type II zinc atoms, which are tetrahedrally coordinated to two chlorine and two sulfur atoms. The lattice water is not coordinated, but the two water protons are hydrogen bonded to Cl(1) and one symmetry related Cl(2) atom (Table V, Figure 2).

Table V. Geometry of the Lattice Water and Hydrogen Bonding[a]

Bond length, Å		Bond angle, deg	
O–H(1O)	0.98 (16)	H(1O)–O–H(2O)	130 (15)
O–H(2O)	0.93 (16)		
H(1O)–Cl(2″)[b]	2.31 (16)		
H(2O)–Cl(1)	2.44 (16)		

[a] See footnotes *a* and *b*, Table I. [b] Cl(2″) chlorine atom related to Cl(2) by symmetry (x, $-\frac{1}{2} - y$, $\frac{1}{2} + z$).

The Zn–S and Zn–N distances in the present structure are normal.[9,10] The bond angles N(1)–Zn–S(1) (110.8°) and N(2)–Zn–S(2) (112.4°) are close to the tetrahedral value, while the bond angles N(1)–Zn–N(2) (87.0°), N(1)–Zn(I)–S(2) (91.8°), and N(2)–Zn(I)–S(1) (91.6°) are similar to the N–Zn–N or N–Zn–S angles found in other zinc complexes containing five-membered chelate ring systems.[10] The tetradentate chelation, however, results in an unusual coordination in which one side of the Zn(I) atom is very open, the S(1)–Zn(I)–S(2) angle being 148.1° (Figure 1). The steric strain that causes this severe distortion from tetrahedral geometry also results in a difference of 0.06–0.07 Å (15–18σ) between the Zn(I)–S and Zn(II)–S bond lengths (Table III). In addition, the dihedral angle between the planes defined by N(1)–Zn(I)–N(2) and S(1)–Zn(I)–S(2) is 75.2 (3)°, compared to the idealized tetrahedral value of 90° or to the unconstrained dihedral angle of 88.1 (1)° between the Cl(1)–Zn(II)–Cl(2) and S(1)–Zn(II)–S(2′) planes.

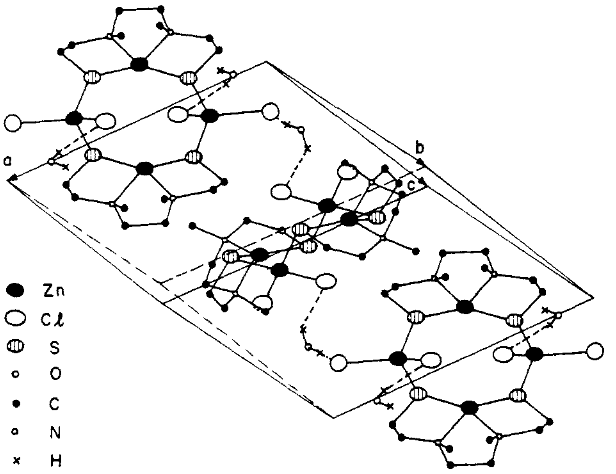

Figure 2. Packing diagram of $[Zn_2Cl_2L]_2 \cdot 2H_2O$ showing hydrogen bonding between the lattice water and chlorine atoms.

The tendency for mercaptide sulfur to form three bonds and bridge metal ions is manifest in the present complex. If the two sulfur atoms of one ZnL unit (S···S bite 4.39 Å) were to bridge to a second zinc atom, an impossibly short nonbonded Zn···Zn contact distance would result. Instead, the two sulfur atoms bridge to different zinc atoms, the result being the observed tetranuclear array.

The present structure clearly shows the constraining stereochemical properties of the tetradentate ligand, providing important information relevant to the current investigation of iron derivatives.[1]

Acknowledgment. We are grateful to the National Institutes of Health for support of this research under Grant GM 16449.

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[9] L. F. Lindoy, D. H. Busch, and V. Goedken, *Chem. Commun.*, 683 (1972).

[10] (a) A. Mawby and H. M. N. H. Irving, *Anal. Chim. Acta*, **55**, 269 (1971); (b) A. Mawby and H. M. N. H. Irving, *J. Inorg. Nucl. Chem.*, **34**, 109 (1972).

