π^* excitations can be located, INDOUV transition energies are in general agreement with experimental spectra to within ±1.0 eV. Other $\sigma \rightarrow \pi^*$ excitations appear in regions consistent with available experimental and ab initio data. Unlike several other semiempirical methods, $n \rightarrow \sigma^*$ states are calculated to be well above the $\pi \rightarrow \pi^*$ state. This aspect of state ordering cannot be confirmed, but it is in accord with almost all ab initio calculations. Also unique to our results is the determination that the weakly allowed $n\sigma \rightarrow \pi^*$ transition takes place at lower energy than the $n \rightarrow \sigma^*$ transition. This feature is apparent in the experimental spectrum of formaldehyde and is ostensibly present as an underlying band in other carbonyl spectra. To be sure, our calculated state energies are too low to obtain an accurate state ordering of the $n\sigma \rightarrow \pi^*$ state relative to the $\pi \rightarrow \pi^*$ state. Yet the prediction of $n\sigma \rightarrow \pi^*$ as a low-lying state is surprisingly consistent with ab initio calculations.

Thus, our previously stated goal of relative state orderings accurate to ±1.0 eV seems to have been substantially met by the INDOUV formalism. In addition, the qualitative effects of perturbations on the carbonyl chromophore by methyl, vinyl, and cyclopropyl substituents appear to be correctly represented.

Acknowledgment. The services of the Academic Computer Services, Southeastern Massachusetts University, are acknowledged. I also express appreciation and grateful thanks to Dr. F. A. Van-Catledge for providing the INDOUV program, assistance, and critical comments.

On Conformational Sensitivity in the Ultraviolet Spectra of Cyclopropyl Ketones and Olefins

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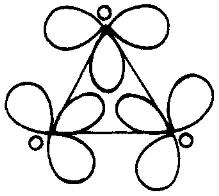
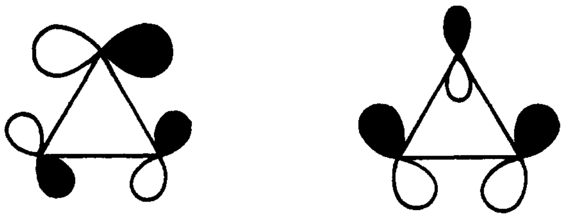
Selected cyclopropyl ketones and olefins have been prepared to approximate the three principal conformers (*s*-trans, *s*-cis, and gauche) of vinylcyclopropane and cyclopropanecarboxaldehyde. The model systems are as follows: for the *s*-cis form, 4-oxo- (VI) and 4-methylene-1(*E*)-methylspiro[2.5]octane (VII); for the *s*-trans form, 2-oxo- (IV) and 2-methylene-1-methylbicyclo[4.1.0]heptane (V); for the gauche form, 2-oxo- (VIII) and 2-methylenetricyclo[5.2.1.$0^{3,5}$]decane (IX). The geometries of IV–IX were taken from empirical force-field calculations. Spectral measurements on the ketones give support to the notion of conformational sensitivity in that the λ_{max} values are in the expected order, VI > IV > VIII. Further, the sensitivity of λ_{max} to solvent polarity supports the earlier assignment of the ketone band as $\Delta \rightarrow \pi^*$ in nature. For the olefins the ultraviolet maxima are in the order IX > V > VII. On the basis of the calculated geometries, IX is felt to be anomalous, and a rationale is given to account for this. It is concluded that the internal coordinate governing the value of λ_{max} is the dihedral angle defining the *s*-cis–*s*-trans relationship.

The conjugative interaction of the cyclopropane ring with neighboring p orbitals is a well-documented phenomenon. Of the several models[2-7] proposed for bonding among the ring carbons, the Walsh model,[5,6] based on the union of three sp^2-hybridized carbons (I), permits the simplest interpretation of the origin of this interaction and its conformational requirements. A simple description of the bonding is as follows. Interaction among the inward-pointing sp^2 hybrids leads (in D_{3h} symmetry) to an a_1' bonding level (Δ_σ) and a doubly degenerate e′ antibonding level (Δ_σ^*). The p orbitals yield an e′ bonding level (Δ_p) and an a_2' antibonding level (Δ_p^*). These symmetry orbitals are depicted in Figure 1. The six electrons corresponding to the carbon–carbon bonds are assigned to the Δ_σ and Δ_p levels. Formation of molecular orbitals for the carbon–carbon bonds should lead to mixing of Δ_p and Δ_σ^*. Indeed, Hoffmann and Davidson[7] have given a better representation of the Δ_p orbitals as in II.



I



A S

II

On the basis of these orbital representations, the symmetric conformation (IIIb) is preferred if a neighboring p orbital is doubly occupied, while single occupancy or vacancy will stabilize the bisected conformation (IIIa). The general features outlined above find ample experimental support for cationic,[8-25] radical, and anionic[26-28] systems.

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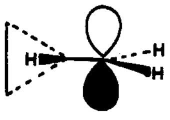
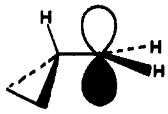


IIIa



IIIb

Moreover, ab initio and semiempirical molecular orbital studies[25,29-33] corroborate these experimental findings.

It is well-known that ultraviolet spectroscopy may serve as a sensitive probe of molecular electronic structure. One would expect, therefore, to find clear documentation of conformational effects in UV spectra due to cyclopropyl interaction. Phenylcyclopropane derivatives generally exhibit a bathochromic shift of the ^1L_a band, relative to that of the parent phenyl derivatives.[34-39] However, the conformational dependence implied by the Walsh model is relatively small for simple phenylcyclopropanes[37,39b] but is significant for 2-arylcyclopropanecarboxamides[36] and nitrated phenylcyclopropanes.[39] The far-ultraviolet spectra of carbonyl compounds also show bathochromic shifts and marked conformational effects upon introduction of the cyclopropyl group.[34,40-45] Simple cyclopropyl olefins, on the other hand, show the bathochromic shift but no clear evidence for conformational effects.[46,47] The auxochromic effect of the cyclopropyl group also has been observed for conjugated enones, dienones, dienes, and various acrylic acid derivatives.[48,49] Pete[50] has provided an extensive review and compilation of UV spectra of a large number of these conjugated cyclopropyl compounds. Conclusions derived from this experimental work may be summarized as follows: (a) Interaction of cyclopropyl with a π system in the bisected geometry will always produce a bathochromic shift of the UV maximum (excepting the $n \rightarrow \pi^*$ maximum of carbonyl groups, which is hardly affected).

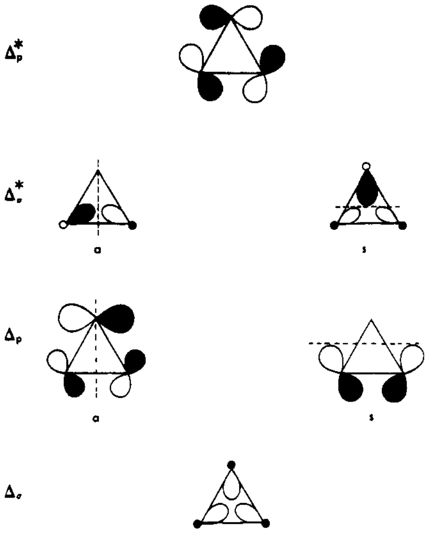


Figure 1. Symmetry orbitals for the carbon–carbon bonds of cyclopropane, based upon the Walsh model.

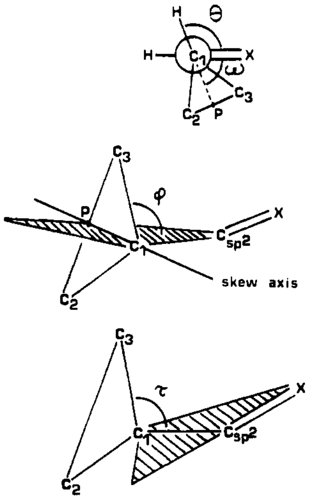


Figure 2. Planes and dihedral angles employed in discussions of conformations of cyclopropyl ketones and olefins: (a) top, the dihedral angle relationship as measured by θ or ω; (b) center, the angle ϕ as a measure of cyclopropyl "skewing" or Pete's criterion;[50] (c) bottom, the angle τ as a measure of the "parallel" relationship.

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(b) If the basic chromophore is hydrocarbon in nature (e.g., vinyl or phenyl), apparent conformational effects are minimal.

