

Ab Initio Theoretical Calculations on the Circular Dichroism Spectra of *trans*-Cyclooctene

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Abstract: Ab initio configuration interaction wave functions were calculated for several excited states of ethylene distorted from its planar geometry in order to examine the circular dichroism on monoolefinic systems. The ethylene was distorted by a 10° twist to D_2 symmetry and was also given the C_2 geometry of the double bonded carbon structure in *trans*-cyclooctene. Excitation energies, oscillator strengths, rotatory strengths, and $\langle X^2 \rangle$ are reported. Correspondence to the spectra of *trans*-cyclooctene is presented using spectral shifts obtained from calculations on distorted *trans*-2-butene.

I. Introduction

Experimental circular dichroism (CD) spectra in the vacuum ultraviolet have become increasingly available in recent years, thereby providing an additional source of information for the assignment of the electronic states of chromophoric groups. Among the most heavily studied such moieties is the carbon-carbon double bond, the simplest model for which is the ethylene molecule. The CD spectrum of this group has been obtained both in the case where optical activity is induced through distortion of the bond by twisting, thus introducing an inherently dissymmetric screw axis, and by the inclusion of an asymmetric carbon in the situation where the chromophoric group is planar as in ethylene itself. An example of the first case is *trans*-cyclooctene,¹ while spectra of α - and β -pinene¹ and (*S*)-3-methyl-1-pentene² are examples of the second. The CD spectra obtained in these two cases, while both intimately related to the electronic structure of the basic chromophore, the ethylenic group, differ in that *trans*-cyclooctene exhibits two major dichroic bands while the planar situation leads to three.

The CD spectrum of *trans*-cyclooctene has previously been considered by Yaris, Moscowitz, and Berry,³ who used a semiempirical method and twisted ethylene as a model, by Robin et al.,⁴ who used the same model and SCF calculations in the virtual orbital approximation, by Bouman and Hansen,⁵ who used the random phase approximation in an ab initio fashion, but who did not include Rydberg type functions in their computation, and by Rauk et al.,⁶ who used a variety of methods of comparable accuracy.

In this paper we report a series of extensive ab initio CI calculations directed toward a complete elucidation of the *trans*-cyclooctene CD spectrum. These calculations deal with CI problems ranging up to 23 322 configurations, utilizing a partitioning approach described elsewhere.^{7,8} The energies, rotatory strengths, and oscillator strengths of the excited electronic states have been calculated for ethylene in the planar, 10° twisted (D_2), and in the *trans*-cyclooctene (C_2) double bond geometry.

While the states of this model system should have a one-to-one correspondence to the states of *trans*-cyclooctene in the energy range considered, the perturbation due to the six carbon saturated portion of the ring does induce sizable energy shifts which vary in magnitude from state to state. These shifts have been calculated using *trans*-2-butene in the *trans*-cyclooctene geometry as a model for *trans*-cyclooctene. This leads to results which differ in energy from those observed by not more than 0.15 eV.

II. Computational Details

The orbital designations and geometric conventions of Merer and Mulliken⁹ are used throughout this paper. This geometry

for planar ethylene corresponds to centering the molecule on the origin of a cartesian coordinate system so that the C-C bond is on the z axis and the x axis is perpendicular to the molecular plane. Molecular distortions such as twisting the C-C bond and bending ethylene to the *trans*-cyclooctene geometry are made symmetrically so that the x axis remains a C_2 symmetry axis. In addition to the normal planar geometry of ethylene¹⁰ with $R_{CC} = 1.34 \text{ \AA}$, $R_{CH} = 1.086 \text{ \AA}$, and $\angle CCH = 121.2^\circ$, two other distorted geometries were used to compute the rotatory properties of ethylene. One distorted geometry is the same as the planar geometry except for a 10° twist in the C=C double bond, a geometry used in previous theoretical studies. The other ethylene geometry corresponds to the double bond geometry of *trans*-cyclooctene determined by x-ray crystallography and refined by empirical force field calculations.^{11,12} The x-ray and force field geometries for *trans*-cyclooctene agree well enough that there is no sacrifice in choosing the computed geometry over the experimental one. The calculated geometry is constrained to be symmetric, and properly represents a gas-phase molecule. Figure 1 illustrates the geometry of twisted ethylene while Figure 2 illustrates the *trans*-cyclooctene geometry.