A Theoretical Study of the Perturbation of Hydrocarbon Chromophores by Cyclopropyl

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Abstract: Transition energies and oscillator strengths have been calculated for the lower excited states of cyclopropane, benzene, and various conformers of vinylcyclopropane and phenylcyclopropane using an SCMO–CI technique based upon intermediate neglect of differential overlap (INDO). Reasonable agreement with experiment was obtained for cyclopropane and benzene. The phenylcyclopropane spectrum is found to be relatively insensitive to the dihedral angle, as has been demonstrated experimentally. In vinylcyclopropane conformational dependence of the spectrum was found, but only within a rather narrow range (60–120°) of the dihedral angle. This result is in keeping with the experimental observation that the uv maximum is only moderately affected by alkyl substitution on the vinyl group. The 1-methyl-1-vinylcyclopropanes, however, exhibit hypsochromic shifts relative to the unmethylated derivatives. This implies that 1-methyl substitution is necessary to significantly populate any but the s-trans conformation.

There is abundant experimental evidence for the conformational dependence of cyclopropyl interaction with neighboring p orbitals, derived primarily from solvolytic studies.[1] The conclusion drawn regarding

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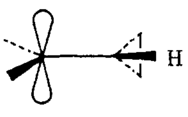
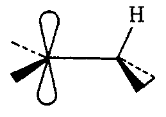
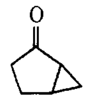
[1] (a) B. R. Bree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970), and the references cited therein; (b) see also ref 4 of L. D.

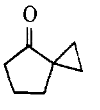
the conformational preferences are that the bisected conformation (Ia) is the favorable one, relative to the symmetric conformation (Ib). It has been anticipated

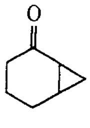

Ia ($\theta = 0°$)

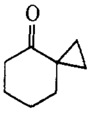

Ib ($\theta = 90°$)

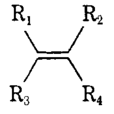
that this conformational preference should manifest itself in the ultraviolet spectra of suitably substituted chromophores. It is well documented that cyclopropyl substitution produces a bathochromic shift in the spectra of monoolefins,[2] ketones,[3] benzene,[4] dienes,[5a] and various β-substituted-α,β-unsaturated carbonyl derivatives.[5b,c] The early evidence for a conformational dependence of the auxochromic effect of the cyclopropyl group was derived from studies of 2-phenylcyclopropylcarboxamides by Perold.[6] These studies showed that the band near 220 nm in these compounds disappeared when phenyl was replaced by *o*-tolyl. In the studies of rigid, presumably unstrained, cyclopropyl ketones (II → V),[3] the spectral evidence, based on the shifts in the absorption maximum for the $\pi \rightarrow \pi^*$ transition[7] of the ketone, supports the idea of the bisected conformation being the one in which maximum conjugative interaction can occur. (Spurious maxima are known to occur in this region that arise from instrument problems. The spectra of the cyclopropyl ketones, the vinylcyclopropanes, and the β-cyclopropyl acrylic esters were taken under conditions such that these artifacts are avoided.) These results are in line with the early predictions by Walsh.[8] An important feature of the results obtained by Dauben and Berezin is the indication that the auxochromic effect of the cyclopropyl group is quite sensitive to substitution on the group itself.[3a] This makes it somewhat difficult to factor out the basic cyclopropyl effect, as the basic systems necessarily incorporate some such substitution. In an effort to gain insight into the cyclopropyl auxochromic effect, some relatively simple systems (VI) were studied by Heathcock and Poulter[2] and Jorgenson and Leung.[5c] In these two studies, the effect of the cyclopropyl group was evaluated relative to a compound having isopropyl in the same position. The working hypothesis was that the alkylation pattern of the double bond should distort the isopropyl group from the equilibrium conformation in roughly the same manner as the cyclopropyl group, and the relative spectral shift should show a change upon successive substitution if the conformational dependence is a reality. The somewhat surprising result obtained was that in the case of the simple olefins the relative shift was fairly constant, while in the case of the acrylic esters the spectral shift varied over a range of some 30 nm. This, coupled with the earlier results of Goodman and Eastman,[4b] seems to imply that in hydrocarbon systems there is little conformational dependence of the auxochromic effect of the cyclopropyl group. This is, to our mind, a curious result and was the impetus for the study that we report herein.