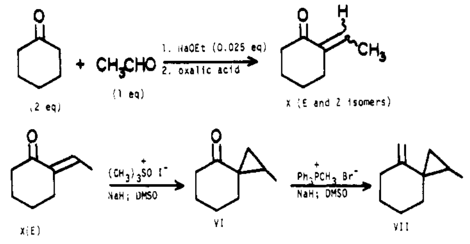
Although there are numerous theoretical studies of the excited states of the isolated cyclopropyl[51] and π[52-56] chromophores, theoretical efforts to understand the spectral implications of cyclopropyl coupled systems have been minimal. In earlier work, we have calculated the conformational dependence of the UV spectra of vinylcyclopropane[30] and cyclopropyl methyl ketone[53] using the INDOUV method,[52] a modification of INDO.[57] The geometric parameter under consideration was the dihedral angle θ, which basically involves rotation about the CC single bond joining the cyclopropyl and vinyl or carbonyl moieties. Angle θ depicted in Figure 2 is effectively a torsional angle formed by (1) H attached to C_1 of the cyclopropyl ring, (2) C_1, (3) the sp^2 carbon atom, and (4) the group X (where X $\equiv$ CH_2 for vinylcyclopropane and X $\equiv$ O for cyclopropyl ketones). (Alternately, other researchers have used the angle ω, where $\omega = \pi - \theta$.) For both vinylcyclopropane and cyclopropyl methyl ketone the calculations predict that (a) of the two possible bisected forms the *s*-cis ($\theta = 180°$) conformer (if attainable) should show the longer wavelength maximum and that (b) conformational dependence in the UV spectrum of vinylcyclopropane or cyclopropyl methyl ketones may be observed, provided we are able to generate a geometric arrangement within 30° of the "symmetric" (gauche, $\theta = 90°$) conformation.

To test the role of geometry experimentally, we chose polycyclic model systems in which the dihedral angle could be rigidly fixed. Our method is unique in providing a means of systematically assaying dihedral angle effects. The spectrum of each conformation can be obtained with relatively little contamination from other conformers, in contrast to previous attempts with vinylcyclopropanes.[46] Although spectra of some rigid cyclopropyl ketones have been recorded, there was no quantitative treatment of conformational effects in these studies.[42,43] Furthermore, cyclopropyl ketones within ~40° of the gauche ($\theta = 90°$) conformation are lacking. Hence, our study considers each conformation of interest in both cyclopropyl ketones and olefins in a more systematic, quantitative manner than in earlier treatments.

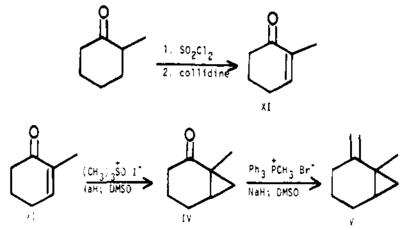
Results

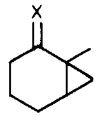
Selection of Spectral Models. Our study centers on three critical regions of dihedral angle, the *s*-trans (θ = 0–30°, ω = 150–180°), the *s*-cis (θ = 150–180°, ω = 0–30°), and the gauche conformation ($\theta \simeq 90°$, $\omega \simeq 90°$). Since we wish to consider cyclopropyl ketones as well as vinylcyclopropanes, we have restricted our selection to systems in which the double bond is exocyclic. The bicyclo[*n*.1.0]alkane framework (*n* = 3, 4)[42,43] provides dihedral angles approximating the *s*-trans conformation. We have, therefore, chosen 2-oxo-1-methylbicyclo[4.1.0]heptane (IV) and its 2-methylene analogue (V). In like manner, cisoid arrangements are obtained by incorporating the chromophores into the spiro[2.*n*]alkane systems (n = 4, 5).[42,43] (If an endocyclic double bond is permitted, the cisoid arrangement may also be obtained in the bicyclo[*n*.1.0]alkane series.) Hence, our models are 4-oxo-1-methylspiro[2.5]octane (VI) and the corresponding olefin (VII). Our models, 2-oxotricyclo[5.2.1.0^{3,5}]decane (VIII) and the methylene derivative (IX), employ an added bridging group to achieve the gauche arrangement. Actually there are four species (XB, NC, XC, NB) corresponding to this general structure, VIII or IX. First, the seven-membered ring may adopt either a boat (B) or chair (C) conformation. Second, the cyclopropyl ring may be either endo (N) or exo (X) on the seven-membered ring. Of the four possibilities, only the endo–boat (NB) and exo–chair (XC) arrangements have the desired dihedral angle. Fortunately, as anticipated from Dreiding models, the endo–chair (NC) and exo–boat (XB) species can be excluded due to adverse hydrogen van der Waals interactions. Force-field calcu-

Scheme I

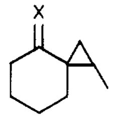


Scheme II

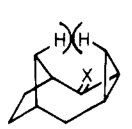




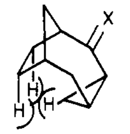
IV, X = O
V, X = CH_2



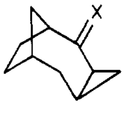
VI, X = O
VII, X = CH_2



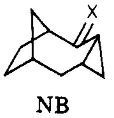
XB



NC



XC



NB

VIII, X = O
IX, X = CH_2

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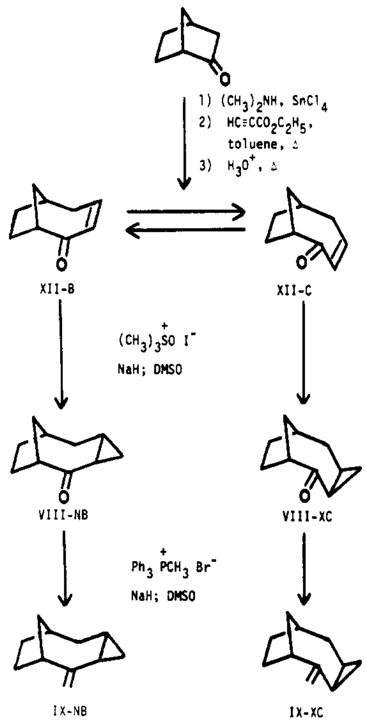
Scheme III



lations (vide infra) on these molecules show that the endo-chair (NC) conformer is distorted and exists at a high-energy minimum on the potential energy hypersurface. The exo-boat species (XB) is neither at a minimum nor at a saddle point on the energy hypersurface. It is an unstable, high-energy species, decaying spontaneously to the exo-chair (XC) conformer.

Syntheses. The synthetic routes to our model compounds appear in Schemes I-III. Our preparation of the cyclopropyl ketones from the corresponding α,β-unsaturated ketones by the Corey procedure[58] constitutes a more expeditious method than that employed in the previous preparation of VI and IV.[59] The new cyclopropyl ketone (VIII), also synthesized by the Corey method, may exist as either the endo-boat (NB) or exo-chair (XC) isomer. Our ^{1}H NMR studies,[60] however, indicate that the boat (B) conformation is preferred for the precursor XII. Hence, VIII-NB is the probable isomeric product of cyclopropanation. However, *even if* the product is a mixture of VIII-NB and VIII-XC isomers, force-field calculations (vide infra) predict that the two isomers (and the olefins IX-XC or IX-NB derived therefrom) should have very similar dihedral angles and should be spectroscopically indistinguishable. Thus, provided with ketones IV, VI, and VIII, we were able to generate the new olefins V, VII, and IX by treatment with methylenetriphenylphosphorane.[61] The previous method[62] for obtaining 2-ethylidenecyclohexanone (X) gives a mixture of products and ultimately poor yields. We found that X could be prepared much more satisfactorily by a controlled aldol condensation of acetaldehyde with cyclohexanone followed by dehydration with oxalic acid.[63] 2-Methylcyclohex-2-en-1-one (XI) was obtained by a modification of the method of Warnhoff and Johnson.[64] Finally, bicyclo[4.2.1]non-3-en-2-one (XII) was conveniently synthesized by using a procedure we previously developed.[60]

Molecular Mechanics Calculations. In order to precisely establish the geometries of the molecules studied, we have employed molecular mechanics, a method which has proved accurate for a wide variety of compounds.[65] The usual methods of conformational analysis are ineffectual or inapplicable for the cyclopropyl ketones and olefins studied here. Molecular mechanics is an empirical method, originally applied by Westheimer,[66] which considers the molecule to be a collection of particles held together by oscillator forces and subject also to van der Waals forces over nonbonded, nongeminal pairs.[65-73] The steric energy of the molecule, E_{steric}, is calculated in terms of van der Waals interactions and torsional and deformation energies for all bonds and angles. The quantity E_{steric} is minimized, giving the equilibrium geometry of the molecule. Further details of the Allinger 1973 force field, used here, are to be found elsewhere.[65] Modifications for cyclopropyl derivatives are described in the Appendix.

