calculated by the RHF-SCF method using the basis set described in the previous section is −115.830 23 hartrees. The

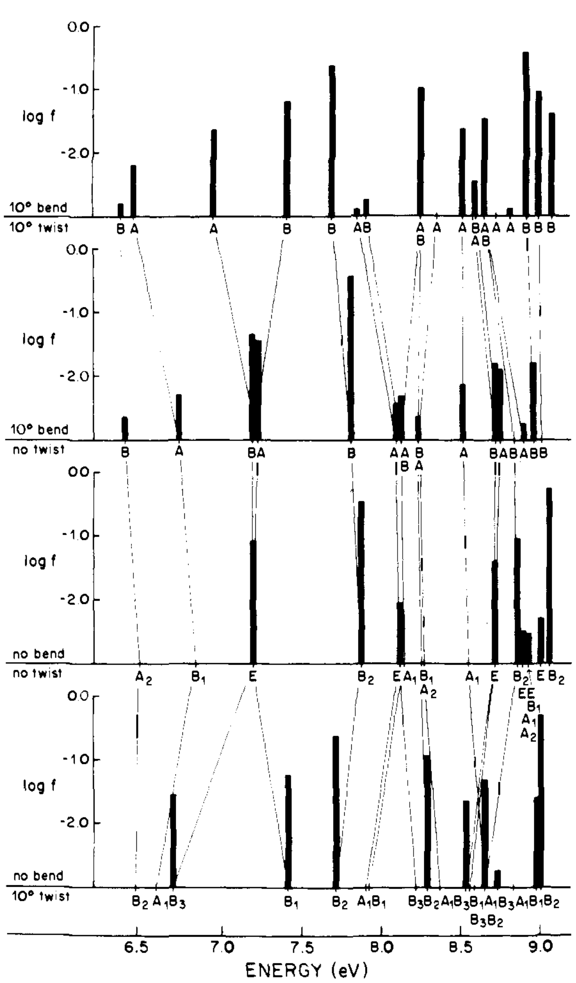


Figure 1. The effect of bending and twisting of the allene molecule on the calculated UV spectrum. The absorption energies are displayed horizontally and the states are labeled according to the point group appropriate to each deformation. The oscillator strengths, *f*, are displayed as bar graphs on a logarithmic scale (truncated at $f = 0.001$). The bend and twist are in the sense shown in Figure 4.

ground-state configuration is $(1a_1)^2(1b_2)^2(2a_2)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1e)^4(2e)^4$. The energies of the 1e and 2e molecular orbitals are $\epsilon_{1e} = -0.6123$ and $\epsilon_{2e} = -0.3783$ hartree, respectively. The first two bands of the photoionization spectrum of allene have maxima at 10.02 and 14.75 eV.[26,27] The first band appears to be Jahn-Teller split, the second component occurring at 10.60 eV. Similar values for the first ionization potential have also been obtained from convergence of Rydberg series (10.10[9,10] and 10.02 eV[11]) and by electron impact spectroscopy (10.16 eV[28]). These values are in reasonable agreement with estimates by Koopmans' theorem[29] for the potentials for vertical ionizations from the $2e(\pi)$ and $1e(\sigma_{CH})$ levels, 10.3 and 16.7 eV, respectively.

Allene Singlet Excited States. As stated in the Introduction, the singlet states of allene which are reached by vertical $\pi \rightarrow \pi^*$ transitions are generally believed to occur in the order $A_2 < B_1 < B_2$. The position of the fourth $\pi \rightarrow \pi^*$ state (of A_1 symmetry) has remained in doubt. The results of our calculations are given in Table I and the effects of various bending and twisting deformations are shown in Figure 1. The principal features of the experimental vacuum UV spectrum of allene, obtained by Iverson and Russell[11] and by Rabalais et al.,[10] are four broad bands at 6.72 (ϵ_{max} 980), 7.30 (ϵ_{max} 8400), 8.20 (ϵ_{max} 2200), and 8.78 eV (ϵ_{max} 5050). Each band is highly structured, the structure consisting apparently of a mixture of vibronic transitions and transitions to Rydberg states.[11]