λ_{max}^{HOH} 197 nm
II


λ_{max}^{HOH} 206 nm
III


λ_{max}^{HOH} 209 nm
V


λ_{max}^{HOH} 200 nm
IV


R_1 = *i*-Pr or *c*-Pr
VIa, R_2, R_3, R_4 = H or alkyl
VIb, R_2 = COOEt; R_3, R_4 = H or alkyl
VIc, R_4 = COOEt; R_2, R_4 = H or alkyl

In order to understand the preference for the bisected conformation, we must consider the molecular orbital interactions that couple a cyclopropyl group to a π system. Considering the problem from the point of view of perturbation theory, the interactions that would dominate the second-order energy correction are outlined in Figure 1. (The use of equal coefficients is a matter of convenience only!) Confining our attention to the electronic ground state for the moment, the 3e′ level for the cyclopropyl system would be the highest occupied level. Its interaction with the π level of another fragment will result in the formation of a symmetric (in-phase) and antisymmetric (out-of-phase) combination between the 3e′ and π levels. In the case of a cyclopropyl carbocation, this interaction should be a large, stabilizing, interaction as the lower combination of these two orbitals will be the only one occupied. For neutral systems, such as phenylcyclopropane or vinylcyclopropane, both of these new levels will be occupied and one would anticipate that the stabilization would be severely diminished. Using the original INDO specification of Pople, *et al.*,[9] we have calculated the relative energies for a variety of conformations of cyclopropyl carbocation, phenylcyclopropane, and vinylcyclopropane (see Figure 2). In keeping with our analysis, the two neutral molecules have reduced barriers relative to

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Kispert, C. Engleman, C. Dyas, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **93**, 6948 (1971).

[2] C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968).

[3] (a) W. G. Dauben and G. H. Berezin, *ibid.*, **89**, 3449 (1967); (b) E. M. Kosower and M. Ito, *Proc. Chem. Soc. (London)*, **95** (1962).

[4] (a) M. T. Rogers, *J. Amer. Chem. Soc.*, **79**, 2544 (1947); (b) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

[5] (a) S. Julia, M. Julia, and P. Graffin, *Bull. Soc. Chim. Fr.*, 3218 (1964); (b) S. Julia, M. Julia, S. Y. Tehen, and P. Graffin, *ibid.*, 3207 (1964); (c) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).

[6] G. W. Perold, *J. S. Afr. Chem. Inst.*, 6, 29 (1953); **8**, 107 (1955); **10**, 11 (1957); *Chem. Abstr.*, **48**, 4314c (1954); 36, (1956); **59**, 1074 (1958).

[7] The referees have questioned this assignment for the uv maximum in this region. One has suggested an $n \rightarrow \sigma^*$ assignment; another has suggested that it is $\pi \leftrightarrow \sigma$ in nature. While it is true that one of these is the probable assignment in simple carbonyl compounds (*e.g.*, formaldehyde and acetone), it is our understanding that in conjugated and quasi-conjugated carbonyl compounds this is in fact the $\pi \rightarrow \pi^*$ transition.

[8] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[9] (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, Chapter 3; (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

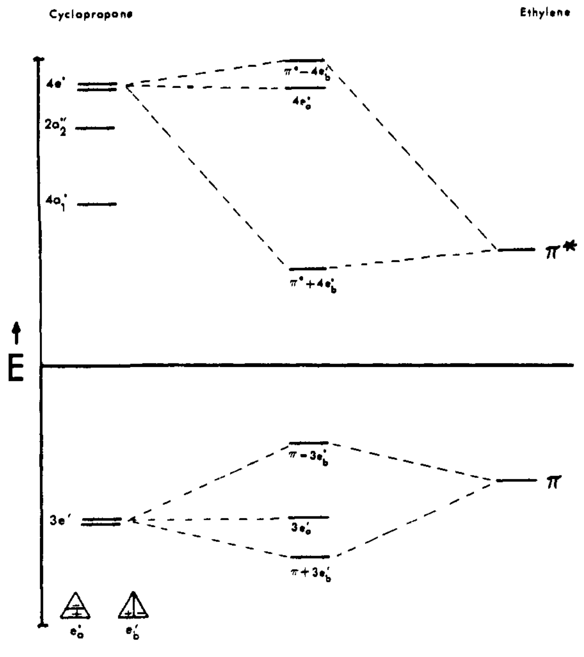

Figure 1. Diagrammatic representation of the dominant orbital interactions coupling cyclopropane to the π system of ethylene.