The Gaussian basis set used in these calculations was selected to be roughly equivalent to the basis used previously by Buenker, Peyerimhoff, and Kammer.¹³ This basis consists of a (9s,5p) carbon basis set contracted to a [4s,2p] set as defined by Dunning,¹⁴ augmented with s and p diffuse basis functions each with $\alpha = 0.02$ for the Gaussian exponential parameter, and a (5s) hydrogen atom basis set contracted to a single function¹⁵ and scaled by 1.414. The complete molecular basis set contains 32 functions.

With this molecular basis set, Hartree-Fock self-consistent field (SCF) wave functions were computed for the closed-shell ground state at each geometry. The orbital energies from these calculations are listed in Table I. The SCF molecular orbitals (MO) were used to transform the atomic orbital (AO) basis integrals to the MO basis representation which was used for all the states considered in the subsequent CI calculations regardless of the base configuration occupancy. Using only ground-state orbitals in this way, instead of determining new SCF MOs for each state, should not be a serious approximation since all valence single and double excitation configurations from each base occupancy were included in the CI wave functions. The four molecular orbitals representing the two core and two virtual carbon 1s orbitals were not included in the transformation or the CI calculations.

After the transformation, the CI calculations were completed using only the D_{2h} irreducible representations A_g , B_{1u} , B_{1g} , and B_{3u} for planar ethylene, and the D_2 irreducible representations A , B_1 , and B_3 for twisted ethylene. These representations are chosen since they correspond to the symmetry of the ground state and excited states of the ($\pi \rightarrow \pi^*$), ($\pi \rightarrow 3s$),

Table I. Ethylene Orbital Energies

Geometry: Symmetry group:	Planar ^a <i>D</i> _{2h}	10° twisted ^a <i>D</i> ₂	<i>trans</i> -Cyclooctene ^b <i>C</i> ₂			
Orbital designation and orbital energy, au	1a _g (1s + 1s)	-11.2395	1a	-11.2398	1a	-11.2399
	1b _{1u} (1s - 1s)	-11.2379	1b ₁	-11.2382	1b	-11.2383
	2a _g (2s + 2s)	-1.0358	2a	-1.0360	2a	-1.0409
	2b _{1u} (2s - 2s)	-0.7918	2b ₁	-0.7919	2b	-0.7901
	1b _{2u} (p _y + p _y)	-0.6465	1b ₂	-0.6460	3b	-0.5824
	3a _g (p _z - p _z)	-0.5893	3a	-0.5845	3a	-0.5824
	1b _{3g} (p _y - p _y)σ _{CH}	-0.5031	1b ₃	-0.5054	4a	-0.5103
	1b _{3u} (p _x + p _x) π	-0.3729	2b ₃	-0.3703	5a	-0.3619
Total SCF energy, au		-78.0064		-78.0041		-77.9865

^a *R*_{CC} = 1.34 Å, *R*_{CH} = 1.086 Å, ∠CCH = 121.2°, ∠HCH = 117.6°. See ref 10. ^b *R*_{CC} = 1.338 Å, *R*_{CH} = 1.086 Å, ∠CCH = 121.2°, ∠CCH' = 117.9°, ∠H'CCH' = 138°, ∠HCCH = 177.6°. See ref 11.