We find that the first two states, $1A_2$ (6.49 eV) and $1B_1$ (6.84 eV), arise from $\pi \rightarrow \pi^*$ excitations both of which are electric dipole forbidden. Both transitions gain weak dipole strength from the bending vibrational mode. When the bend is 10°, $f(^1A_1 \rightarrow {}^1A_2)$ is 0.0023 and $f(^1A_1 \rightarrow {}^1B_1)$ is 0.0051. Neither transition gains dipole strength from the twisting vibration. We assign the weak first band at 6.72 eV[11] as arising partly from the $^1A_1 \rightarrow {}^1B_2$ transition and partly from the $\pi \rightarrow$ 3s Rydberg transition (see below). From the calculated values of $\langle \pi^* | r^2 | \pi^* \rangle$, 14.1·$(1A_2)$, and 16.1 bohr^2 $(1B_1)$, both $\pi \rightarrow \pi^*$ states have valence rather than Rydberg character.[30] As confirmation one finds that removal of the diffuse functions from the basis leaves the positions of these states essentially unchanged, $^1A_2$ (6.55 eV) and $^1B_1$ (6.91 eV).

The third state is 1^1E ($\pi \rightarrow$ 3s), computed to occur at 7.21 eV and to have an oscillator strength $f = 0.082$. Such a state may be Jahn-Teller unstable, the degeneracy being removed by coupling to vibrations of b_1 symmetry.[31] Sutcliffe and Walsh[9] assign a value of 7.16 eV to the first member of a Rydberg series with quantum defect $\delta = 1.06$. This number is corroborated by model potential calculations of Betts and McKoy.[12] Iverson and Russell[11] have calculated the value of 6.87 eV as the first number of an alternate series with $\delta = 0.97$ which converges to the same ionization potential. Robin[32] argues from photoelectron spectroscopic data and by analogy with term values observed for other three-carbon chromophores that the lower component of the Jahn-Teller unstable ^1E state should occur at the position of the weak band at 6.72 eV. This assignment is consistent with a recent MCD study of allene by Schnepp[33] in which no A term could be found in the range 6.5-7.5 eV and which revealed partial Rydberg character for the band at 6.72 eV. Although a complete vibronic analysis is not feasible in the present study, our calculations demonstrate (Figure 1) that a 10° twist (the b_1 vibrational mode) leads to a separation of 0.72 eV of the $\pi \rightarrow$ 3s Rydberg states, the lower component moving to 6.7 eV. As stated above, we prefer to assign the band at 6.72 eV as a composite of valence $\pi \rightarrow \pi^*$ ($A_1 \rightarrow B_1$) and Rydberg $\pi \rightarrow$ 3s (Jahn-Teller separated $A_1 \rightarrow E$). The calculated oscillator strength of the lower $\pi \rightarrow$ 3s component at a twist of 10° is 0.029, in good agreement with the experimental estimate $f = 0.03$.[32]

The two components of the ^1E ($\pi \rightarrow$ 3s) are individually strongly optically active. As will be seen in the next section, the removal of the degeneracy by vibronic coupling will play a prominent role in the explanation of the observed optical activity of chiral allenes.

The fourth excited singlet state is found to be 1^1B_2 ($\pi \rightarrow \pi^*$) with energy 7.88 eV relative to the ground state. The transition $^1A_1 \rightarrow {}^1B_2$ must correspond to the 7.30 eV second band[9-11] which must also contain the higher energy $\pi \rightarrow$ 3s transition in its lower energy side. The calculated oscillator strength is $f = 0.334$ for the D_{2d} structure, and $f = 0.287$ for the D_2 structure. In the latter case, the value cited is the sum of the oscillator strengths of $\pi \rightarrow \pi^*$ ($A_1 \rightarrow B_2$, $f = 0.229$) and $\pi \rightarrow$ 3s ($A_1 \rightarrow B_1$, $f = 0.058$). Both values are in good agreement with the experimental estimate, $f = 0.34$.[32] The $^1B_2$ state has considerable Rydberg character.[30,34] Without the diffuse functions in the basis, the energy of this state increases by 0.79 eV. Secondly, $\langle \pi^* | r^2 | \pi^* \rangle = 80.0$ bohr^2.