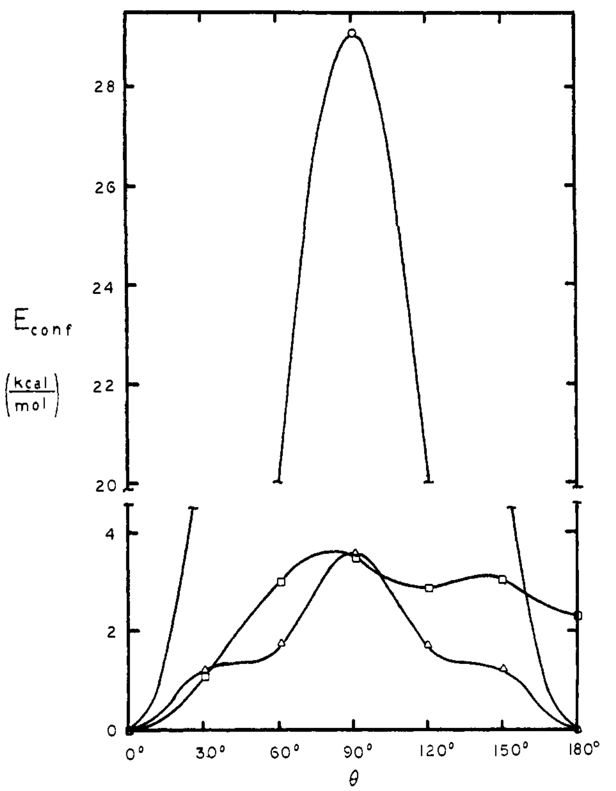

Figure 2. Conformational energies as a function of the dihedral angle for cyclopropyl carbocation (○), phenylcyclopropane (△), and vinylcyclopropane (□).

the cyclopropyl carbocation. While the conformational energy of the latter system showed essentially a cos 2θ dependence, the additional features appearing in the energy profiles for phenylcyclopropane and vinylcyclopropane merit some comment. In phenylcyclopropane, the ortho hydrogen steric effect appears as a perturbation on the simple potential energy curve at θ = 30 and 150°. In vinylcyclopropane (s-trans = 0°) we observed a three-well potential such has been previously proposed on the basis of nmr studies.[10] As we did not minimize the energy with respect to internal coordinates, we probably do not obtain the proper energy relationship between the s-cis conformation and the gauche conformation. Nonetheless, these overall trends confirm the type of analysis that we have given. Further, in considering the barrier heights predicted for cyclopropyl carbocation (~29 kcal/mol) *vs.* vinylcyclopropane (~3.5 kcal/mol), we find their *relative* magnitudes in good agreement with the experimental results (~1.0 kcal/mol for the latter;[10] 12-14 kcal/mol for tertiary cyclopropyl carbocations[11]).

The overall conclusions to be drawn from this are that these levels we have designated "b" may interact with the π system quite well in the bisected conformation, but interactions in the symmetric conformation are poor. The interesting aspect of this is that such arguments apply as well to π^* interacting with 4e' (Figure 1), and we would anticipate on this simple basis that there should be a conformational dependence of the auxochromic effect of the cyclopropyl group in *any* cyclopropyl-substituted π system. The point which we shall attempt to resolve in the subsequent sections of this paper is the question of the magnitude, and hence the experimental observability, of such an effect in the two prototype hydrocarbon systems.

Results and Discussion

The results we report herein have been obtained from all-valence-electron SCMO-CI calculations including up to 100 singly excited configurations. The SCMO's were obtained *via* calculations within a modified INDO framework.[12] In order to develop a suitable basis for comparisons, we have calculated the spectra for cyclopropane itself and benzene.[13]

The early spectral calculations on cyclopropane and its derivatives[14] usually included only the carbon-carbon binding orbitals as defined by the Walsh model.[8] The most recent calculations are included in an experimental and theoretical study of electronic excitations in saturated hydrocarbons.[15] The theoretical aspects of this work were based on a C-C and C-H bond orbital model appropriate to normal alkanes. Our method, though semiempirical in nature, permits the use of a complete valence-shell basis set and assumes no localized bonds. The optical spectrum[15] exhibits two maxima below 9 eV, which have been assigned as E' (7.0 eV) and A_1' (7.8 eV) states, on the basis of the earlier calculations.[14b,15] The presence of a symmetry-forbidden state of possible A_2' symmetry at *ca.* 6.7 eV was also reported. This feature was not apparent, however, in the trapped-electron excitation spectra.[16] We find that our results (Table I) are consistent with

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(10) G. R. DeMare and J. S. Martin, *J. Amer. Chem. Soc.*, **88**, 5033 (1966).

(11) (a) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2988, 5123 (1965); (b) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

(12) F. A. Van-Catledge, *ibid.*, **93**, 4365 (1971).

(13) See ref 12 for calculation of the ethylene spectrum in this approximation.