Table II. Base Occupancies and Number of Configurations Used in CI Calculations on Ethylene

Geometry: Ground state occupancy:	Planar 1a _g ² 1b _{1u} ² 2a _g ² 2b _{1u} ² 1b _{2u} ² 3a _g ² 1b _{3g} ² 1b _{3u} ² σ _{CH} π	Twisted 1a ² 1b ₁ ² 2a ² 2b ₁ ² 1b ₂ ² 3a ² 1b ₃ ² 2b ₃ ² σ _{CH} π	<i>trans</i> -Cyclooctene structure 1a ² 1b ² 2a ² 2b ² 3b ² 3a ² 4a ² 5a ² σ _{CH} π
Base occupancies ^a and number of generated con- figurations ^b for each symmetry	Ground state 1b _{3u} → 2b _{3u} , 2b _{3g} , 3b _{3u} , 3b _{3g} , 4b _{3g} 9241	Ground state 2b ₃ → 3b ₃ , 4b ₃ , 5b ₃ , 6b ₃ , 7b ₃ 18,819	Ground state 4,491
¹ A _g		¹ A	A
¹ B _{1g}	1b _{3u} → 2b _{2u} , 1b _{2g} , 2b _{2g} 1b _{3g} → 2b _{2u} , 1b _{2g} , 2b _{2g} 9775	¹ B ₁	A
¹ B _{1u}	1b _{3u} → 2b _{2u} , 1b _{2g} , 2b _{2g} 1b _{3g} → 2b _{2u} , 1b _{2g} , 2b _{2g} 9833	¹ B ₃	B
¹ B _{3u}	1b _{3u} → 4a _g , 5a _g , 6a _g 7046		A
			B
			A

^a Base occupancies are indicated by an orbital excitation from the ground-state occupancy. ^b All single and double excitations were generated from each base occupancy.

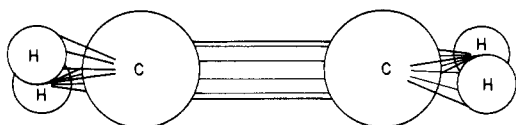


Figure 1. Twisted ethylene geometry. *R*_{CC} = 1.34 Å, *R*_{CH} = 1.086 Å, ∠CCH = 121.2°, ∠HCCH = 170°. See ref 10.

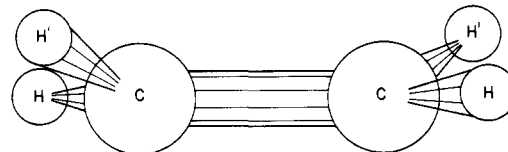


Figure 2. *trans*-Cyclooctene geometry for ethylene. *R*_{CC} = 1.338 Å, *R*_{CH} = 1.086 Å, ∠H'CC = 117.9°, ∠HCC = 121.2°, ∠HCCH = 177.6°, ∠H'CCH' = 138°. See ref 11 and 12.

and ($\pi \rightarrow p_y$) transitions in ethylene. All of the irreducible representations, A and B, for the *C*₂ group symmetry of *trans*-cyclooctene must be considered for the third geometry, owing to its lower symmetry, and this brings in a state of ¹B_{2g} symmetry in the planar case. Configuration selection for the *D*_{2h} and *D*₂ groups included base occupancies for the dominant *D*₂ configurations in the low-lying states of interest, plus all single and double excitation configurations from these base occupancies. The *C*₂ group calculations with *trans*-cyclooctene geometry were not done in this fashion since the lower symmetry leads to a relatively large number of important base occupancies and the single and double excitation configuration space generated from all of them of a given symmetry would be too large to handle economically. Each state was therefore treated individually with configuration spaces generated from those base occupancies which were dominant for a single state. Table II shows the base occupancies and the number of configurations used in the CI calculations for each symmetry in this case. The base occupancies involve an excitation of the ground-state π electron in each case except in the ¹B_{1u} (*D*_{2h}), ¹B₁ (*D*₂), and ¹B (*C*₂) cases where there was a low-lying solution involving an excitation from the next lower ground state

orbital. This orbital is constructed from antibonding P_y carbon functions and is bonding to the hydrogen atoms. The bonding nature of this orbital has led to its description as the σ_{CH} orbital by other authors.⁹ A core basis of 50 configurations is selected from the configurations of Table II for exact treatment in each calculation.^{7,8} The selection uses first-order perturbation theory to find the most important configurations mixing with the dominant configurations for the states of interest in a given calculation. The remainder of the configurations are mixed into the final CI wave function by using the iterative perturbation scheme of Segal and Wetmore.^{7,8}