The next four states, 2E, $2A_1$, $2B_1$, and $2A_2$, all arise from $\pi \rightarrow$ 3p excitations and fall in the narrow range 8.13-8.26 eV. Except for the first, $^1A_1 \rightarrow 2^1E$ ($\pi \rightarrow 3pa_1$), none of the transitions to the 3p Rydberg states is electric dipole allowed in the D_{2d} point group symmetry. The $^1A_1 \rightarrow 2^1E$ transition has weak oscillator strength, $f = 0.0088$. Sutcliffe and Walsh[9] have two series with quantum defects suggestive of $\pi \rightarrow$ np transitions beginning at 8.03 and 8.15 eV, respectively. Iverson and Russell[11] have identified one series with a quantum defect, $\delta = 0.372$, beginning at 8.05 eV. We assign the transition at 8.05 eV as $^1A_1 \rightarrow 2^1E$ ($\pi \rightarrow 3pa_1$) as did McKoy and Betts.[12]

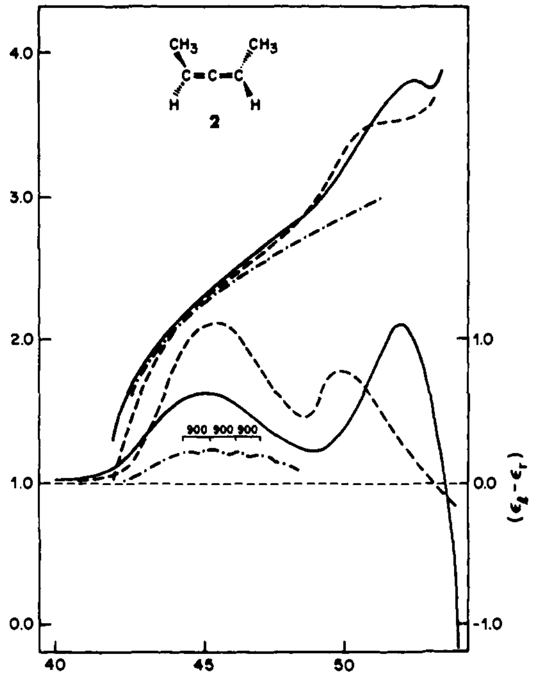


Figure 2. The UV and CD spectrum of (R)-(−)-1,3-dimethylallene: —, gas phase, ambient temperature; - - -, solution in 3-methylpentane at 23 °C; -·-, solution in 3-methylpentane at −182 °C.

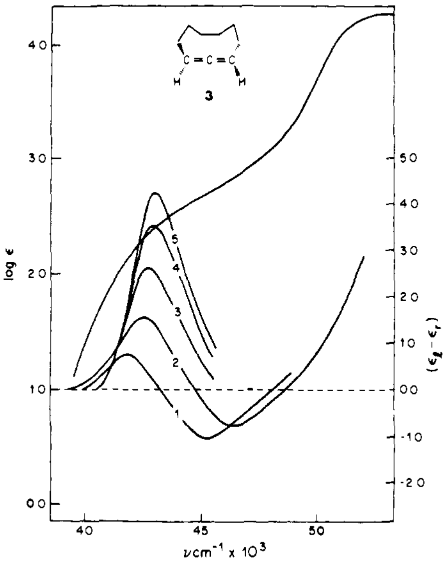


Figure 3. The UV and CD spectrum of (R)-(+)-1,2-cyclononadiene: 1, gas phase, ambient temperature; 2, solution in 3-methylpentane at 20°; 3, at −100 °C; 4, at −145 °C; 5, at −182 °C.

The 2^1A_2 state has the same symmetry as the 1^1B_2 state, namely, B_2, when the symmetry of the molecule is reduced to D_2 by twisting vibrations. The calculations indicate that the two transitions couple strongly, sharing dipole intensity. At a twist angle of 10°, $f(^1A_1 \rightarrow 2^1A_2) = 0.116$ while $f(^1A_1 \rightarrow 1^1B_2) = 0.228$. We suggest that the third diffuse band at 8.20 eV in the allene spectrum be assigned as $^1A_1 \rightarrow 2^1A_2$ ($\pi \rightarrow$ 3pe) and predict that the intensity of this band should decrease with lowering of the temperature with a concurrent increase in intensity of the second band, assigned as $^1A_1 \rightarrow 1^1B_2$.