We now focus on the pertinent aspects of the geometries and energies calculated for our spectroscopic models and summarized in Table I. With the exception of VII, all calculated values of θ (or ω) are within 15° of the predictions based on molecular models. (This difference is in fact quite acceptable as the minima associated with torsional coordinates are quite broad. Such a difference is within the range available via thermal energies.) We note also that the dihedral angles θ for the two ketone (VIII-NB and VIII-XC) and olefin (IX-NB and IX-XC) isomers are within 3° of each other. Hence, they are effectively indistinguishable spectroscopically. Further, the anomalous behavior of VII is predictable. Molecular models indicated that severe hydrogen-hydrogen interactions might induce distortions in VII, i.e.,

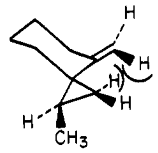


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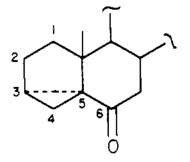
Table I. Force-Field Results for the Cyclopropyl Olefins and Ketones

	E_{steric}, kcal/mol	$\Delta H_f°$(calcd), deg kcal/mol	E_{strain}, kcal/mol	θ, deg	$\lvert\phi - \pi/2\rvert$, deg	$\lvert\tau - \pi/2\rvert$ deg
			Ketones			
IV	10.01	−30.46	32.67	17.5	2.2	6.4
VI	11.68	−35.69	33.03	140.2	3.6	14.6
VIII-NB	26.98	−15.52	47.20	102.4	3.3	29.4
VIII-XC	26.18	−16.32	46.39	99.7	0.1	31.2
XIII[a]				131.8	3.2	20.0
XIV[a]				127.2	6.7	16.9
			Olefins			
V_a	20.28	23.95	40.03	13.7	2.4	11.3
V_b	20.67	24.34	40.42	76.9	1.3	31.2
VII	18.89	15.67	37.34	120.7	5.5	26.2
IX-NB	33.60	35.26	50.92	86.1	2.2	37.1
IX-XC	31.93	33.58	49.24	87.8	3.6	38.4

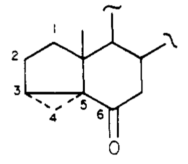
[a] The dihedral angles are based on experimental geometries determined by X-ray diffraction (see ref 74).

Unfortunately, the olefin V was found to exist in two distinct conformations differing in energy by ~0.4 kcal/mol. We have attempted to assay the spectral consequences of such a conformational mixture using the spectral simulation technique described by us earlier.[30] We tentatively concluded that the spectrum of V should resemble that of the low-energy conformer (θ = 13.7°) with some hypsochromic shifting.

The X-ray structural data[74] on the cyclosteroidal ketones XIII and XIV provide a range (albeit limited) of bond angles (C_{cp}–C_{cp}–C_{sp^2}) and bond lengths (C_{cp}–C_{cp}) with which our force field results on IV, VI, and VIII may be compared. With the exception of the 3-5-6 bond angle in XIV (130°), the experimental bond angles (C_{cp}–C_{cp}–C_{sp^2}) in XIII and XIV span the range 114–117°. The calculated C_{cp}–C_{cp}–C_{sp^2} angles in IV, VI, and VIII cover a similar range (112–118°). Both experimental and force-field cyclopropyl bond lengths lie in the range 1.50–1.52 Å. Thus, the ketone geometries, predicted by force-field calculations, are reasonable.



XIII



XIV

We were also interested in comparing the steric energy and strain energy for each of our spectroscopic models. We have previously defined steric energy. Allinger[65g] has defined the strain energy as "the calculate heat of formation minus the heat of formation obtained for the *n*-alkane derivative of the same molecular formula, corrected for chain branching and functionalization". It is evident that the bicyclo[4.1.0] and spiro[2.5] systems have comparable strain (and steric) energies. The tricyclo[5.2.1.0^{3,5}] systems, on the other hand, have 10–15-kcal/mol more strain associated with them. Clearly, some of this increase is inherent in the increased numbers of bonds and angles involved. Substantial amounts of the difference (7–8 kcal/mol) arise nonetheless from an accumulation of unfavorable torsional angles in the tricyclic systems.

Table II. Observed n → π* Maxima for the Cyclopropyl Ketones

compd	$\lambda_{\max}$, nm (ϵ) in C_6H_{12}	$\lambda_{\max}$, nm (ϵ) in H_2O
IV	284.0 (24)	275.0 (33)
VI	289.0 (37)	282.0 (53)
VIII	289.0 (24)	280.0 (37)

Table III. Observed Far-Ultraviolet Maxima for the Cyclopropyl Ketones

ketone		$\lambda_{\max}$, nm (ϵ) in H_2O	$\lambda_{\max}$, nm (ϵ) in C_5F_{13}
IV	$\Delta_p(a) \rightarrow \pi^*$	207.5 (5264)	189.0 (4280)
	$\Delta_p(s) \rightarrow \pi^*$		175.0 (5513)
VI	$\Delta_p(a) \rightarrow \pi^*$	215.0 (4298)	199.0 (3220)
	$\Delta_p(s) \rightarrow \pi^*$		≤172.5 (≥5200)
VIII	$\Delta_p(a) \rightarrow \pi^*$ and/or $\Delta_p(s) \rightarrow \pi^*$	197.0 (5310)	177.0 (5790)

Ultraviolet Spectra. Ketone n → π* Bands. To first-order, the n → π* excitation shows little variation with changes in the conformation of a cyclopropyl carbonyl system. This is consistent with our spectral calculations on cyclopropyl methyl ketone.[53] It is possible, nonetheless, that second-order effects might become evident when considering carefully selected examples such as IV and VI. The n orbital of the carbonyl group should, in the cisoid form, be raised slightly in energy via interaction with the a_1' orbital of the cyclopropane ring. One would expect, therefore, a small red shift in the n → π* maximum of VI relative IV. Such an effect is observed (Table II), with Δλ varying from 5 to 7 nm, depending upon solvent. To be sure, such a small effect may merely reflect differing degrees of solvation in the ground electronic state. The trend is, however, consistent with what one might expect.

Far-Ultraviolet Ketone Bands. According to Meyer et al.,[44] the transition found near 200 nm for ordinary ketones is hypsochromically shifted and obscured by a new band in cyclopropyl ketones. This new band, characterized as $\Delta_p(a) \rightarrow \pi^*$ by our INDOUV calculations,[53] appears in all of the cyclopropyl ketone spectra and exhibits sensitivity to solvent. The "blue shift" observed for the first far-ultraviolet band upon changing from water to perfluoropentane is large (15–20 nm). The relative positions of the maxima in both solvents show pronounced sensitivity to conformation to be discussed below. Dauben and Berezin[43] have previously reported ultraviolet maxima for IV (207 nm) and VI (215 nm) in water which we match quite well. The maximum for VIII is the first reported UV measurement for a gauche cyclopropyl ketone.

In addition to this first far-ultraviolet band, spectra taken in perfluoropentane (Figure 3) show a second band (~170 nm) which is probably the $\Delta_p(s) \rightarrow \pi^*$ transition predicted by our calculations,[53] as well as those of Meyer

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[74] Pettersen, R. C.; Kennard, O.; Dauben, W. G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1929.

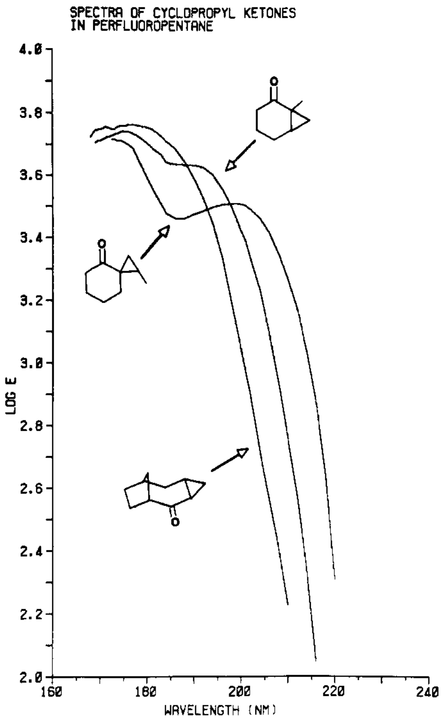

Figure 3. Ultraviolet spectra of (*E*)-1-methyl-4-oxospiro[2.5]-octane (VI), 2-oxo-1-methylbicyclo[4.1.0]heptane (IV), and 2-oxotricyclo[5.2.1.0^{3,5}]decane (VIII) as measured in perfluoropentane.