III. Results and Calculated Transition Properties

A. Ethylene Oscillator Strengths and Rotatory Strengths. The general intensity relationships for the oscillator strength and rotatory strength of an electronic transition are given in ref 5. Three forms for the oscillator strength were used. These are the dipole length f_{ov}^r , dipole velocity f_{ov}^v , and the mixed dipole f_{ov}^{ν} , where o indicates the ground electronic state and ν indicates an excited state. There are two forms for the rotatory

Table III. CI Results on Ethylene

State	Planar group designation	Geometry	Excitation energy, eV	Oscillator strengths			Rotatory strength, cgs $\times 10^{-40}$		$\langle x^2 \rangle$, au ²	$\langle r^2 \rangle$, au ²	Magnitude of tail configurations in CI eigenvector, %
				f_{ov}^x	f_{ov}^y	f_{ov}^z	R_{ov}^x	R_{ov}^y			
Ground state	1A_g	0°							12.4	83.9	6.0
		10°							12.4	83.8	6.1
		TCO									6.6
$\pi \rightarrow 3s$	$^1B_{3u}$	0°	7.30	0.115	0.098	0.106	0.0	0.0	25.0	122.8	6.0
		10°	7.24	0.109	0.094	0.101	-20.0	-21.6	25.3	123.0	6.4
		TCO	6.97	0.097	0.082	0.089	-33.5	-36.6			7.1
$\pi \rightarrow 3p_y$	$^1B_{1g}$	0°	7.92	0.0	0.0	0.0	0.0	0.0	22.1	141.5	6.5
		10°	7.88	0.014	0.007	0.010	-2.9	-4.2	22.2	140.7	7.0
		TCO	7.62	0.015	0.005	0.008	0.33	0.73			7.1
$\pi \rightarrow \pi^*$	$^1B_{1u}$	0°	8.33	0.430	0.204	0.296	0.0	0.0	27.8	120.7	6.9
		10°	8.14	0.334	0.171	0.239	-128.	-179.	24.0	110.8	7.4
		TCO	7.54	0.274	0.150	0.202	-153.	-215.			7.7
$\pi \rightarrow 3d\sigma$	2^1B_{3u}	0°	8.80	0.041	0.034	0.037	0.0	0.0	22.1	161.8	6.2
		10°	8.73	0.038	0.033	0.035	-11.5	-12.3	22.4	162.1	6.5
		TCO	8.46	0.053	0.030	0.040	-17.8	-23.8			7.3
$\sigma_{CH} \rightarrow \pi^*$	2^1B_{1g}	0°	8.90	0.0	0.0	0.0	0.0	0.0	15.8	86.3	7.2
		10°	8.96	0.068	0.026	0.041	92.5	149.	22.8	104.2	8.3
		TCO	9.71	0.353	0.173	0.247	180.	263.			8.8
$\pi \rightarrow 3p_\sigma$	$^1B_{2g}$	TCO	7.70	0.014	0.008	0.011	-1.03	-1.45			7.0
$\pi \rightarrow 3p_x$	2^1A_g	TCO	7.90	0.022	0.0001	0.002	0.16	2.2			7.2

strength which measures the circular dichroism for an electronic transition. These are the dipole length R_{ov}^x , and the dipole velocity R_{ov}^y forms. However, the dipole length form R_{ov}^z of the rotatory strength is, in general, not invariant to a translation of the coordinate system origin when approximate wave functions are used, and may not be reliable for computational purposes. As a check, all forms of these intensity relationships are reported to indicate the level of approximation contained in the wave functions and to indicate the reliability of the rotatory strength calculations.

