On the Orbital Interactions of Three-Membered Rings with π Systems. Electronic Structure of Alkenylidenecyclopropanes[1]

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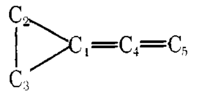
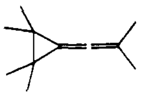
Abstract: The electronic structure and bonding in alkenylidenecyclopropanes have been investigated using He(I) photoelectron spectroscopy and CNDO calculations. The nature and magnitude of the interactions between the Walsh orbitals of the three-membered ring and the two π bonds of the allene chromophore are analyzed, and the forms of the five highest energy MO's are outlined. In addition to the interaction of the σ-type, in-plane Walsh orbital with the terminal allene double bond, our analysis indicates that one of the lower lying, degenerate p_z π-type orbitals interacts significantly with the exocyclic double bond. In prior discussions of the bonding in methylene- and vinylcyclopropanes, and related systems, the effect of interactions with the p_z π-type orbitals has been ignored. Substituent effects on the energies of the MO's are analyzed and are used to confirm orbital assignments. The interaction parameter δ for the interaction of the terminal π system with the in-plane Walsh orbital is 1.0, indicating that the resonance interaction in the alkenylidenecyclopropanes is ~83% that in 1,3-butadiene.

Photoelectron spectroscopy[2] has been successfully used to characterize the nature of the electronic structure of a variety of conjugated systems,[3] a number of which involve small rings.[4-7] In these laboratories studies of the chemistry of alkenylidenecyclopropanes have indicated a significant interaction between the cyclopropyl and C_4-C_5 π systems. In order to gain a more quantitative evaluation of the extent of this interaction, the He(I) photoelectron spectra of a series of these (**1-9**) and related compounds (**10** and **11**) have been measured.

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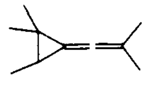
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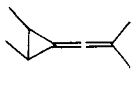
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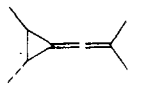
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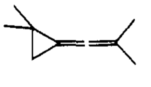
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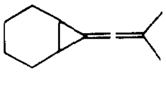
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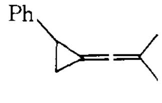

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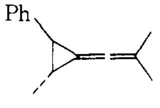

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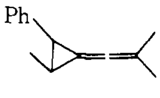

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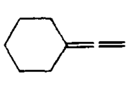
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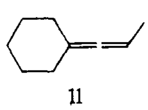
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Results for the cyclopropane-containing systems are given in Table I; typical spectra are shown in Figure 1. In all cases only the bands of lowest ionization potential are given, and attention is focused on the first five bands. These bands fall at ionization potentials lower than that expected for typical σ- and π-type orbitals.[2] In compounds **1-6** the areas of these five bands are approximately the same, thereby indicating the same occupancy.[8] The second band is sharp and in most cases exhibits vibrational fine structure with a spacing of about 1100-1300 cm^{-1}. This frequency is close to the symmetric stretching frequency of allene[9] and, apparently, this excited state of the radical cation behaves similarly to the cation produced by ionization of a symmetrically substituted allene.

These molecules are amenable to the application of the linear combination of bond orbitals (LCBO) method[10] which provides a simplified, but useful, description of the orbital interactions between portions of molecules. We begin by considering interactions between those orbitals of the same symmetry that are closest in energy. In this fashion, the highest energy occupied orbitals of an alkenylidenecyclopropane result from the linear combination of the π orbitals of an allene with the degenerate pair of highest energy Walsh orbitals[11] of cyclopropane.[12] As illustrated in Figure 2, the C_4-C_5 π orbital interacts with one of the σ-type Walsh orbitals of appropriate symmetry in a bonding and an antibonding manner. The splitting $\Delta_{1,2}$, and $\Delta_{3,4}$, is, thus, a measure of the magnitude of this interaction (see Table I for the values of the Δ's). According to this model the second highest orbital is the C_1-C_4 π-type, which is effectively isolated from the methyl substituted ends of the molecule and their associated, low-frequency vibrational modes. Therefore, one expects to see characteristic ethylenic vibrational structure in this band, with a frequency in the range 1000-1500 cm^{-1} as observed.