Table IV. Observed $\pi \rightarrow \pi^*$ Maxima for the Cyclopropyl Olefins

olefin	λ_{max}, nm	ϵ
V	201.0	14 850
VII	193.0	8 740
IX	203.0	11 550

et al.[44] In contrast to the $\Delta_p(a) \rightarrow \pi^*$ band, this second band shows little or no conformational dependence.

Olefinic $\pi \rightarrow \pi^*$ Band. The UV maxima for the vinylcyclopropane derivatives (Table IV, Figure 4) lie in the range 190–205 nm. When compared with λ_{max} of the parent olefin, methylenecyclohexane (190.9 nm in isooctane[75]), the vinylcyclopropane maxima are bathochromically shifted. The spectral shifts induced by interactions with cyclopropyl are 10 nm for V and only 2 nm for VII. The maximum of IX is anomalous and will be discussed later. However, the other results are consistent with those for the simple models reported by Heathcock and Poulter.[46]

Discussion

Excitation Description. In order to fully understand the nature (in a single configuration approximation) of the excitations we are observing, it is necessary to analyze the interactions generating the MO manifolds of interest in vinylcyclopropane and the cyclopropylcarbonyl system. We will approach this using the ideas of second-order perturbation theory, identifying the orbital energies with the negative of the ionization potentials (IP's) observed in photoelectron spectroscopy. Data are available for cyclopropane (Δ_p, 10.9 eV),[76] ethylene (π, 10.51 eV),[77] formaldehyde (n, 10.9 eV; π, 14.5 eV),[77] vinylcyclopropane [$\pi - \Delta_p(a)$, 9.25 eV; $\Delta_p(s)$, 10.76 eV; $\pi + \Delta_p(a)$, 11.79 eV],[78] and cyclopropyl methyl ketone [n, 9.50 eV, $\Delta_p(a) - \pi$, 10.62 eV; $\Delta_p(s)$, 11.40 eV; $\pi + \Delta_p(a)$, 13.2 eV].[79] For cyclo-

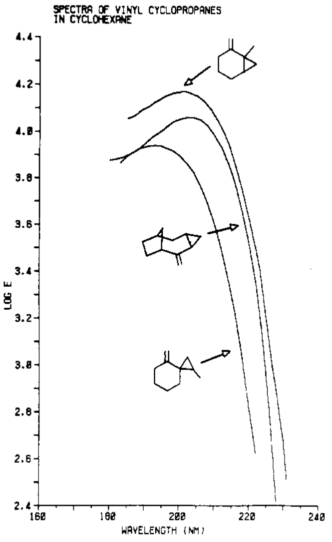

Figure 4. Ultraviolet spectra of (*E*)-1-methyl-4-methylene-spiro[2.5]octane (VII), 2-methylene-1-methylbicyclo[4.1.0]heptane (V), and 2-methylenetricyclo[5.2.1.0^{3,5}]decane (IX) as measured in cyclohexane.

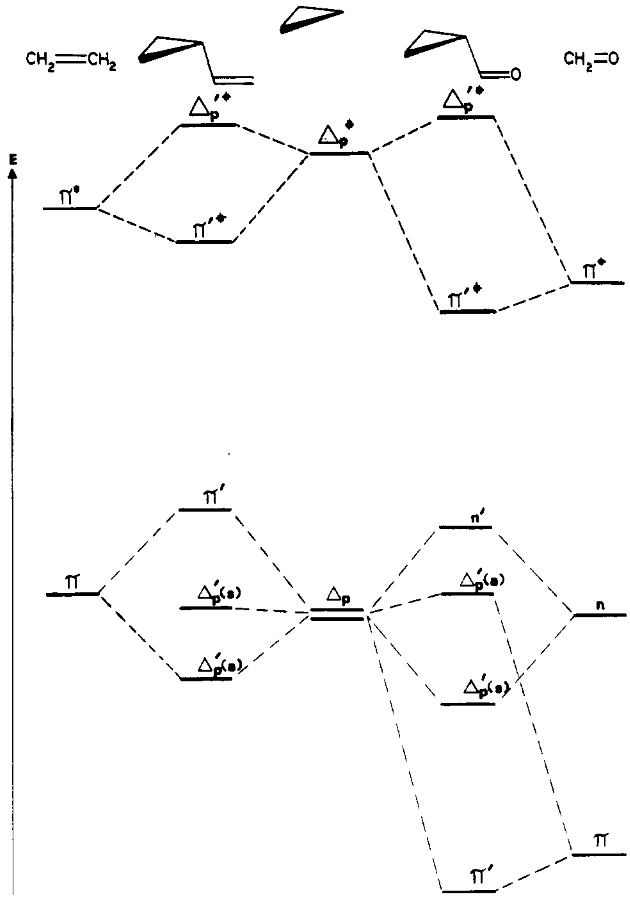

Figure 5. Interaction diagram depicting the coupling of the cyclopropyl Δ_p orbitals to the π orbitals of ethylene (left-hand side) and to the n and π orbitals of formaldehyde (right-hand side). The relative energies are based upon PES data, except for cyclopropanecarboxaldehyde, for which no such data are available.

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(78) Harada, Y.; Seki, K.; Suzuki, A.; Inokuchi, H. *Chem. Lett.* **1973**, 893.

propane we have taken the value for the Δ_p level to be the mean of the observed first and second IP's (10.53 and 11.30 eV; Jahn–Teller splitting). We summarize in Figure 5 the consequences of coupling $\Delta_p(a)$ to π_{CC} and π_{CO} in the bisected conformation. The gauche (or symmetric) conformation, it should be noted, does permit coupling $\Delta_p(s)$ with the π systems in question. As implied by the symmetry orbital (Figure 1) and the "true" representation (II) of Hoffmann and Davidson,[7] however, the $\Delta_p(s)$–π interaction should produce much smaller splittings than those induced by $\Delta_p(a)$.

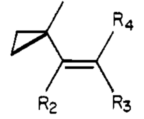
Let us focus upon the orbital in which the "hole" occurs upon excitation. For vinylcyclopropanes this orbital maintains π_{CC} character but undergoes nontrivial mixing with Δ_p. Hence the excitation may be presumed to be "essentially local" provided the upper orbital is mainly π_{CC}^*. In the cyclopropylcarbonyl systems, on the other hand, the orbital in question (subjacent to the n orbital) is predominantly $\Delta_p(a)$ in nature. Thus, the "200-nm band" takes on the features of an intramolecular charge-transfer transition involving excitation from the antisymmetric component of the e′ cyclopropyl orbital to the π^* orbital of the carbonyl moiety. This conclusion, first drawn by Meyer et al.,[44] is certainly consistent with the sensitivity to solvent polarity we find for this band.

It would be most helpful if we could assay the extent of interaction between Δ_p^* and π^* orbitals. This type of information is not, unfortunately, directly accessible. Our observations for the ketone $\Delta_p(s) \rightarrow \pi^*$ band (Table III) suggests that such interactions may show minimal conformational sensitivity. If this proves true, we could conclude that conformational effects in the spectra of cyclopropyl carbonyl and olefin derivatives derive predominantly from interactions among the bonding orbitals of the two chromophoric fragments.

Conformational Effects in Ketones. The ketone data reported herein are consistent with the previously observed conformational requirement for cyclopropyl–p orbital interaction in general. Furthermore our experimental results for the first far-ultraviolet band show significant dependence on the dihedral angle θ, completely in accord with our postulation via INDOUV calculations.[53] The predicted conformational dependence[53] of the maxima for the cisoid and transoid cyclopropyl ketones (cisoid > transoid) is consistent with the experimental findings. Superimposed upon what is essentially an orbital overlap requirement is the charge-transfer character of the excitation. This latter effect may be the major source of the lowering of the transition energy for VI relative to IV. In the cisoid arrangement electrostatic interactions in the excited state are more favorable due to the proximity of the carbonyl and cyclopropyl groups. In addition, the qualitative appearance of the maximum at short wavelengths for gauche cyclopropyl ketones (VIII < IV by 12 nm and VIII < VI by 22 nm) is in agreement with the theoretical predictions[53] (gauche < transoid by 17 nm and gauche < cisoid by 22 nm). In the case of the gauche cyclopropyl ketone VIII, it is not clear experimentally whether the $\Delta_p(a) \rightarrow \pi^*$ band merely shifts to shorter wavelengths or whether it disappears into the long-wavelength tail of the $\Delta_p(s) \rightarrow \pi^*$ band. This second scenario is supported by our spectral calculations.