Values for the oscillator strength and rotatory strength calculated for important low-lying transitions in ethylene and distorted ethylene are given in Table III. These transition properties are computed from the 50 core configurations selected as a starting point for the perturbation theory treatment which involves the remainder of the configuration space. Therefore, the calculated properties do not directly account for the effect of the tail configurations (configurations other than the 50 core configurations) which were omitted for reasons of economy. Truncation of the CI eigenvectors in this fashion should not be a serious approximation for present purposes, since the tail configurations do not contribute more than 8.8% to the magnitude of the eigenvector in the worst case. This indicates that, for the worst case, the truncation error should be on the order of 18%. In most cases the truncation was about 7% and the corresponding error in the properties could be as much as 14%. The experimental rotatory strengths may well be in error by this amount owing to the difficulty in extracting them from overlapping bands. Furthermore, rotatory strengths are quite sensitive to the precise molecular environment of the chromophoric group. Since we have used model systems, the best that can be hoped for is agreement with experiment with respect to order of magnitude and sign. A more extensive calculation of this quantity is therefore unwarranted.

B. Circular Dichroism Spectrum of *trans*-Cyclooctene. The distorted ethylene spectrum in Table III must be compared to the experimental spectra of twisted monoolefins, in this case *trans*-cyclooctene. The absorption and circular dichroism spectrum of *trans*-cyclooctene has been reported by Mason and Schnepf.¹ In order to make this comparison more quantitative, and to analyze the effect of the saturated hydrocarbon substituents on the excitation energies, additional calculations

on *trans*-substituted ethylene were performed. These calculations used a minimal STO-4G basis set¹⁶ on the carbon and hydrogen atoms with the addition of the s and p Rydberg-like ($\alpha = 0.02$) functions on the olefinic carbons and the molecules ethylene and *trans*-2-butene were treated in this basis set. In each case, the molecule was given the geometry from ref 11 for the corresponding atoms in *trans*-cyclooctene. The basic approximation involved here is that a more extensive basis set than STO-4G is necessary to calculate the excitation energies of twisted ethylene, but this lower level basis is adequate for the calculations of the *shifts* in state energies due to the presence of a saturated hydrocarbon moiety. These shifts were calculated with all single and double excitation configurations from the ground-state A configuration for A states and the ($\pi \rightarrow 3p\sigma$) B configuration for B states. The shifted ethylene spectrum is calculated and compared to the experimental *trans*-cyclooctene spectrum in Table IV, which also compares the calculated and observed rotatory and intensity parameters. Some additional calculations were carried out at the STO-4G level on *trans*-3-hexene, but the shifts from *trans*-2-butene were very small, so that it was concluded that the perturbation introduced by the methyl groups in *trans*-2-butene is sufficient to model *trans*-cyclooctene. Table IV shows that the ethylene spectrum is red shifted by 1.0–1.5 eV in *trans*-cyclooctene owing to the effects of *trans* substitution on ethylene.

IV. Discussion

trans-Cyclooctene exhibits two principal dichroic bands. The first of these, with a maximum at 6.32 eV in both rotation and absorption, is assigned to the V state of ethylene, ($\pi \rightarrow \pi^*$), which is calculated at 6.18 eV in the TCO geometry as shown in Table IV. The calculated rotatory strength, -150×10^{-40} cgs, agrees in both sign and order of magnitude with experiment, while the calculated oscillator strength, 0.202, is consistent with the strong absorption observed. While Yaris et al.³ find that this peak represents the superposition of two states, we find, in agreement with all other calculations and the assignment of Mason and Schnepf,¹ that the feature is due to the V state alone.