In order to identify the molecular orbitals giving rise to the other ionizations, we have examined in detail the effects of substituents on the three-membered ring on the band positions. A discussion of such effects involves a number of complications which must be considered first. Substituent effects may affect the stability of the ion or molecule, or both. A second complication is that, in the photoelectron spectrum of both allene and cyclopropane, the first band is split by a final state effect, the Jahn-Teller distortion of the ion.[2] Consequently, the net result of the final state effect and the substituent effects must be considered. In the following we show qualitatively that these complications may be understood, and that the simple model of Figure 2 is basically correct.

For our purposes, the pragmatic approach of Brogli et al. is most useful.[13] These authors note that, as the symmetry of the molecular ground state is removed by substituents, the Jahn-Teller effect becomes relatively less important and substituent effects become more important. For small substituent interactions, the magnitude of the splitting reaches a limiting value of about 0.5 eV. This behavior is modeled in terms of two parameters: one constant parameter for the Jahn-Teller splitting and one for the substituent effect. It was found that the latter parameter was numerically similar to that found in systems free from Jahn-Teller effects.[13]

Table I. Ionization Potentials of Alkenylidenecyclopropanes

Band notation	1 IP, eV	1 ν, cm^{-1}	2 IP, eV	2 ν, cm^{-1}	3 IP, eV	3 ν, cm^{-1}	4 IP, eV	4 ν, cm^{-1}	5 IP, eV	5 ν, cm^{-1}	6 IP, eV	6 ν, cm^{-1}
1	7.87 7.46[a]		8.00 7.57[a]		8.16 7.76[a]		8.13 7.70[a]		8.08 7.65[a]		8.01 7.60[a]	
2	8.78	1230 0 → 1[b]	8.90	~1200	9.00	1260 0 → 1[b]	8.98	1300 0 → 1[b]	8.96	1190 0 → 1[b]	8.88	1280 0 → 1[b]
3	9.42		9.72		10.05		10.10		10.07		9.79	
4	10.78		10.96		11.09		11.08		11.24		10.84	
5	11.21		11.63		11.75		~11.9		11.95		11.72	
$\Delta_{1,2}$	0.91		0.90		0.84		0.85		0.88		0.87	
$\Delta_{1,4}$	2.91		2.96		2.93		2.95		3.16		2.83	
$\Delta_{3,4}$	1.36		1.24		1.04		0.98		1.17		1.05	

Band notation	7 IP, eV	7 ν, cm^{-1}	8 IP, eV	8 ν, cm^{-1}	9 IP, eV	9 ν, cm^{-1}
1	8.15 7.73[a]		8.12 7.63[a]		8.11 7.65[a]	
Ph	8.80		8.80		8.78	
2, Ph	9.16		9.12		9.06	
3	10.67		10.44		10.49	
4	11.45		11.24		11.29	
$\Delta_{1,2}$	1.01		3.30		0.78	
$\Delta_{1,4}$	1.00		3.12		0.80	
$\Delta_{3,4}$	0.95		3.18		0.80	

[a] Adiabatic ionization potential. [b] Vibrational line of maximum intensity.

Table II. Photoelectron Ionization Potentials of Compounds 10 and 11

Band	10 IP, eV	10 $\nu_{(0\to1)}$, cm^{-1}	11 IP, eV	11 $\nu_{(0\to1)}$, cm^{-1}
1	8.80 (8.69)[a]	1270	8.66 (8.41)[a]	1670
2	9.56		9.10	
3	10.81		10.80	
$\Delta_{1,2}$	0.76		0.44	

[a] Adiabatic ionization potential.