(14) (a) J. F. Music and F. A. Matsen, *J. Amer. Chem. Soc.*, **72**, 5256 (1950); (b) R. D. Brown and V. G. Krishna, *J. Chem. Phys.*, **45**, 1482 (1966).

(15) J. W. Raymonda and W. T. Simpson, *ibid.*, **47**, 430 (1967).

(16) H. H. Brongersma and L. J. Oosterhoff, *Chem. Phys. Lett.*, **3**, 37 (1969).

Table I. Calculated Transition Energies for Cyclopropane

State symmetry	ΔE, eV	λ, nm	f
A_1'	10.06	123	0.000
A_2'	10.87	114	0.000
E'	8.53	145	0.568
	10.86	114	0.352
E''	9.97	124	0.000
	10.66	116	0.000

this interpretation, except for the low-energy A_2' state. The low energy transition in our calculations corresponds to excitation to an E' state, being followed by two, near-degenerate, states of A_1' and E'' symmetry.

Table II. Calculated Transition Energies for Benzene

State symmetry	ΔE, eV	λ, nm	f
$B_{2u}{}^a$	5.29	234	0.000
$B_{1u}{}^a$	5.63	220	0.000
$E_{1u}{}^a$	7.30	170	1.754
$A_{1u}{}^b$	6.16	201	0.000
$A_{2u}{}^b$	6.17	201	0.010
$E_{2u}{}^b$	6.17	201	0.000

[a] These correspond to the well-known $\pi \rightarrow \pi^*$ states. [b] These are $\sigma \rightarrow \pi^*$ states whose positions have yet to be established.

Calculations on benzene produced some rather unusual results (Table II) as we encountered excitations that were predominantly $\sigma \rightarrow \pi^*$ in nature in the region of the B_{1u} state. The accepted assignments for this molecule are $^1B_{2u}$ (^1L_b), 4.90 eV; $^1B_{1u}$ (^1L_a), 6.19 eV; $^1E_{1u}$ ($^1B_{a,b}$), 6.94 eV.[17] This ordering has been confirmed numerous times by calculations in the π-electron approximation. Our current results are most directly comparable with those of Del Bene and Jaffé,[18] Clark and Ragle,[19] and Giessner-Prettre and Pullman.[20] Retention of unscaled repulsion integrals[19,20] tends to weight the $\sigma \rightarrow \sigma^*$ and $\sigma \leftrightarrow \pi$ transitions rather heavily. The Del Bene and Jaffé parameterization, on the other hand, seems to eliminate them from consideration altogether. On the basis of our previous results,[12] it would seem that our method lies somewhere in between. We are unable to evaluate the significance of these results as there is no nonempirical calculation of the spectrum of benzene including $\sigma \rightarrow \sigma^*$ and $\pi \leftrightarrow \sigma$ configurations.[21] These calculated states may merit investigation, as attempts to derive the "best" parameters for π-electron calculations of the benzene spectrum (in a least-squares sense) result in a particularly poor fit for the B_{1u} transition energy.[22] The experimental evidence is, at this time, inconclusive. Studies of crystalline hexamethylbenzene[23] have demonstrated the presence of an out-of-plane polarized transition in this region, but it was ascribed to excitation of an out-of-plane vibrational mode (b_{2g}) in the upper (B_{1u}) state. We can only point out that the intensity (relative to the E_{1u} state) is approximately the same as that which we have calculated. Current interpretation of the spectrum of matrix-isolated benzene, however, *does not* require the presence of such states in this region.[24]

Overall, the spectra that our computational scheme predicts are qualitatively in line with the types of assignments that have been made for these molecules. (We reiterate that our primary goal is a relative ordering accurate to ±1.0 eV.[12])

Table III. Calculated Transition Energies for Vinylcyclopropane

State		Dihedral angle 0°	30°	60°	90°	120°	150°	180°
$\pi \rightarrow \pi^{*a}$	ΔE, eV	6.58	6.56	6.54	6.55	6.50	6.33	6.24
	λ, nm	188	189	190	189	191	196	199
	f	0.721	0.526	0.162	0.003	0.183	0.321	0.350
$\sigma \rightarrow \pi^{*a}$ (CH)	ΔE, eV	6.79	6.79	6.83	6.99	7.04	6.95	6.91
	λ, nm	183	183	182	177	176	178	179
	f	0.027	0.097	0.207	0.189	0.042	0.013	0.020
$\sigma \rightarrow \pi^{*a}$ (CC)	ΔE, eV	7.87	7.70	7.41	7.20	7.31	7.40	7.45
	λ, nm	157	161	167	172	170	168	166
	f	0.022	0.029	0.104	0.262	0.285	0.095	0.027
Fitted first maximum^b	λ_{max}, nm	188	188	185	174	191	196	199
	Log ε	4.34	4.24	3.95	4.08	3.74	3.98	4.02