There has been much discussion in the literature about the degree of Rydberg character in the V state of ethylene.^{13,17-22} Large-scale all valence electron calculations have given mixed results as to the character of this transition.^{20,22} The value of

Table IV. CI Results for Spectral Shift from Ethylene to *trans*-2-Butene

Transition	Excitation energies, eV			TCO geometry		Rotary strength		Oscillator strength calcd	Exptl ϵ
	Ethylene STO-4G + Ryd	<i>trans</i> -2-Butene STO-4G + Ryd	Ethylene DZ + Ryd	<i>trans</i> -Cyclo-octene calcd ^a	<i>trans</i> -Cyclo-octene exptl	<i>trans</i> -Cyclo-octene, 10 ⁻⁴⁰ cgs calcd	exptl ^b		
$\pi \rightarrow 3s$ $^1B_{3u}$	6.07	5.04	6.97	5.94	5.96	-33.5		0.089	Shoulder 2300
$\pi \rightarrow 3p_{\sigma}$ $^1B_{2g}$	6.48	4.98	7.70	6.20		-1.0		0.011	
$\pi \rightarrow \pi^*$ $^1B_{1u}$	7.51	6.15	7.54	6.18	6.32	-153	-92 ^c	0.202	Broad max 7600
$\pi \rightarrow 3p_x$ 2^1A_g	6.99	5.48	7.90	6.39		0.2		0.002	
$\pi \rightarrow 3p_y$ $^1B_{1g}$	6.59	5.59	7.62	6.62		0.3		0.008	
$\pi \rightarrow 3d_{\sigma}$ 2^1B_{3u}	7.66	6.29	8.46	7.09	6.95-7.08	-17.8		0.040	Structure 8000
$\sigma \rightarrow \pi^*$ 2^1B_{1g}	12.37	10.64	9.71	7.98	7.95	180	88 ^c	0.247	

^a Ethylene DZ + Rydberg shifted; see text. ^b See ref 1. ^c The signs of the rotatory strength have been made to correspond to the (-) enantiomer of *trans*-cyclooctene.

$\langle x^2 \rangle$ for the $^1(\pi \rightarrow \pi^*)$ state obtained here for the planar ethylene geometry is 27.8 au.² This is in basic agreement with the latest calculations by other workers.^{21,22} The absorption maximum for the V state in ethylene lies at 7.66 eV,¹⁰ while most calculations, including ours, place the vertical transition energy at about 8.3 eV. It has therefore been argued that the observed ethylene V state spectrum represents a nonvertical transition.²¹ The fact that this state, which we calculate at 8.33 eV in planar ethylene, is calculated at 6.18 eV at the *trans*-cyclooctene geometry including the shift due to the saturated hydrocarbon geometry would seem to lend strength to the belief that the calculated vertical V state transition energy is, in fact, essentially correct.

The second major dichroic band is observed at 7.95 eV.¹ It displays a large extinction coefficient and a large rotational strength which is opposite in sign to that of the 6.32-eV band. These observations are well correlated with our calculations for the transition to the ($\sigma_{CH} \rightarrow \pi^*$), the 2^1B_{1g} state which, as shown in Table IV, is calculated to be at 7.98 eV, to have a large rotatory strength opposite in sign to the V state, and to have a large oscillator strength. This assignment is in agreement with that of all previous theoretical work and ref 1. This state is calculated to be at 8.90 eV in planar ethylene and is dipole forbidden but magnetically allowed, thus accounting for the large rotatory strength on twisting.

The ($\pi \rightarrow 3s$), $^1B_{3u}$ Rydberg transition is calculated to lie at 5.94 eV in *trans*-cyclooctene and 7.30 eV in planar ethylene. The calculated rotatory strength is of the same sign as that of the V state and roughly one-fifth as large while the oscillator strength is 0.089. This is in good agreement with the shoulder observed in *trans*-cyclooctene in both CD and absorption at 5.96 eV, the CD being of the same sign as the 6.32-eV band. This transition is observed in ethylene itself at 7.11 eV.¹⁰