The ninth state, $3A_1$, at 8.56 eV is the fourth member expected from the $\pi \rightarrow \pi^*$ valence transitions and, indeed, is found to be valence-like:[30] $\langle \pi^* | r^2 | \pi^* \rangle = 31.$ bohr^2; energy, without diffuse functions, 8.53 eV. This state derives negligible intensity from vibronic coupling and is not observed in the experimental spectrum.[11]

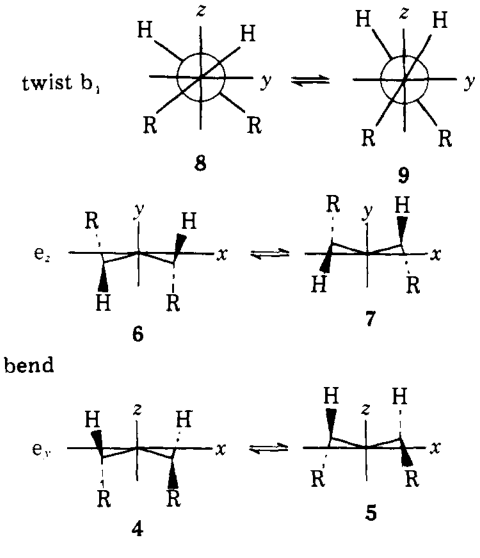
Assignments of more highly excited states than those discussed above become less certain because of basis set limitations. The $^1A_1 \rightarrow 2^1B_2$ ($\pi \rightarrow$ 3pe) and $^1A_1 \rightarrow 3^1B_2$ ($\pi \rightarrow$ 3de), with energies 8.86 and 9.07 eV, respectively, are calculated to have the highest intensities, $f = 0.093$ and 0.535, respectively. We tentatively assign the latter as corresponding to the fourth diffuse band at 8.78 eV in the allene spectrum.[11] The strong, sharp peak at 8.58 eV at the beginning of the third diffuse band was assigned as the $n = 4$ member of the $\pi \rightarrow ns$ series by Iverson and Russell[11] and also by Sutcliffe and Walsh[9] but is calculated to be relatively weak, $f(^1A_1 \rightarrow 6^1E) = 0.0052$, though not broadened by vibronic coupling. Our results indicate that the $^1A_1 \rightarrow 6^1E$ and $^1A_1 \rightarrow 2^1B_2$ transitions exchange positions when the molecule is twisted through 10° (Figure 1). We tentatively assign the 8.58-eV peak as due to the overlapping transitions $^1A_1 \rightarrow 2^1B_1$ ($\pi \rightarrow$ 3pe) and $^1A_1 \rightarrow 6^1E$ ($\pi \rightarrow$ 4s).

In summary, all of the transitions of allene below 9 eV originate from π(2e) excitations. Three of the $\pi \rightarrow \pi^*$ excitations are expected to give valence-like states, namely, $1B_1$, $1A_2$, and $3A_1$. The strongly electric dipole allowed $\pi \rightarrow \pi^*$ transition, $A_1 \rightarrow 1B_2$, has considerable Rydberg character. There appears to be a substantial Jahn–Teller splitting of the $^1E(\pi \rightarrow 3s)$ Rydberg state.

Optical Activity of Chiral Allenes. The temperature and solvent dependence of the UV and CD spectra of (R)-(−)-**2** and (R)-(+)-**3** are shown in Figures 2 and 3, respectively. The gas-phase CD spectrum of **2** reveals a band at 6.00 eV which is little affected when **2** is dissolved in 3-methylpentane and a band at 6.17 eV which experiences a marked blue shift to 6.45 eV in the condensed phase. It is apparent that the two terminal states are of valence and Rydberg character, respectively, and that they have the same sign for the rotational strength, opposite to that observed for the intense CD absorption above 6.7 eV which apparently is responsible for the sign of optical rotation at the sodium D lines. It is apparent also that the rotatory strength of the first transition is considerably attenuated upon cooling to −182 °C, in accord with the predictions for the CD of the $A_1 \rightarrow A_2$ transition based on the dynamic coupling model (see the Introduction).