We have also considered geometrical factors previously[40,42,43,50] thought to be important in determining spectral shifting in cyclopropyl ketones. Both angles τ and ϕ (Figure 2) measure deviation from the condition of best interaction of the cyclopropyl ring with the π system. The angle τ is formed between the plane of the cyclopropyl ring and the nodal plane of the π system (described by the atoms C_1, the sp^2 carbon atom, and the group X). Attention was focused on this so-called "parallel" relationship by Cromwell,[40] Dauben,[43] and Kosower.[42] In Table I we have recorded deviations from the "parallel" condition ($\tau = \pi/2$) as function of $|\tau - \pi/2|$. On this basis VI should absorb at *shorter* wavelength than IV, while the opposite is definitely the case. This cannot, then, be the geometric parameter of primary importance. Pete[50] suggested another spectral-shift factor, which we feel is best described by the angle ϕ. This angle is effectively a "skewing" about an axis through the carbon C_1 and the midpoint P between C_2 and C_3 of the ring. It can also be described as the angle between the cyclopropyl plane and the plane formed by (1) C_1, (2) the midpoint P, and (3) the sp^2 carbon. Table I again presents deviations $|\phi - \pi/2|$, from the optimum condition ($\phi = \pi/2$). The values of $|\phi - \pi/2|$ throughout the series are all comparable while the spectral maxima vary widely. Hence, the angle ϕ cannot be of primary importance. It is interesting to note the case of the two cyclosteroidal ketones (XIII and XIV). Whereas the dihedral angles ϕ are similar (Table I), the maximum of XIV is hypsochromically shifted over 15 nm relative to that of XIII.[43,80] However, the observed value of $|\phi - \pi/2|$ for the badly deformed cyclosteroid XIV is quite different (~7°) from those of the other cyclopropyl ketones. Thus, the angle ϕ can take on importance since it reflects indirectly whatever C_{cp}–C_{cp}–C_{sp^2} bond angle deformations are present in the system. Nevertheless, it is clear that the location of λ_{max} will be primarily controlled by the angle θ.

Conformational Effects for Olefins. Let us first focus on V and VII which approximate the *s*-trans and near-gauche conformations, respectively. The experimental maxima for V and VII appear to be qualitatively in accord with the semiempirical computations.[30] The results for VII confirm the deformation from a cisoid to a near-gauche geometry, which was predicted by force-field calculations (vide supra). In addition, our results support our interpretation[30] of the data of Heathcock and Poulter[46] in that VII approaches fairly closely the conformation one would anticipate for XV ($R_1 = CH_3$), due to steric interactions with R_4 (either H or CH_3). All of these data combine, in our judgement, to support the proposition that there is a detectable degree of conformational dependence in the UV spectra of cyclopropyl olefins. The principal characteristic of this effect is its small magnitude, relative to that for the related ketones. This outcome is related to the negligible degree of charge-transfer character in either the ground or excited state for the olefins.



XV

$\Delta\lambda_{max}$ for $[(R_1 = H) \rightarrow (R_1 = CH_3)] = -4$ to -7 nm

We have thus far excluded IX from our discussion. The position of the UV maximum for IX was at surprising variance with our theoretical calculations. We would have expected the maxima for V and IX to be reversed. Either the theoretical predictions[30] are in error or factors not previously taken into account are operative. The success

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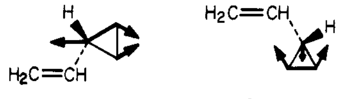
[79] Kelder, J.; Cerfontain, H.; Higginson, B. R.; Lloyd, D. R. *Tetrahedron Lett.* 1974, 739.

[80] XIV exhibits only end absorption (in water) while XIII is comparable to VI (see ref 43).

of the INDOUV method with the cyclopropyl ketones suggests that the calculations are valid. Although strain factors might be invoked to account for this, we prefer a rationale based on Franck–Condon factors.

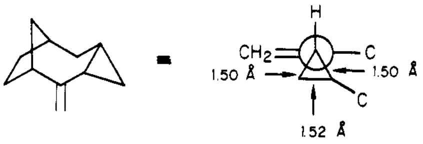
The evidence available suggests that the cyclopropyl group retains local C_3 symmetry in simple carbonyl and olefin derivatives. Given that this is true, let us consider the bond-length changes that might occur upon excitation, assuming that a Δ_p orbital contributes significantly to the "hole" MO. Bonds bisected by nodes in Δ_p will shorten while those having phase continuity will lengthen. To the extent that a Δ_p orbital contributed to the "hole" MO, the equilibrium geometry of the excited state will correspond to loss of C_3 symmetry in the cyclopropyl group. Clearly, the sense of distortion will depend upon which Δ_p orbital is involved. The two possibilities are depicted in XVI.



s-trans; $\Delta_p(a)$ gauche; $\Delta_p(s)$

XVI

None of the derivatives discussed herein maintain strict C_3 symmetry in the cyclopropyl ring, but the tricyclo[5.3.1.0^{3,5}] systems (either NB or XC) are unique. In each case, ketone or olefin, the cyclopropyl ring is predicted to be distorted by the constraining framework in the sense appropriate to an excited-state gauche conformer (compare XVI and XVII). Hence the ground-state energy of the chromophore has been increased by strain, and vertical excitation leads to an excited state at or near its equilibrium geometry. We suggest that these two factors produce the anomalously high value of λ_{max} for IX-NB. Indeed, further INDOUV calculations with distorted cyclopropyl rings tend to support this conclusion.[81] In contrast, these effects do not render the ketone VIII-NB anomalous. We presume that this is because the "200-nm band" in the ketone does not converge to a ~190-nm olefin band (in the limit of complete decoupling) but rather to either the $\Delta_p(s) \rightarrow \pi^*$ (~170 nm) or another carbonyl excitation (~170 nm). In this shorter wavelength range the decrease in expected transition energy observed for IX would not be sufficient to render VIII anomalous.



XVII

Accuracy of the Theoretical Predictions. It is worthwhile to consider briefly the extent to which experimental facts conform to the predictions for vinylcyclopropanes[30] and cyclopropyl ketones (contained in part in the preceding paper).[53] The principal characteristic, namely, a bathochromic shift of the UV maximum upon cyclopropyl substitution, is certainly contained in the theory. The predicted magnitude of the shift for the *s*-trans conformer (14 nm for vinylcyclopropane and 17 nm for cyclopropyl methyl ketone) is well in line with experiment (10 nm for V, 9–15 nm for various simple systems, and 12 nm for IV). In addition, the predicted conformational dependence of the maxima for the cisoid and transoid cyclopropyl ketones (cisoid > transoid by 5 nm) is completely consistent with the experimental findings (VI > IV by 10 nm). Furthermore, the calculated maximum at shorter wavelengths for the gauche cyclopropyl ketone is clearly found experimentally. Thus, our earlier conclusion,[53] that the INDOUV method performs reasonably well for carbonyl transitions other than n → π*, is borne out in these experimental results.

Returning to the vinylcyclopropanes, the predicted conformational dependence, while confirmed in a qualitative sense, is not exhibited by VII relative to V. The prediction is that VII should absorb at slightly longer wavelength and V. Detailed analysis[82] of the configuration interaction calculations shows that the difficulty arises from a low-lying $\sigma \rightarrow \pi^*$ configuration. (The σ orbital is mainly the C_{cp}–C_{sp^2} bonding MO.) The effect of this is to induce improper state splitting and spurious distributions of oscillator strength for conformers in the range $60° \leq \theta \leq 120°$. This problem does not arise for the *s*-cis and *s*-trans conformers by virtue of the plane of symmetry in these forms. We conclude, therefore, that the computational method, while qualitatively useful, tends to overemphasize the importance of $\sigma \rightarrow \pi^*$ excitations in hydrocarbons. We find this somewhat discouraging since a comparison of our method with other all-valence-electron methods shows it to be one of the more accurate for spectral calculations.[82]

Conclusion

It is confirmed that the UV spectra of cyclopropylcarbonyl and olefin derivatives manifest conformation sensitivity. The internal coordinate of primary importance is the dihedral angle, θ, defined in Figure 2. The excitation observed in the carbonyl derivatives exhibits marked sensitivity to conformation and to solvent polarity as is consistent with its proposed $\Delta_p(a) \rightarrow \pi^*$ charge-transfer character. The excitation observed for the olefinic derivatives is felt to be a perturbed $\pi \rightarrow \pi^*$ excitation, as evidenced by the relatively small shift and reduced conformational sensitivity. A consequence of these characteristics of the olefin band is a marked dependence upon the distortions imposed on the vinylcyclopropane moiety by the constraining framework.

Experimental Section

Ultraviolet Spectra. The UV spectra of the cyclopropyl ketones (IV, VI, and VIII) and vinylcyclopropanes (V, VII, and IX) were taken on a Cary 15 UV–visible spectrophotometer operating in the double-beam mode. The slit program was followed carefully to avoid the inclusion of spurious maxima. Base-line corrections from a solvent–solvent run were collected for each solution–solvent run. The final plots of log ϵ vs. λ_{max} were prepared by processing these data on the CDC-6600 computer of the University of Minnesota by using the Varian Statos 31 plotting system.