The experimental CD and absorption spectra of *trans*-cyclooctene exhibit structure to the blue of the ($\pi \rightarrow \pi^*$) state from 6.95 to 7.08 eV. The rotation of at least one of these three weak features is of the same sign as the V state, but smaller in magnitude. The $^1(\pi \rightarrow 3d_{\sigma})$ transition is calculated to lie at 7.09 eV, in good agreement with this observation. The calculated rotatory strength is roughly one-ninth that of the V state and of the same sign, while the oscillator strength is 0.04. This state is calculated to lie at 8.80 eV in planar ethylene but is dipole forbidden and the importance of this state to the CD spectrum has not previously been recognized. This, however, is the spectral region in which the $^1(\pi \rightarrow 4s)$ state would be expected to lie. This state cannot be represented in our calculation since we did not incorporate 4s Rydberg basis functions. The spectrum may therefore represent the superposition of these two states.

The previous theoretical treatments have variously been able to piece together the qualitative aspects of the CD spectrum of *trans*-cyclooctene. Yaris et al. were not able to correctly

account for the sign and the magnitude of the $^1(\pi \rightarrow \pi^*)$ rotatory strength, and attributed the rotation to the ($1b_{3u} \rightarrow 2b_{2u}$) $^1(\pi \rightarrow \gamma)$ transition. We do not agree and, in fact, our $^1(\pi \rightarrow \gamma)$ transition does not have a large rotatory strength. A number of comments about this state are in order. While $^1(\pi \rightarrow 3p_y)$ is calculated to be on the red side of $^1(\pi \rightarrow \pi^*)$ in twisted ethylene itself, the perturbation shifts it to the red far less than it does $^1(\pi \rightarrow \pi^*)$ so that it lies to the blue of $^1(\pi \rightarrow \pi^*)$ in *trans*-cyclooctene. This is in agreement with the spectra of α - and β -pinene, planar double bonds, where the dichroism is induced by an asymmetric carbon rather than an internal screw axis. In these cases, a third CD band appears to the blue of $^1(\pi \rightarrow \pi^*)$ which has been ascribed to the $^1(\pi \rightarrow 3p_y)$ state.¹ The weak rotatory strength of this state in *trans*-cyclooctene is somewhat surprising, since this state would be expected to have a sizable transition magnetic moment and the transition electric moment borrowed from the intensely absorbing $^1(\pi \rightarrow \pi^*)$ state on twisting is expected to be parallel to the transition magnetic moment. The small rotatory strength exhibited by $^1(\pi \rightarrow 3p_y)$ in our calculation is due to the fact that it is a Rydberg state of large dimension ($\langle y^2 \rangle = 57.9 \text{ au}^2$) so that the transition magnetic moment is small owing to the extended nature of the upper state. The mixing with the $^1(\pi \rightarrow \pi^*)$ is primarily with the Rydberg component of that state, so that the transition electric dipole moment is also small. This may differ from the behavior of this state in situations where the double bond is planar and dichroism is induced by an asymmetric carbon. A moderate increase in valence character of the state would sharply increase the rotatory strength, thus accounting for the third band observed in CD. This point is currently under study.

The calculations reported here account for the bands observed in the CD spectrum of *trans*-cyclooctene with respect to energy, rotatory strengths, and oscillator strength. Given the sensitivity of rotatory strengths to molecular environment, this calculation appears to be in good agreement with the observed facts, although the almost quantitative agreement with experimental transition energies seems better than could be hoped for. Nevertheless, given the extensive agreement between these calculations and experiment, we believe that this work firmly establishes the assignment of the *trans*-cyclooctene CD spectrum. We intend to extend the techniques used here to other chromophoric groups and to molecules exhibiting magnetic circular dichroism spectra.

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Theoretical Studies of the Cubane Molecule

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Abstract: Molecular orbital calculations were performed on cubane using ab initio STO-3G, SCF-X α , MINDO/3, and INDO methods. The photoelectron ionization energies were calculated from the above by Koopmans' theorem and, in addition, by Slater's transition-state approximation in the SCF-X α method. An analysis of the molecular orbital energy splitting pattern has been made utilizing the concept of interactions between symmetry-adapted combinations of localized CC and CH orbitals.