The gas-phase CD spectrum of **3** (Figure 3) reveals a couplet of oppositely signed CD bands at 5.19 and 5.59 eV. Both bands experience blue shifts to 5.27 and 5.77 eV, respectively, upon solution of the compound in 3-methylpentane. Upon cooling,

Scheme I



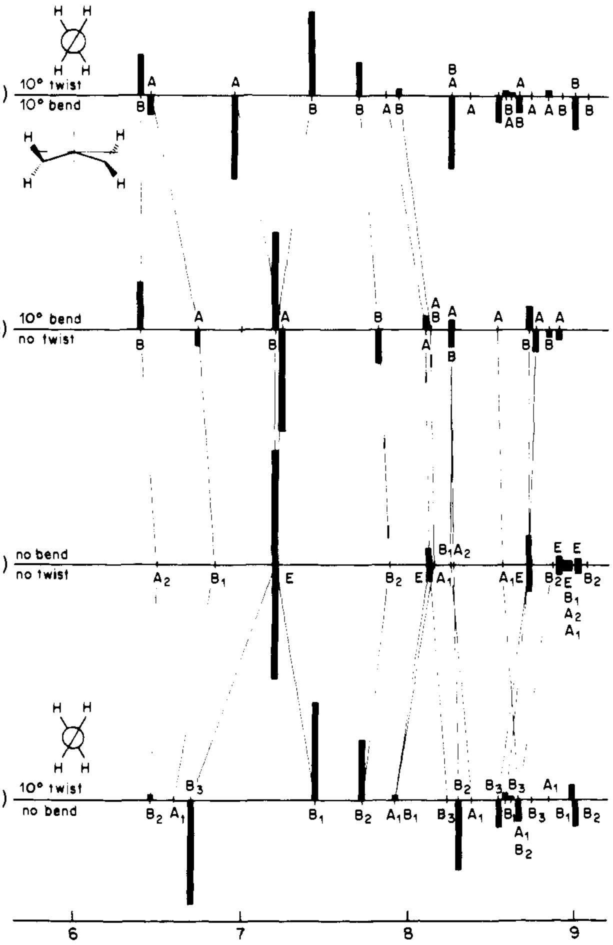


Figure 4. The effect of bending and twisting of the allene molecule on the calculated CD spectrum. The absorption energies are displayed horizontally and the states are labeled according to the appropriate point group. The rotational strengths $[R]^r$ are displayed as bar graphs where lengths are proportional to the magnitude of the rotatory strength. Row (d) corresponds to (*R*)-(+)-**3**.

the first band grows in intensity and shifts further to 5.33 eV at −183 °C. Although the data are incomplete, the second band apparently disappears as the temperature is lowered. As in the case of **2**, there is a transition above 6.6 eV with larger rotational strength which may be responsible for the sign of optical rotation at the sodium D lines. This last transition has CD of opposite sign to its analogue in **2**, although the spatial arrangement of the five carbon atoms which make up the chromophore has the same helicity.

In order to rationalize the applicability of the model we wish to use to explain the optical activity of **2** and **3**, it is necessary to examine the stereochemistry of the vibronic deformations that render **1** instantaneously chiral. We concentrate on the lowest frequency vibronic modes of e and b symmetry,[36,37] the *bend* of e symmetry which has a vibrational progression of 335 cm^{-1}, and the *twist* of b_1 symmetry which has spacings of 865 cm^{-1}. Both modes are illustrated in Scheme I. The terminal points **6** and **7** of the bending vibration labeled e_z are chiral and identical. The terminal points **4** and **5** of the e_y bend are chiral and have the same local handedness, but are *not* equivalent if R ≠ H. The chiral structures along the coordinate e_x are antipodal to those along e_y (i.e., **6** (R = H) is the mirror image of **4** (R = H)). Since **6** and **7** are identical, the time-averaged structure along e_z is one in which there is no bend at the central carbon. Since **4** and **5** are *not* equivalent if R ≠ H, then the geometry local to the chromophore of (*R*)-(−)-**2** and (*R*)-(+)-**3** will have a bend in the sense shown in **4** (or **5**). The terminal points of the b_1 twist, **8** and **9**, are chiral with opposite handedness. If R ≠ H the vibrational motion will favor one or the other. As we shall discover, the observed optical activity of (*R*)-(−)-**2** can be rationalized if the time-averaged structure corresponds to **8** (R = CH_3), while the optical activity of (*R*)-(+)-**3** is consistent with having a twist as in **9** (R, R = $-(CH_2)_6$). A recent study of the structure of **3** by molecular mechanics calculations suggested a bend of 10° in the sense of **4** and a twist of 2° in the sense of **9** as the static geometry of the most stable conformation.[38]