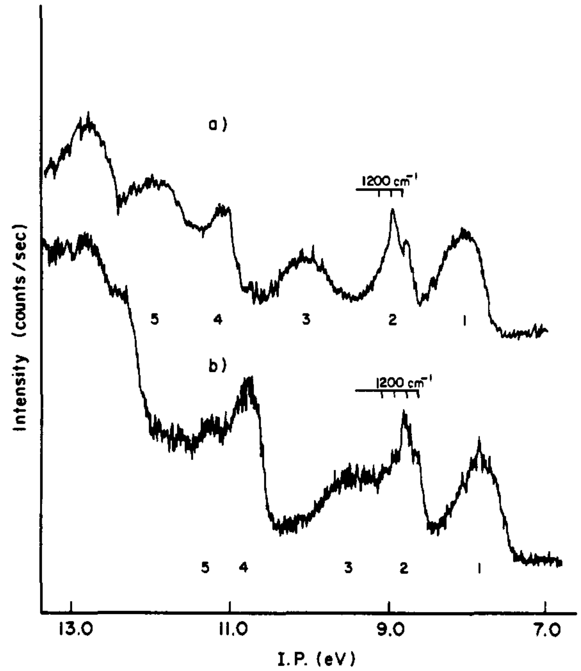


Figure 1. He(I) photoelectron spectra of 2,2-dimethyl- (**5**) and 2,2,3,3-tetramethylisobutenylidenecyclopropane (**1**).

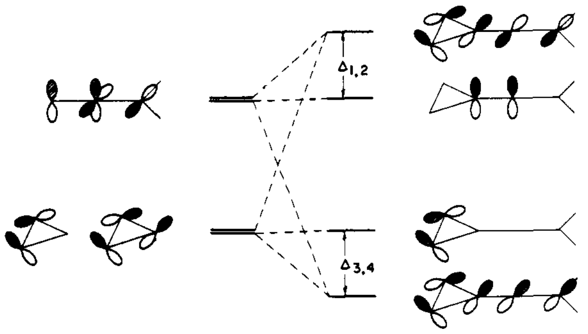


Figure 2. LCBO model for alkenylidenecyclopropanes.

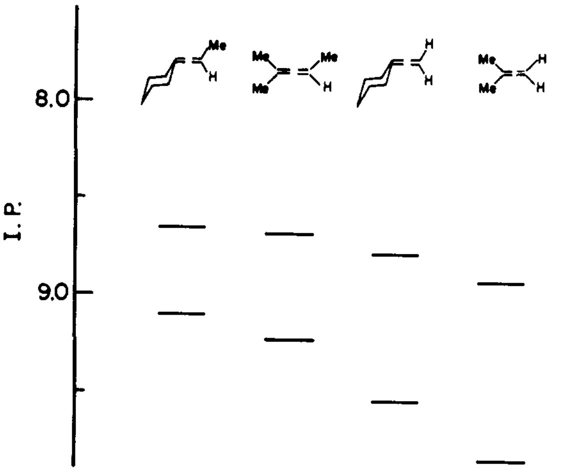


Figure 3. Line spectral comparison of the IP's of the two highest energy MO's of **10**, **11**, and 1,1-dimethyl- and 1,1,3-trimethylallene.

We choose to approach the analysis of the alkenylidenecyclopropanes from the point of view of substituted allenes because of the existence of the previous work on substituted allenes,[13] and also because we have measured the spectra of two alkenylidenecyclohexanes (**10** and **11**). A significant conjugative interaction of the type in interest here (Figure 2) is not expected in these latter compounds. Their IP's are given in Table II, and line spectra are compared with the related methyl-substituted allenes in Figure 3. Clearly, the

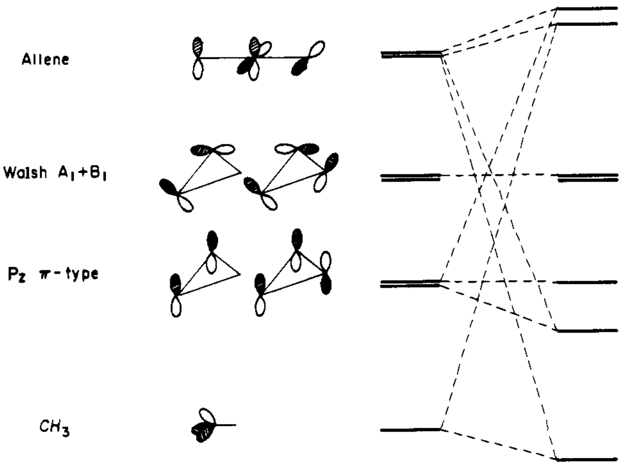
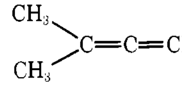