General Methods. Melting points were obtained with a Mel-Temp apparatus and are corrected. Boiling points are uncorrected unless indicated as corrected (cor). Infrared (IR) spectra were determined on a Perkin-Elmer Model 257, Beckmann Model 33, or Beckman Model 18A spectrophotometer and are recorded in wave numbers. Nuclear magnetic resonance (NMR) spectra (^{1}H) were measured on a Varian Associates A-60D or XL-100 instrument. Chemical shift values are recorded in parts per million (δ) downfield from tetramethylsilane (internal standard). Mass spectra were obtained on an AEI MS-30 double-beam, double-focusing instrument by the Mass Spectrometry Laboratory of the University of Minnesota. Elemental analyses were obtained from MHW Laboratories, Garden City, MI. Vapor-phase chromatographic (VPC) data were obtained with a Varian Aerograph

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Model 90-P and a Varian Associates Model 30 recorder. The VPC data given are column temperature (CT), helium carrier flow rate (FR), retention time relative to air peak (t_R), and sample injection size in microliters (SIS). Ultraviolet spectra of compounds (described below) were obtained on either a Beckmann Model DK-2A (λ_{max} > 215 nm) or a Cary Model 15 (λ_{max} < 215 nm) spectrophotometer.

(*E*)-2-Ethylidenecyclohexanone (X). In a 1-L three-necked flask fitted with a magnetic stirrer, dropping funnel, and condenser was placed 184 g of cyclohexanone. A solution of 1.05 g of sodium in 25 mL of absolute ethanol was added, while maintaining a temperature of ~0 °C. To this solution was added (over 2.5 h) a solution of 82.6 g of acetaldehyde in 184 g of cyclohexanone. The solution was stirred for an additional 45 min, at which time 150 mL of water was added, and the mixture was washed with a solution of 2.91 g of oxalic acid dihydrate in 50 mL of water. Oxalic acid dihydrate (3.11 g) was added to the organic layer, which upon vacuum distillation gave 59.9 g of X (26%). Chromatography on silica gel (pentane–ether, 3:2) permitted separation of the *E* and *Z* isomers of X. Analytical samples were prepared by VPC on a 6 ft × 0.25 in. 15% Apiezon L on Chromosorb P column (CT = 91 °C, FR = 240 mL/min, t_R = 33.0 min, SIS = 50 μL): bp 48–54 °C (1.5 nm); n^{24}_{D} 1.4903; UV (C_2H_5OH) λ_{max} 245 nm (ϵ 7480); IR (neat) 3024, 2936, 2864, 1691, 1621, 1456, 1438, 1413, 1380, 1346, 1313, 1270, 1259, 1146, 1073, 995, 958, 911, 886, 867, 837, 812, 683; NMR (CCl_4) 1.7–2.0 (m, 3.9 H), 1.83 (d, 3.0 H, J = 7.8 Hz) 2.2–2.7 (m, 4.0 H), 6.74 (q of t, 0.9 H, J = 7.8, 2.2 Hz) [lit. bp 68–70 °C (17 mm);[62] n^{23}_{D} 1.4925;[62] UV (EtOH) λ_{max} 250 nm (ϵ 4000);[62] NMR 6.62[91]].

(*E*)-1-Methyl-4-oxospiro[2.5]octane (VI). A 53% NaH in mineral oil dispersion (5.77 g) was rinsed with pentane in a 250-mL, three-necked, round-bottomed flask. The flask was fitted with a condensor, magnetic stirrer, and dropping funnel, evacuated, and filled with nitrogen. Trimethylsulfoxonium iodide (28.0 g) dissolved in 100 mL of Me_2SO was then admitted slowly. After hydrogen evolution had subsided 15.0 g of X in 40 mL of Me_2SO was added. The mixture was stirred for ~3 h at room temperature and at ~55 °C for 1 h. The reaction mixture was poured onto 250 mL of ice–water and extracted with 250 mL of ether. The ethereal layer was washed with 200 mL of H_2O, dried over Na_2SO_4, and evaporated in vacuo, leaving 13.7 g of oil. Purification by column chromatography on silica gel (pentane) gave 8.8 g of VI (53%). Analytical samples were prepared by VPC on a 9 ft × 0.25 in. 25% FFAP on Chromosorb W column (CT = 152 °C, FR = 88 mL/min, t_R = 19.9 min, SIS = 50 μL): bp 79–83 °C (8 mm); n^{23}_{D} 1.4753; UV (H_2O) λ_{max} 215 nm (ϵ 4298); IR (neat) 3076, 3000, 2940, 2870, 1697, 1453, 1397, 1369, 1320, 1299, 1241, 1138, 1099, 1033, 1014, 985, 976, 894, 803, 749; NMR ($CDCl_3$) 0.1–0.5 (m, 1.0 H), 1.0–1.3 (m, 3.0 H), 1.3–1.7 (m, 2.2 H), 1.7–2.2 (m, 6.0 H), 1.84 (d superimposed on m, 3.0 H, J = 1.6 Hz), 2.2–2.6 (m, 2.0 H) [lit.[43] bp 78 °C (10 mm); n^{25}_{D} 1.4770; UV (H_2O) λ_{max} 215 (ϵ 3360); IR (CCl_4) 1695].

(*E*)-1-Methyl-4-methylenespiro[2.5]octane (VII). A 53% NaH in mineral oil dispersion (1.47 g) was rinsed with pentane in a 100-mL, three-necked, round-bottomed flask fitted with a condenser, magnetic stirrer, and septum. After evacuation of the flask and filling with nitrogen, 20 mL of Me_2SO was added and stirred for ~40 min at 70–80 °C. Methyltriphenylphosphonium bromide (10.57 g) dissolved in 28 mL of Me_2SO was added (by syringe), the resulting solution being stirred for 10 min. A solution of 2.32 g of VI in 2 mL of Me_2SO was then added, and the flask was maintained at 50–60 °C for 6.5 h. The cooled reaction mixture was poured onto 80 mL of ice and extracted with three 50-mL portions of pentane. After filtration to remove triphenylphosphine oxide, the pentane solution was washed with 40 mL of a 1:1 water–Me_2SO solution and then with 80 mL of saturated NaCl solution and was dried over $MgSO_4$. Fractional distillation gave 1.77 g of VII (77%). Analytical samples were prepared by VPC on a 20 ft × 0.25 in. 25% FFAP on Chromosorb W column (CT = 117 °C, FR = 118 mL/min, t_R = 17.7 min, SIS = 40–50 μL): bp 172–173 °C (cor); n^{24}_{D} 1.4707; UV (c-C_6H_{12}) λ_{max} 193 nm (ϵ 8736); IR (neat) 3080, 3066, 2996, 2988, 2970, 2933, 2875, 2856, 1788, 1650, 1460, 1447, 1394, 1243, 1190, 1098, 1090, 1031, 1015, 997, 941, 915, 885, 829, 803, 772; NMR ($CDCl_3$) –0.1–0.1 (m, 1.0 H), 0.6–1.0 (m, 2.2 H), 1.0–1.3 (m, 3.0 H), 1.3–1.9 (m, 6.2 H), 2.1–2.4 (m, 1.9 H), 4.49 (m, 2.0 H). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.93; H, 11.91.

2-Oxo-1-methylbicyclo[4.1.0]heptane (IV). A 53% NaH in mineral oil dispersion (3.35 g) was rinsed with pentane in a 250-mL, three-necked, round-bottomed flask. The flask, after being fitted with a condenser, magnetic stirrer, and dropping funnel, was evacuated and filled with nitrogen. Trimethylsulfoxonium iodide (15.22 g) was added followed by careful addition of 87 mL of Me_2SO. After hydrogen evolution had subsided, 7.21 g of XI in 10 mL of Me_2SO was added. The mixture was stirred at room temperature for 2.5 h and at 70–80 °C for 2 h. The reaction mixture was poured onto 270 mL of ice and extracted successively with 250 and 100 mL of ether. The ether was washed with three 100-mL portions of water, dried over Na_2SO_4, and distilled in vacuo, yielding 6.65 g of crude product. Chromatography on silica gel (pentane–ether, 3:2) gave 4.29 g (53%) of VI. Analytical samples were prepared by VPC on a 6 ft × 0.25 in. 15% Apiezon L on Chromosorb P column (CT = 151 °C, FR = 45 mL/min, t_R = 11.0 min, SIS = 50 μL): bp 53–57 °C (1.5 mm); n^{24}_{D} 1.4806; UV (H_2O) λ_{max} 207.5 nm (ϵ 5264); IR (neat) 3088, 3010, 2960, 2930, 2865, 1689, 1477, 1463, 1447, 1378, 1360, 1330, 1126, 1099, 1086, 1022, 974, 913, 845, 825, 752; NMR (CCl_4) 0.7–1.0 (m, 0.8 H), 1.19 (s, 3.0 H), 1.3–1.6 (m, 1.7 H), 1.6–2.4 (m, 5.9 H) [lit.[43] bp 76 °C (10 mm); n^{25}_{D} 1.4794; UV (H_2O) λ_{max} 207 nm (ϵ 5800); IR (CCl_4) 1692].