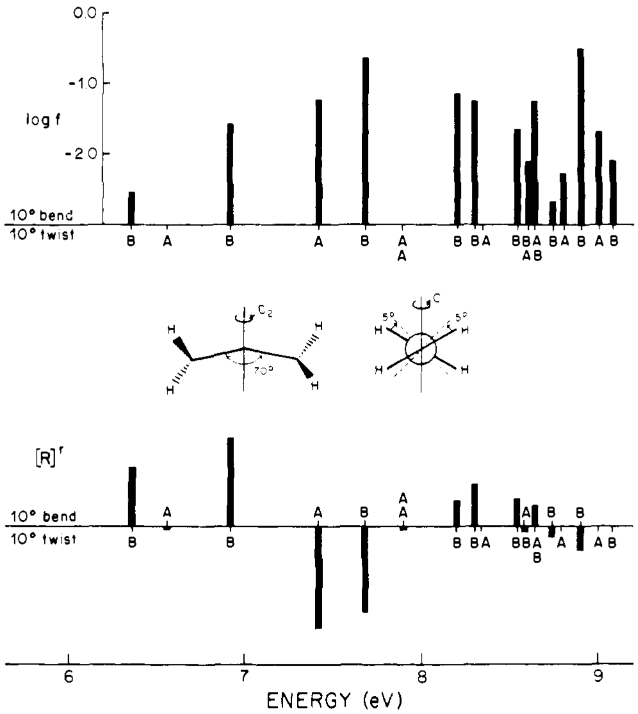


Figure 5. The effect of bending and twisting of the allene molecule on the calculated UV and CD spectra. The absorption energies are displayed horizontally and the states are labeled according to the point group C_2. Oscillator strengths are displayed as in Figure 1 and rotatory strengths $[R]^r$ as in Figure 4. The distortions are those expected for the time-averaged structure of vibrationally excited (*R*)-(−)-**2**.

The results of the deformation studies on the allene moiety are shown in Figure 4. As argued above, neither **2** nor **3** can have a linear arrangement of the C=C=C bonds. The data displayed in Figure 4 represent the consequences of the principal deformation modes available to the cumulene. Several points are immediately apparent. Bending of the chromophore, in the sense of **4** (R = H), causes the $A_1 \rightarrow A_2$ allene transition to shift to lower energy by 0.1 eV and to gain appreciable rotational strength, $[R]^r = +27.2$,[40] principally by gaining electric dipole intensity from the $A_1 \rightarrow A_2$ transition. As is expected from the coupling of the two transitions, the latter has $[R]^r = -20.1$. The $A_1 \rightarrow B_1$ intra-valence-shell transition also gains some rotational strength, $[R]^r = -8.4$, from one of the components of the $A_1 \rightarrow 1E$ transition. As anticipated earlier[31] a bend of 10° is ineffective in removing the degeneracy of the E state of allene and thus the large rotational strengths associated with the components of this transition will almost cancel.

On the other hand, twisting of one end relative to the other (the b_1 torsional mode) leads to little shift in the $A_1 \rightarrow A_2$ transition and does not induce mixing of the $1A_2$ and $1B_2$ states. As a consequence little optical activity is expected for the $A_1 \rightarrow A_2$ transition from the twist alone. However, $1B_2$ and $2A_2$ ($\pi \rightarrow 3pe$) interact under the twist perturbation and a CD couplet results: $[R]^r = +35.7$ and -40.8, respectively. Of greater significance is the fact that the degeneracy of the $A_1 \rightarrow E$ transition is removed, the resultant B_1 and B_3 states being separated by 0.73 eV when the twist is 10°, but the rotational strength of each is not diminished. A large CD couplet results with the lower energy $A_1 \rightarrow B_3$ transition having $[R]^r = -62.2$ and the $A_1 \rightarrow B_1$, $[R]^r = +58.6$ when the twist is the sense of **9** (R = H).