Figure 4. Illustration of the partial cancellation of the $\overline{W}_\pi$–$\pi_{1,4}$ interaction by the $CH_{3\pi}$–$\pi_{4,5}$ interaction in the absence of W_σ–$\pi_{4,5}$ interaction and Jahn–Teller effects.

cyclohexyl group behaves like two methyl groups, but with a somewhat smaller substituent interaction parameter. In these molecules the splitting $\Delta_{1,2}$ between the first two IP's may be described[13] by

$$\Delta_{1,2} = \sqrt{\delta^2 + 4\tau^2}$$

where δ is the substituent interaction parameter and τ the Jahn-Teller splitting parameter. With τ = 0.25 eV,[13] **10** and **11** possess substituent parameters of 0.6 and ≤0.3 eV compared to 0.8 and ≤0.3 eV for **12** and **13**.



$(CH_3)_2C{=}C{=}CH_2$

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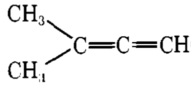

$(CH_3)_2C{=}C{=}CHCH_3$

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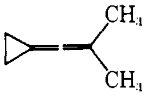
For the cyclopropyl derivatives (Table I), both $\Delta_{1,2}$ and $\Delta_{1,4}$ are essentially independent of the degree of methyl substitution in **1**–**6**. Therefore, we can take $\Delta_{1,2}$ for the parent ring unsubstituted compound **14** as 0.9 eV. This $\Delta_{1,2}$ in



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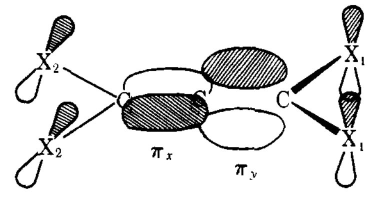
the two-parameter model (with τ = 0.25 eV) yields δ = 0.7 eV. This is clearly larger than the parameter for the cyclohexyl compounds (≤0.3 eV), and we attribute the difference to the interaction of the C_4–C_5 π system with the in-plane cyclopropyl Walsh orbitals.

A more detailed analysis based on the results of CNDO calculations indicates that one of the next lower lying p_z π-type orbitals of the three-membered ring interacts with the C_1–C_4 π orbital. This interaction would tend to reduce $\Delta_{1,2}$ (Figure 4). Let us consider first a tetrasubstituted allene. The energy of π_y will be affected by interaction with



the orbitals on X_1, and similarly π_x, by the orbitals on X_2. When X_1 and X_2 are the same, the effects on the energy of π_x and π_y will be the same, and π_x and π_y will be split mainly by the Jahn-Teller effect. In the specific case X_1 = X_2 = CH_3 the *net* interaction parameter is ≤0.3 eV. In the case of the cyclopropyl compound **14** (X_2 = X_2 = $-(CH_2)_2-$, X_1 = CH_3), in the absence of any special interaction with σ-type Walsh orbital, the magnitude of the interaction of the p_z π-type orbital with π_x should be roughly the same as the interaction of π_y with the methyls (X_1 = CH_3), and the π_x and π_y MO's will be split mainly by the Jahn–Teller effect. In reality the two interactions do not exactly compensate each other, and we later calculate that π_x is destabilized by ~0.1 eV relative to π_y (Figure 4). This indicates that a better value for δ is 1.0 eV. Considering that δ = 1.2 eV in 1,3-butadiene, the value of δ for the alkenylidenecyclopropane system indicates considerable conjugative interaction between the σ-type, in-plane Walsh orbitals and the C_4–C_5 π orbital. This observation is consistent with the results of related studies.[4-7]