[a] In the region 60–120° the state assignment becomes somewhat arbitrary. [b] These values were obtained using the following equation, where α was selected to give a half-band-width of 2000 cm⁻¹: $\epsilon(\bar{\nu}) = 30{,}000\Sigma_i f_i \exp[-\alpha(\bar{\nu} - \bar{\nu}_i{}^0)^2]$.

Let us first look at our results for vinylcyclopropane. As one might anticipate, a conformational dependence of the ultraviolet spectrum is found that is similar to that predicted for butadiene.[25] We have increased the dihedral angle in 30° increments until we reached the s-cis conformation. We found the near ultraviolet region to be dominated by three excited states, one being the "local" $\pi \rightarrow \pi^*$ excitation, the other two being "intramolecular charge-transfer" excitations originating in the σ-framework of the cyclopropyl ring. As indicated in Table III, the distinction among these states becomes quite blurred at 60 and 90°, the assignment being made on the basis of the coefficients of the

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(17) J. Koutecky, "Modern Quantum Chemistry," Istanbul Lectures, Vol. I, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 215.

(18) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807, 4050 (1968).

(19) D. A. Clark and J. L. Ragle, *ibid.*, 46, 4235 (1967).

(20) C. Giessner-Prettre and A. Pullman, *Theor. Chim. Acta*, **13**, 265 (1969).

(21) The most extensive *ab initio* SCF–CI calculation reported thus far involves a "frozen σ-core" approximation; see R. L. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2961 (1968).

(22) F. A. Van-Catledge, unpublished results.

(23) R. C. Nelson and W. T. Simpson, *J. Chem. Phys.*, **23**, 1146 (1955).

(24) B. Katz, M. Brith, B. Scharf, and J. Jortner, *ibid.*, **52**, 88 (1970).

(25) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **86**, 2811 (1964).

CI wave function. Note should be taken of the change in character of the most intense bands as a function of the dihedral angle. At 0 and 180° the π orbital is in fact the antisymmetric (out-of-phase) combination of π and the 3e′ orbital nodal in the plane of the double bond. No such cyclopropyl orbital exists in the range 60 and 120°; hence the π orbital is mixed extensively *via* "σ-like" interaction into the C–C bonding orbitals of the cyclopropyl ring. This explains the trend in intensities over this range of the dihedral angle.

The data as presented are of interest, but not particularly useful to the experimentalist. What one obtains in the laboratory is a composite consisting of the superposition of the various transitions with their accompanying intensities. To obtain a more useful representation of the consequences of these predictions for the experimentalist, we have "synthesized" vinylcyclopropane spectra based on the transition energies and oscillator strengths given. In the last line of Table III we present the first maxima that would be observed and the accompanying extinction coefficient, given that our calculations provide a reasonable description of the behavior of the various excited states upon changing the dihedral angle. What we find is a predicted variation of the first absorption maximum over approximately 25 mn, but the important feature to note is that the most abrupt changes occur in a relatively narrow range, between 60 and 120° (see Figure 3).

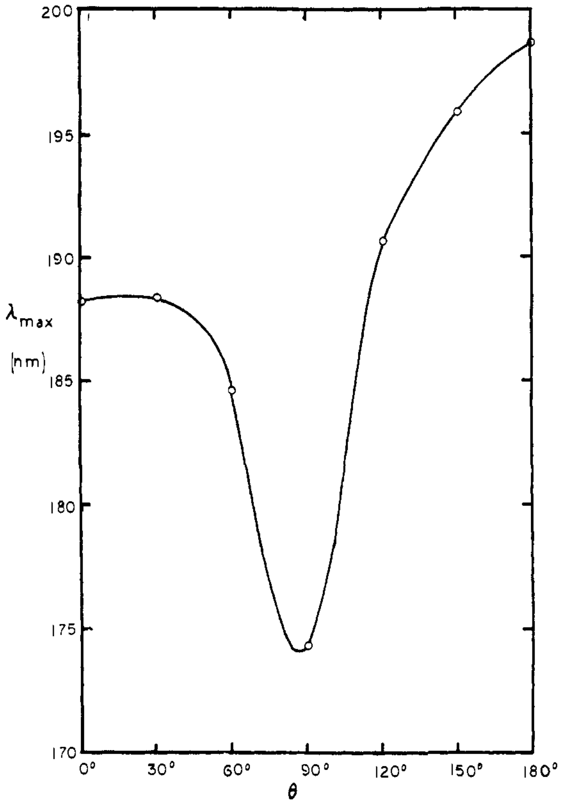


Figure 3. The predicted first ultraviolet maximum as a function of the dihedral angle for vinylcyclopropane.