The top row, (d) of Figure 4 shows the resulting optical activity when the chromophore is both twisted and bent in the sense expected for (*R*)-1,2-cyclononadiene **3** (**4** + **9**). The first band, which originates from the $A_1 \rightarrow A_2$ ($\pi \rightarrow \pi^*$) allene transition, has a positive rotatory strength $[R]^r = +23.9$ because of the C-C-C bend. The next, $A_1 \rightarrow B_1$ ($\pi \rightarrow \pi^*$), is strongly shifted to lower energies by the twist and has a small rotational strength of opposite sign imposed by the bend. The next two bands, with $[R]^r = -51.2$ and $+51.1$, are the two components of the $A_1 \rightarrow E$ ($\pi \rightarrow 3s$) Rydberg transition of allene which are spread apart by the twist. The separation, 0.46 eV, is similar to the separation, 0.65 eV, of the two highest occupied π molecular orbitals of the structure with 10° bend and twist. The $A_1 \rightarrow B_2$ ($\pi \rightarrow \pi^*$) transition has a weaker positive rotatory strength $[R]^r = +20.1$. Comparison of lines a and c reveals that the bend (**4**) and twist (**9**) tend to induce oppositely signed rotational strengths on this transition.

Finally, the results of the calculations of the optical and circular dichroism spectra of the chromophore when it is bent in the sense of **4** and twisted in the opposite sense, i.e., as in **8**, are shown in Figure 5. This configuration, discussed above, corresponds to the time-averaged structure of (*R*)-(−)-**2**. The first bend has positive rotational strength $[R]^r = +32.9$ because of the bend. The next transition has negligible optical activity. However, the principal difference between the results shown in Figure 5 and those shown in Figure 4b is that the Rydberg ($\pi \rightarrow 3s$) components have moved in the opposite direction. The second *observable* band ($A_1 \rightarrow B$, $\pi \rightarrow 3s$) in both the UV and CD spectrum also has positive rotatory strength $[R]^r = +49.5$. To higher energy is a region of large negative rotatory strength arising from $A \rightarrow A$, the second component of the $A_1 \rightarrow E$ ($\pi \rightarrow 3s$) Rydberg transition $[R]^r = -58.19$, and $A \rightarrow B$ (from the allene $A_1 \rightarrow B_2$ ($\pi \rightarrow \pi^*$) transition) $[R]^r = -48.8$.

The temperature-dependent behavior of the spectra of both **2** (Figure 2) and **3** (Figure 3) can now be rationalized. In the case of **2**, at room temperature, both the low-frequency bending and twisting vibrational modes are populated giving the molecule a time-averaged bent and twisted structure, the chirality of which is enhanced by anharmonicity of the nuclear motion. Both vibrational modes would be damped as the temperature is lowered and the molecule would approach its equilibrium geometry which has a bend of 1.4° and a twist of less than 0.01° (according to the results of an optimization of the bend and twist angles of **2** using GAUSSIAN 70[40] with the STO-3G basis[41]). A calculation on the ground state of **2** using the full double ζ valence basis shows that 1,3-alkylation does not lead to a separation of the π orbitals ($\Delta\epsilon = 0.000\ 07$ hartree) and thus, presumably, not of the ($\pi \rightarrow 3s$) states either. Therefore, **2**, in its lowest vibrational state, should be virtually optically inactive.

The chromophore of **3** has a permanent twist of 2° and bend of 10° because of constraints imposed by the nine-membered ring,[38] and one need not assume that either bending or twisting vibrational modes are appreciably excited at room temperature. One can rationalize the temperature dependence displayed in Figure 3 by considering that the valence $^1A \rightarrow {}^1B$ and Rydberg $^1A \rightarrow {}^1A$ transitions overlap less and less as the Rydberg transition is blue shifted first by solution of the compound and then by the increased density that accompanies lowered temperatures. The apparent disappearance of the Rydberg CD band is due to increasing overlap with the larger CD band of opposite sign which lies above 6.6 eV.