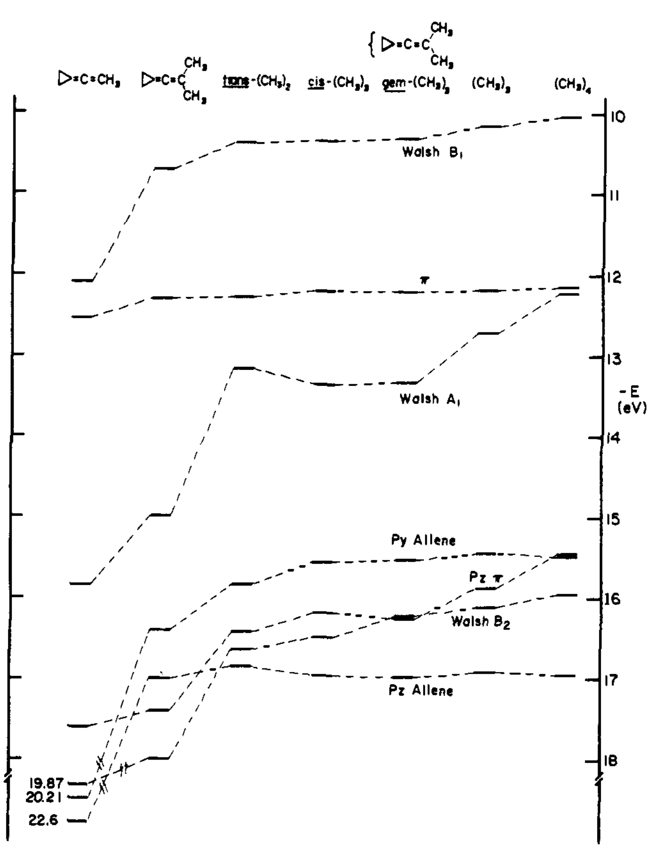
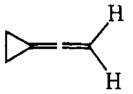


Figure 5. Orbital energies and assignments of the highest energy MO's of various substituted alkenylidenecyclopropanes.

The replacement of X_1 by hydrogen removes the substituent destabilization of π_y relative to π_x and results in a net substituent interaction parameter of 0.7 eV for methyl[13] and 0.6 eV for $-CH_2-$ (see above). Although experimental data are not available[14] for **14** and **15**, CNDO calculations



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(see Figure 5) indicate that the removal of the C_5 methyl groups of **13** results in a substantial lowering in the energy of the Walsh B_1 MO (the in-plane Walsh–π_y combination), but only a small lowering in the energy of the π MO (the p_z π-type–π_x combination). Having established that δ = 1.0 eV for the interaction between the in-plane Walsh orbital and π_y (i.e., the C_4–C_5 π system), the removal of π_y from **14** to give methylenecyclopropane will lower the energy of the Walsh B_1 MO *below* the π_x MO. Thus, the HOMO of methylenecyclopropane is not the in-plane Walsh-type or-

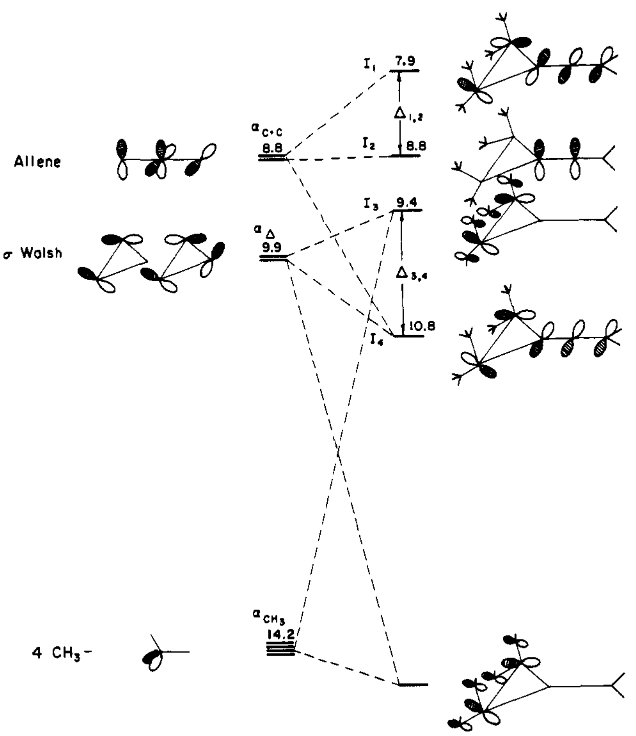


Figure 6. LCBO model for alkenylidenecyclopropane with interaction of ring methyls. The experimental values for **1** are given. The value of $\alpha_{C=C}$ is about equal to the ionization potential of tetramethylallene as expected. Only one of the degenerate CH_3 group orbitals is shown for simplicity. In addition, the C_5 methyl and p_z π-type interactions (Figure 4) are ignored.