Our calculations from phenylcyclopropane are summarized in Table IV. The new band generally associated with this substitution we perceive as being derived from the $^1B_{1u}$ (^1L_a) state, which can be seen to vary in position over a range of only 9 nm. Even less variation is observed for the other $\pi \rightarrow \pi^*$ excitations usually associated with the interpretation of the benzene spectra. The unverified $\sigma \rightarrow \pi^*$ states likewise exhibit this insensitivity to conformation. We do not consider the observed shift significant, as the B_{1u} (^1L_a) state sits on the low-energy wing of the lower component (^1B_b) of the original E_{1u} transitions. This would make any attempt to obtain conformation information from the position of this peak a chancy proposition. In sum, our results conform to the experimental findings of Goodman and Eastman[4b] and give us a measure of confidence in the predictions that we make regarding the simple vinylcyclopropanes.

Table IV. Calculated Transition Energies for Phenylcyclopropane

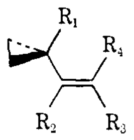
State		Dihedral angle			
		0°	30°	60°	90°
$^1L_b{}^a$	ΔE, eV	5.07	5.10	5.15	5.19
	λ, nm	244	243	241	239
	f	0.099	0.008	0.005	0.003
$^1L_a{}^a$	ΔE, eV	5.38	5.43	5.53	5.62
	λ, nm	230	228	224	221
	f	0.110	0.091	0.046	0.022
$^1B_b{}^a$	ΔE, eV	6.84	6.90	7.05	7.18
	λ, nm	181	180	176	173
	f	0.875	0.883	0.935	1.166
$^1B_a{}^a$	ΔE, eV	7.13	7.14	7.19	7.22
	λ, nm	174	174	173	172
	f	0.808	0.726	0.618	0.586
$\sigma \rightarrow \pi^*$	ΔE, eV	5.88	5.89	5.88	5.93
states^b	λ, nm	211	211	211	209
	f	0.002	0.001	$\sim 10^{-4}$	$\sim 10^{-5}$
	ΔE, eV	6.20	6.15	6.09	6.05
	λ, nm	200	202	204	205
	f	0.002	0.003	0.003	0.002
	ΔE, eV	5.95	5.94	5.93	5.86
	λ, nm	208	209	209	212
	f	$\sim 10^{-4}$	$\sim 10^{-4}$	0.002	$\sim 10^{-5}$
	ΔE, eV	6.13	6.07	5.98	5.87
	λ, nm	202	204	208	211
	f	$\sim 10^{-4}$	0.008	0.005	$\sim 10^{-4}$

[a] See footnote *a*, Table II. [b] See footnote *b*, Table II. It was not possible to make a one-to-one correspondence for these states.

Conclusions

Our calculations seem to confirm the experimental result that the conformationally dependent spectral shifts in phenylcyclopropane will be so small as to render them essentially useless in obtaining conformational information.

Our results for vinylcyclopropanes seem to hold somewhat more promise in that large deviations from the equilibrium dihedral angle ($\theta = 0°$) are shown to be, in principle, detectable *via* uv spectroscopy. The conditions necessary for observing this phenomenon by this technique are (1) incorporation of the vinylcyclopropane system into a rigid, unstrained framework that imposes marked deviation from the s-trans conformation, or (2) producing a large population of the gauche conformation ($\theta \sim 90°$) by appropriate substitution patterns. (It should be noted in this regard that the nmr studies place the dihedral angle for the second potential well at 95–100°.) The first condition has yet to be met, and we are currently attempting to design and synthesize systems that fulfill this criterion. The second condition *seems* to have met in the original study,[2] although the data were not interpreted from this point of view. If we consider structure VII, it should be possible, by a



VII

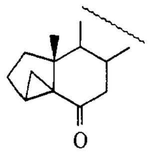
suitable selection of R_1 and/or R_4, to destabilize the s-trans conformation, thereby meeting the second condition. The result should be a hypsochromic shift in λ_{max}, and such an effect is observed when R_1 is changed from H to CH_3.[2] (For the ketones II and IV, a bathochromic shift is observed for the equivalent change.[3]) These data are summarized in Table V. It is also of interest that, as our "synthesized" spectra infer, the intensity of the absorption is fairly insensitive to the changes in conformation population. We feel that the data offer support for the type of spectral behavior that we have predicted.