2-Methylene-1-methylbicyclo[4.1.0]heptane (V). A 50% NaH in mineral oil dispersion (1.45 g) was rinsed with pentane in a 100-mL, three-necked, round-bottomed flask that was subsequently fitted with a condenser, magnetic stirrer, and septum. After evacuation and filling with nitrogen, 15 mL of Me_2SO was added by syringe and the mixture stirred at 70–80 °C for 40 min. Methyltriphenylphosphonium bromide (10.4 g) in 25 mL of Me_2SO was added to the cooled solution over 10 min. A solution of 2.08 g of IV in 2 mL of Me_2SO was added by syringe and the reaction mixture stirred for 6.5 h. The reaction mixture was poured onto 80 mL of ice and extracted with three 50-mL portions of pentane, and the pentane solution was filtered to remove triphenylphosphine oxide. The pentane solution was washed with 40 mL of a 1:1 water–Me_2SO solution and 80 mL of saturated NaCl solution and then was dried over $MgSO_4$. The pentane was removed by fractional distillation, leaving 1.31 g (64% crude yield) of oil. Distillation of this oil gave V with trace amounts of 1,2-dimethylbicyclo[4.1.0]hept-2-ene. Analytical samples were prepared by VPC on a 20 ft × 0.25 in. 25% FFAP on Chromosorb W column (CT = 90 °C, FR = 136 mL/min, t_R = 33.8 min, SIS = 40 μL): bp 156–157 °C (cor); n^{23}_{D} 1.4795; UV (c–C_6H_{12}) λ_{max} 201 nm (ϵ 14850); IR (neat) 3083, 3066, 2996, 2948, 2932, 2858, 1638, 1469, 1451, 1375, 1354, 1156, 1114, 1099, 1086, 1015, 936, 905, 888, 872, 837, 820, 755; NMR ($CDCl_3$) 0.5–0.8 (m, 1.9 H), 0.8–1.2 (m, 1.0 H), 1.24 (s, 3.2 H), 1.3–1.6 (m, 1.9 H), 1.6–2.2 (m, 4.0 H), 4.9 (d, 2.0 H, J = 1.2 Hz). Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.58; H, 11.43.

2-Oxotricyclo[5.2.1.0^{3,5}]decane (VIII). A 50% NaH in mineral oil dispersion (2.27 g) was rinsed with pentane in a 250-mL, three-necked, round-bottomed flask that was subsequently fitted with a condenser, magnetic stirrer, and septum. Trimethylsulfoxonium iodide (10.29 g) was placed in the flask under a nitrogen atmosphere, and 60 mL of Me_2SO was added cautiously by syringe. The solution was stirred for 30 min after hydrogen evolution had subsided. A solution of 6.00 g of XII in 10 mL of Me_2SO was added by syringe, and the reaction mixture was stirred at room temperature for 3.2 h. The reaction mixture was poured onto 200 mL of ice and extracted with two portions of ether (200 and 75 mL). The ether solution was washed with three 70-mL portions of water, was dried over $MgSO_4$, and was stripped of solvent in vacuo, leaving 4.74 g of crude oil. Chromtography on silica gel (pentane–ether, 3:2) gave 3.10 g of VIII (36%). Analytical samples were prepared by VPC on a 9 ft × 0.25 in. 25% FFAP on Chromosorb W column (CT = 182 °C, FR = 193.5 mL/min, t_R = 25.0 min): mp 64–66 °C; UV (H_2O) λ_{max} 197 nm (ϵ 5310); IR (polycryst) 3022, 2938, 2853, 1666, 1480, 1453, 1362, 1338, 1285, 1217, 1164, 1123, 1031, 1009, 996, 966, 945, 911, 880, 855, 795; NMR ($CDCl_3$) 0.9–1.5 (m, 3.0 H), 1.5–2.3 (m, 9.4 H), 2.4–2.7 (m, 1.1 H), 2.8–3.1 (m, 1.0 H). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.97; H, 9.60.

Table V. Force Field Parameters for Cyclopropyl Derivatives[a,b]

Bond Stretching

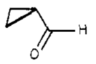
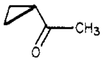
bond	k, mdyn/Å	l_0, Å
C_{cp}-C_{sp^2}(carbonyl)	6.0	1.507
C_{cp}-C_{sp^2}(olefin)	6.0	1.510

Torsional Parameters

torsional angle (ω)	torsional constants, kcal/mol V_1	V_2	V_3
$O{=}C_{sp^2}{-}C_{cp}{-}C_{cp}$	0	5.00	−1.75
$H{-}C_{sp^2}{-}C_{cp}{-}H$	−2.10	0	0.37
$H{-}C_{sp^2}{-}C_{cp}{-}C_{sp^3}$	−2.10	0	0.37
$C_{sp^3}{-}C_{sp^2}{-}C_{cp}{-}C_{sp^3}$	−2.10	0	0.37
$C_{sp^2}{=}C_{sp^2}{-}C_{cp}{-}C_{cp}$	0	6.00	0.30
$C_{sp^3}{-}C_{sp^2}{-}C_{cp}{-}H$	−2.10	0	0.37

[a] C_{cp} represents a cyclopropyl carbon. [b] The Fourier constants are for an equation of the form $E_{torsion} = 0.5[V_1(1 + \cos \omega) + V_2(1 - \cos 2\omega) + V_3(1 + \cos 3\omega)]$.

Table VI. Geometries of Cyclopropanecarboxaldehyde, Methyl Cyclopropyl Ketone, and Vinylcyclopropane[a]

molecule	int coord	obsd	calcd
	Electron Diffraction[b]		
	$r(C{-}H)_{av}$	1.115	1.106
	$r(C{-}C)_{av}$	1.507	1.508
	$r(C{=}O)$	1.216	1.208
	$\theta(C{-}C{=}O)$	122.0	124.5
	$\theta(C{-}C{-}H)_{av}$	117.1	117.2
	Electron Diffraction[c]		
	$r(C{-}H)_{av}$	1.126	1.097
	$r(C{-}C)_{av}$	1.510	1.512
	$r(C{-}O)$	1.225	1.209
	$r(C{-}C{=}O)_{av}$	121.8	121.9
	$\theta(C{-}C{-}H)_{av}$	117.2	116.0
	Electron Diffraction[d]		
	$r(C{-}H)_{av}$	1.099	1.096
	$r(C{-}C)_{av}$	1.510	1.509
	$r(C{=}C)$	1.334	1.339
	$\theta(C{=}C{-}H)_{av}$	119.7	120.1
	$\theta(C{-}C{-}H)_{av}$	116.8	117.0
	$\theta(C_2{-}C_1{-}C_4)$	118.7	118.7
	$\theta(C_1{-}C_4{-}C_5)$	123.8	124.5

[a] All bond lengths are in angstroms, and all bond angles are in degrees. [b] From ref 83. [c] From ref 85. [d] Model I from ref 86.

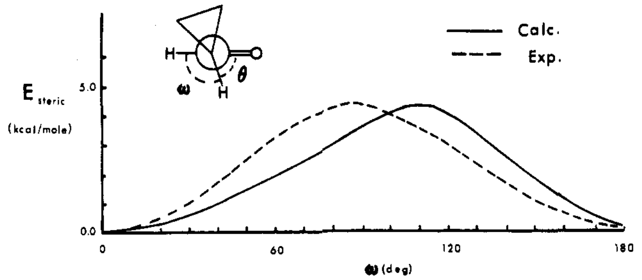


Figure 6. Comparison of the experimental (---) and force-field-determined (—) rotational profiles for cyclopropanecarboxaldehyde.