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References and Notes

(1) (a) University of Calgary; (b) King's College, University of London.
(2) (a) A. Pellégatti, *Theor. Chim. Acta*, **8**, 129 (1967); (b) J. C. Tai and N. L. Allinger, *ibid.*, **12**, 261 (1968); (c) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **50**, 1126 (1969).
(3) A. Albinati, F. Maraschini, and M. Zocchi, *J. Chem. Soc., Faraday Trans. 2*, 798 (1973).
(4) P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, **96**, 779 (1974).
(5) (a) W. Runge, W. Kosbahn, and J. Kroner, *Ber. Bunsenges. Phys. Chem.*, **79**, 371 (1975); (b) W. Runge, W. Kosbahn, and J. Winkler, *ibid.*, **79**, 381 (1975).
(6) H. Dickerson, S. Ferber, and F. S. Richardson, *Theor. Chim. Acta*, **42**, 333 (1976).
(7) R. J. Buenker, *J. Chem. Phys.*, **48**, 1368 (1968).
(8) L. J. Schaad, L. A. Burnelle, and K. P. Dressler, *Theor. Chim. Acta*, **15**, 91 (1969).
(9) L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 899 (1952).
(10) J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, **71**, 73 (1971).
(11) A. A. Iverson and B. R. Russell, *Spectrochim. Acta, Part A*, **28**, 447 (1972).
(12) T. C. Betts and V. McKoy, *J. Chem. Phys.*, **60**, 2947 (1974).
(13) G. Lowe, *Chem. Commun.*, 411 (1965).
(14) S. F. Mason and G. W. Vane, *Tetrahedron Lett.*, 1593 (1965).
(15) J. H. Brewster, *Top. Stereochem.*, **2**, 33 (1967).
(16) P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake, and S. F. Mason, *Chem. Commun.*, 1261 (1971).
(17) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).
(18) W. M. Jones and J. M. Walbrick, *Tetrahedron Lett.*, 5229 (1968).
(19) W. L. Waters and M. C. Casserio, *Tetrahedron Lett.*, 5233 (1968).
(20) W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *J. Am. Chem. Soc.*, **93**, 4932 (1971).
(21) E. G. Hohn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).
(22) A. Rauk, and J. M. Barriel, *Chem. Phys.*, **25**, 409 (1977).
(23) J. W. Moskowitz and L. S. Snyder in "Methods of Electronic Structure Theory", H. F. Schaeffer III, Ed., Plenum Press, New York, 1977, p 387.
(24) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).
(25) A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17**, 136 (1965).
(26) R. K. Thomas and H. Thompson, *Proc. R. Soc. London, Ser. A*, **339**, 29 (1974).
(27) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle in "Photoelectron Spectroscopy", Wiley, New York, 1970, p 169, 184, 185.
(28) J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **79**, 5848 (1957).
(29) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).
(30) It is useful to specify briefly the criteria whereby one may employ the terms "Rydberg", "valence", or "mixed" in the description of electronic states. Inspection of the orbital composition of the wave functions is often confusing when diffuse functions, extra to the ground-state description, are added to the basis set, since these functions will invariably mix with large coefficients. Experimentally, Rydberg states are identified by three principal methods: (1) assignment as members of a convergent series, the limit of which is the ionization potential; (2) observation of a marked "blue" shift upon subjecting the molecule to higher pressures; (3) in the case of transitions characteristic of chromophoric groups in organic systems, by observation of relatively large "red" shifts upon alkylation. Theoretically, two criteria may be applied: (1) the computation of $\langle r^2 \rangle$ for the excited state and (2) comparison of the excitation energy with that obtained when the extra diffuse functions are removed from the basis set. Values of $\langle r^2 \rangle$ much greater than the square of the average molecular dimensions are indicative of Rydberg character. When removal of the diffuse functions leads to a marked increase in the calculated excitation energy, such functions are clearly required for the description of the electronic motion and Rydberg character is indicated.
(31) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1966, p 50.
(32) M. B. Robin, "Higher Excited States of Polyatomic Molecules", Vol. 2, Academic Press, New York, 1975, pp 199-202.
(33) K. Fuke and O. Schnepp. We thank the authors for sending us a preprint of this work.
(34) It is possible that more rigorous calculations will reveal the $^1B_2$ state to be of "mixed"character following the current consensus of theoreticians on the nature of the $\pi \rightarrow \pi^*$ state of ethylene.[22,35]
(35) H. F. Schaeffer III, "Ethylene", paper presented at the American Conference on Theoretical Chemistry, Boulder, Colo., 1978.
(36) (a) R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952); (b) B. Andersen, R. Stolevik, J. Brunvoll, S. J. Cyvin, and G. Hagen, *Acta Chem. Scand.*, **21**, 1759 (1967).
(37) I. M. Mills, W. L. Smith, and J. L. Duncan, *J. Mol. Spectrosc.*, **16**, 349 (1965).
(38) F. A. L. Anet and I. Yavari, *J. Am. Chem. Soc.*, **99**, 7640 (1977).
(39) The units of $[R]^r$ are cgs × 10^{-40} throughout.
(40) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE Program No. 236.
(41) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).