I. Introduction

The present study of cubane, (CH)₈ (Figure 1), concludes a set of investigations on the three (CH)_n molecules whose carbon skeletons form perfect solids, the others being tetrahedrane ($n = 4$)^{2a} and dodecahedrane ($n = 20$).^{2b} Of the three, cubane is especially interesting to chemists since it has already been synthesized^{2c} and its O_h point-group symmetry confirmed.^{2d} However, despite these facts cubane has received surprisingly little theoretical consideration.³ This paper furnishes molecular orbital calculations at the ab initio STO-3G,⁴ SCF-X α ,^{5,6} MINDO/3,⁷ and INDO⁸ levels of approximation and applies the SCF-X α method in Slater's transition state approximation to the calculation of the cubane valence-shell vertical ionization energies. The latter may be compared with the photoelectron spectrum,⁹ as yet incomplete.

An important consequence of the high cubane point-group symmetry is the fact that several of the molecular orbitals are symmetry determined in a minimal basis set treatment. This invites a novel analysis of the molecular orbital splitting pattern in terms of interactions between localized CC and CH orbitals (LMO's), of the Edmiston-Ruedenberg¹⁰ type, for example, which offers some interesting insights into cubane in particular and hydrocarbons generally.

II. Molecular Orbital Descriptions

A. General Aspects. The present molecular orbital studies utilize a minimal basis of atomic orbitals (AOs), i.e., C 1s, 2s, and 2p and H 1s orbitals. The MINDO/3 and INDO methods ignore the C 1s cores, as we shall do in the present discussion. The three 2p orbitals of each carbon can be chosen to be 2p_r pointing radially outward from the molecular midpoint and a pair of 2p_t tangential orbitals perpendicular to 2p_r. This simplifies the reduction into irreducible representations of the

full atomic orbital reducible representation. Each of the three sets of eight radial functions (C2s, C2p_r, and H1s) leads to a_{1g}, t_{2g}, t_{1u}, and a_{2u} symmetry adapted linear combinations; the 16 AO tangential set furnishes e_g, t_{1g}, t_{2g}, e_u, t_{1u}, and t_{2u} symmetry orbitals. Thus, in toto, the full valence AO basis contains in type (and number) a_{1g}(3), a_{2u}(3), e_g(1), e_u(1), t_{1g}(1), t_{2g}(4), t_{1u}(4), and t_{2u}(1) symmetry orbitals.

The ground-state molecular orbital configuration is easily determined by projecting the 12 CC bent σ bonds onto the irreducible representations of O_h , to give a_{1g}(1), e_g(1), t_{2g}(1), t_{1u}(1), and t_{2u}(1) orbitals; projecting out the eight linear combinations of CH σ bonds gives a_{1g}(1), t_{2g}(1), t_{1u}(1), and a_{2u}(1) orbitals. Two important points follow. (1) The e_g and t_{2u} orbitals that occur only once in the occupied set are symmetry-determined combinations of CC LMOs with no CH admixture (they are also symmetry-determined combinations of 2p_t orbitals with no C2s admixture). (2) The a_{2u} orbital is derived from a linear combination of CH LMOs with no CC LMO contribution. Thus, cubane represents the unusual situation where a saturated hydrocarbon has a molecular orbital which is solely CC bonding and another which is solely CH bonding. (By contrast, tetrahedrane and dodecahedrane have symmetry-determined molecular orbitals which are linear combinations of CC LMOs alone, but no orbitals formed exclusively from CH LMOs).

B. SCF-X α Calculations. Before citing the results, it is necessary to give some particulars of the SCF-X α calculations performed here since the parameters of the method have not been standardized. For a general description of the method, its philosophy, and applications, the reader is referred to the papers of Slater⁵ and Johnson.⁶ The quantities specific to the present calculations are (1) the ratio of C to H atomic sphere radii, r_C/r_H , (2) the percent overlap between atomic spheres, (3) the exchange-term prefactors, α_C and α_H for the atomic,