Table V. Observed Uv Maxima for Selected Vinylcyclopropanes[a]

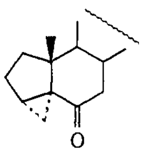
Substituents[b] (see VII)	$R_1 = H$		$R_1 = CH_3$	
	λ_{max}, nm	Log ϵ	λ_{max}, nm	Log ϵ
	192.0	4.00		
$R_2 = CH_3$	196.0	3.99	192.0	4.03
$R_2, R_3 = CH_3$	193.5	4.05	190.0	4.03
$R_2, R_4 = CH_3$	196.0	4.07	189.0	4.00

[a] From ref 2. [b] Hydrogen is implied if the R group is not specified.

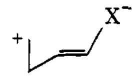
Our conclusions are consistent with the ketone results[3] in that the conformational extremes are approached rather closely by II and IV, on the one hand ($\theta \sim 30°$), which may be compared with III and V ($\theta \sim 180°$). Also, the reported maxima for two isomeric 3,5-cyclo-6-ketosteroids correlate well with the predictions we have made. The β-methano isomer VIII is directly comparable to V. The α isomer, however, is characterized by a dihedral angle of ~120° and exhibits only end absorption in ethanol (see IX). While these data lend support to our results, care must be taken in extending our results to systems in which a polar unsaturated group may interact with the cyclopropyl system. The greater sensitivity to substitution shown by the β-cyclopropyl acrylic esters,[5c] along with recent studies of cyclopropyl nitro aromatics,[26] indicates that conformational dependence of spectra of cyclopropyl derivatives is much more pronounced when there can be significant "intramolecular charge-transfer" character associated with the excitation. This is best understood in terms of the variation of the importance of contributing resonance structures such as X in describing the ground and excited states.[27]



VIII



IX



X

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We wish also to acknowledge a grant-in-aid from the University of Minnesota Computing Center which supported the calculations reported herein. Finally we wish to thank Professor N. A. LeBel (Wayne State University), whose discussion of the results reported in ref 4b with the author several years ago kindled interest in this problem.

Appendix

Molecular Geometries. The geometries used in these calculations are as follows: ethylene $r(C-C) = 1.334$ Å, $r(CH) = 1.085$ Å, $\theta(C-C-H) = 120°$; benzene $r(C-C) = 1.397$ Å, $r(C-H) = 1.085$ Å; cyclopropane $r(C-C) = 1.54$ Å, $r(C-H) = 1.10$ Å, $\theta(H-C-H) = 114°$. In vinylcyclopropane and phenylcyclopropane no deformations were assumed and $r(C_{tet}-C_{tri})$ was taken as 1.501 Å.

Curve-Fitting. The curves displayed in Figures 2 and 3 were obtained by finite expansions in Legendre polynominals $(P_l)(\cos\theta)$; $l_{max} = 6$). The only curve that required smoothing was Figure 2 in the region 0–30° and 130–180°.

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(26) R. C. Hahn, P. H. Howard, and G. A. Lorenzo, *J. Amer. Chem. Soc.*, **93**, 5816 (1971).

(27) NOTE ADDED IN PROOF. We have provided Professor Hahn[26] with a copy of this manuscript prior to publication. He has pointed out that a more positive correlation exists for phenylcyclopropane in that the direction and magnitude of the change in a λ_{max} for the ^1L_b band that we calculate for phenylcyclopropane compare favorably with the data that he has reported. This appears true, but he has taken the conservative view of a predicted 5-nm shift.

Subsequent to the submission of this manuscript, an *ab initio* study of the rotational barrier in vinylcyclopropane has appeared (W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 6592 (1972)). The limited basis set calculation (STO-3G) gives a potential curve quite similar to the one we have calculated. When an extended basis (4–31G) is used, however, the potential minimum at the S-6 conformation is no longer evident. These results confirm the conclusion that the INDO calculation is indeed behaving like a minimum basis set *ab initio* calculation. In addition, however, the existence of a three-well potential for vinylcyclopropane is called into question. Examination of Dreiding models leaves us rather doubtful as to the existence of the gauche conformation as a potential energy minimum.