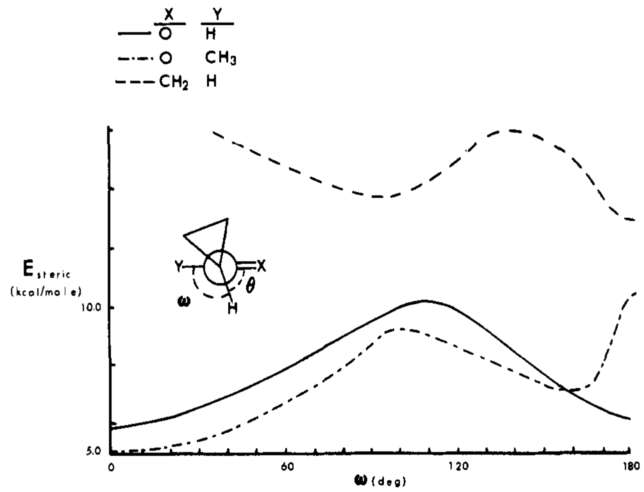


Figure 7. Rotational profiles, based on force-field-determined geometries, for cyclopropanecarboxaldehyde (—), methylcyclopropyl ketone (-·-) and vinylcyclopropane (---).

2-Methylenetricyclo[5.2.1.0^{3,5}]decane (IX). A 50% NaH in mineral oil dispersion (1.47 g) was rinsed with pentane in a 100-mL, three-necked, round-bottomed flask that was subsequently fitted with a magnetic stirrer, condenser, and septum. The system was placed under a nitrogen atmosphere, 20 mL of Me_2SO was added by syringe, and the mixture was stirred for 40 min at 70–80 °C. After the mixture cooled somewhat, a solution of 10.57 g of methyltriphenylphosphonium bromide in 28 mL of Me_2SO was added by syringe. After the mixture was stirred for 10 min, 2.50 g of VIII in 2 mL of Me_2SO was added by syringe. The reaction mixture was stirred at 50–60 °C for 5.5 h and at 70–80 °C for 1 h. The reaction mixture was poured onto 80 mL of ice and extracted with three 50-mL portions of pentane. The pentane solution was washed with 40 mL of a 1:1 water-Me_2SO solution and 80 mL of saturated NaCl solution and was then dried over $MgSO_4$. Fractional distillation gave 1.63 g of IX (66%). Analytical samples were prepared by VPC on a 9 ft × 0.25 in. 25% FFAP on Chromosorb W column (CT = 132 °C, FR = 240 mL/min, t_R = 16.0 min, SIS = 50–60 μL): $n^{23}{}_D$ 1.5238; UV (c-C_6H_{12}) λ_{max} 203 nm (ϵ 11 550); IR (neat) 3074, 3005, 2925, 1617, 1476, 1449, 1318, 1308, 1182, 1170, 1128, 1095, 1054, 1019, 995, 974, 877, 836, 797, 689, 671; NMR ($CDCl_3$) 0.4–1.3 (m, 2.7 H), 1.4–3.3 (m, 9.4 H), 3.3–3.6 (m, 0.9 H), 2.8–3.1 (m, 1.1 H), 4.77 (m, 1.9 H). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.08; H, 11.05.

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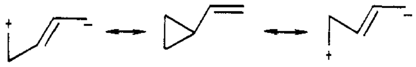
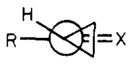
Appendix

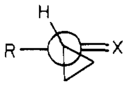
Methods. The main features of the Allinger force-field techniques are adequately detailed in the literature[65] and will not be reviewed here. Cyclopropanes have been studied in Allinger's laboratory,[65h] and our work represents an extension in some detail of the application of the method to the calculation of the conformational properties of cyclopropyl derivatives. Parameters needed in this work are at first approximated by those from the analogous acyclic compounds (i.e., treating C_{cp}, cyclopropyl carbons, the same as C_{sp^3} carbons). However, certain modifications are necessary. These parameters are listed in Table V. The most important new parameters turned out to be the Fourier constants necessary for the torsional functions for bonds between an sp^2 carbon and a cyclopropyl carbon. One feature of the torsional functions merits comment. The large V_2 values for torsions about C_{sp^2}–C_{cp} bonds are 30–40% of that required for carbon–carbon double bonds (15.00 kcal/mol).[65d] The necessity for this parameter is consistent with the interaction (Δ_p–π) whose spectral effect we are attempting to assay, and with the following scheme



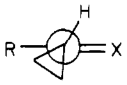
One other modification was necessary for proper fitting of the model systems. The stretching force constant k-(C_{sp^2}–C_{cp}) was fixed at 6.0 mdyn/Å, a value intermediate between those for "pure" single (4.4 mdyn/Å) and double (9.6 mdyn/Å) bonds. As with the V_2 terms, this parameter relfects the coupling of cyclopropyl to unsaturated systems. By partioning the overall coupling in this fashion we have, on the basis of the model systems results, adequately accounted for the principal effects of this important interaction. The principal conformers encountered are depicted below.



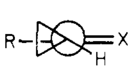
XVIIIa
s-cis



XVIIIb
gauche



XVIIIc
anti-gauche



XVIIId
s-trans

Results for Model Systems. For cyclopropanecarboxaldehyde (XVIII, R = H, X = O) we find the cis form ($\theta = 180°$, $\omega = 0°$) to be favored by 0.2 kcal/mol. Electron-diffraction results[83] have been rationalized in terms of a mixture, 55% cis, 45% trans (ΔH^{298}(cis ⇄ trans) = 0.53 kcal/mol). Microwave studies indicate a rotational barrier of 4.4 kcal/mol,[84] to be compared with our calculated value of 4.3 kcal/mol. In Figure 6 we display the experimental and calculated rotational profiles. It should be noted that there is substantial disagreement as to the position of the barrier. The experimental curve is in fact derived from considerations of the behavior of the molecule near its potential minima. As has been pointed out before,[65e] such a procedure fails to allow for the relaxations which must accompany large deviations from the rotational minima. Hence we consider our calculated profile to have validity comparable to that derived from experiment.

Electron-diffraction results for methyl cyclopropyl ketone[85] (XVIII, R = CH_3, X = O) are best explained in terms of a conformational mixture 80:20 cis/anti-gauche [ΔH^{298}(cis ⇄ anti-gauche) = 1.23 kcal/mol]. Our calculations, on the other hand, predict the *s*-cis conformer to be more stable by 2.1 kcal/mol. The anti-gauche species is found to correspond to $\theta = 35°$ ($\omega = 145°$; see Figure 7). No experimental estimate of this angle is available for comparison. The calculated conformational energy for the anti-gauche form appears to be less satisfactory, but sufficient data are not available for evaluating its reliability.

Vinylcyclopropane (XIX; R = H, X = CH_2) was originally felt to be analogous to cyclopropanecarboxaldehyde in terms of its rotational profile. Evidence for a gauche minimum was provided by electron-diffraction,[86] NMR,[87,88] and Raman[89] studies. Best estimates from electron-diffraction[86] and Raman[89] results predict a conformtional mixture: ~75% *s*-trans and 25% gauche at 20 °C [ΔH^{293} (*s*-trans ⇄ gauche) = 1.04 kcal/mol (electron diffraction) and 1.43 kcal/mol (Raman)]. A lower limit of 1.8 kcal/mol was set for the barrier between these two forms by Codding and Schwendeman.[90] The more recent Raman study places the barrier at 3.92 kcal/mol.[89] We calculate the *s*-trans vinylcyclopropane to be 1.0 kcal/mol lower in energy than the gauche form, the barrier being 3.4 kcal/mol. Of particular importance is the position of the gauche minimum. The first estimate[86] was $120° > \theta > 110°$ ($60 \leq \omega \leq 70°$), but NMR studies[88] led to two possible values, $\theta = 101°$ or 94° ($\omega = 79°$ or 86°). Our calculated minimum (θ or $\omega \simeq 90°$) agrees more closely with the NMR results. Finally it should be noted (Figure 7) that the *s*-cis conformer *does not* correspond to an energy minimum. This aspect of the problem has been studied via SCF-MO calculations. While minimum basis sets [ab initio (STO-3G)[31] and INDO[30]] predict such a minimum, use of a more flexible basis set (4-31G)[31] results in the disappearance of this feature. None of the SCF–MO calculations were carried out with geometry optimization, but no experimental evidence for the *s*-cis conformer has been reported.

The geometries calculated for these model systems are summarized in Table VI. As can be seen, in all cases reproduction of the experimental data is quite satisfactory. We are confident, therefore, that reasonable geometries are obtained for the molecules of interest.

Registry No. IV, 14845-40-0; V, 82554-84-5; VI, 14845-49-9; VII, 82554-85-6; VIII-NB, 82554-83-4; VIII-XC, 82597-42-0; IX-NB, 82554-86-7; IX-XC, 82597-43-1; (*E*)-X, 7417-55-2; (*Z*)-X, 7417-54-1.

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