bital, but is an orbital arising from the interaction of the p_z π-type orbital with the π system. The importance of the lower lying p_z π-type orbitals of cyclopropan in orbital interactions has not been recognized in the past.[4-7]

In the interaction scheme depicted in Figure 2, $\Delta_{1,2}$ and $\Delta_{3,4}$ should remain constant; however, such is not the case (see Table I). In the approach outlined in Figure 2, substituent effects on the orbital energies are ignored, and it is doubtful the substituents should affect the energies of all of the MO's to the same extent. Inspection of the data presented in Table I reveals that $\Delta_{3,4}$ increases with increasing methyl substitution on the ring. If one parameterizes this interaction (illustrated in Figure 6 for **1**) in terms of

$$\beta = -[(\alpha_\Delta - I_3)(\alpha_{CH_3} - I_3)]^{1/2}$$[10]

where α_Δ is taken to be $I_4 - \Delta_{1,2}$ and $\alpha_{CH_3} = 14.2$ eV,[10] and plots β as a function of the number of methyl groups attached to the three-membered ring, one obtains Figure 7. The important conclusion derived from this correlation is that $\Delta_{3,4} - \Delta_{1,2}$ is predicted to be very small (~0.02 eV) in the absence of methyl groups on the three-membered ring. The plot in Figure 7 can be forced to go through the origin by arbitrarily increasing $\Delta_{1,2}$ from 0.9 to about 1.0 eV. The difference, 0.1 eV, is suggested to result from the relative destabilization of the C_1–C_4 π orbital by interaction with the out-of-plane, p_z π-type orbital compared to the interaction of the C_4–C_5 π orbital interaction with the methyls attached to C_5, as discussed above.

CNDO calculations (see Experimental Section for bond lengths and angles used) confirm the assignment of the nature of the five highest energy occupied orbitals and provide additional insight concerning the orbital interactions and substituent effects on orbital energies. Figure 8 outlines the general forms and energies of the highest energy occupied MO's of ethenylidenecyclopropane. The HOMO and π-type MO's are formed as indicated in Figures 2 and 4.

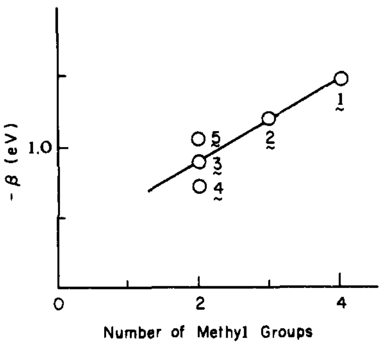


Figure 7. Plot of substituent interaction parameter vs. number of methyl groups attached to the three-membered ring.

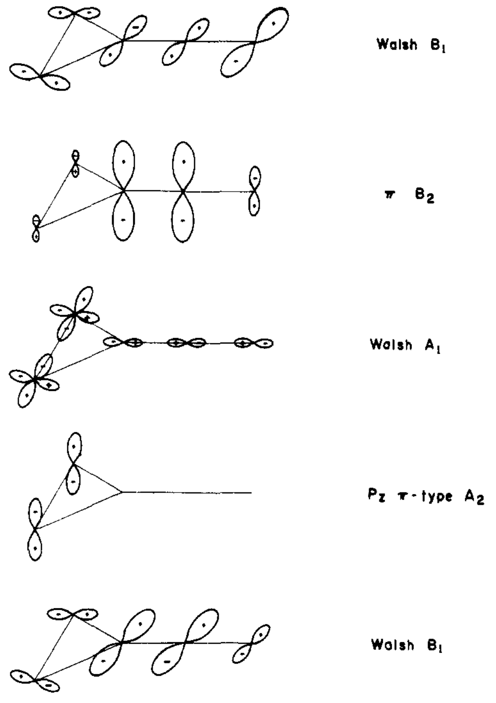


Figure 8. Highest occupied MO's of ethenylidenecyclopropane.

Although it is well known that the CNDO method overestimates orbital energies,[15] and that they are not comparable to experimental IP's, the MO's themselves, however, give a reasonable description of the bonding scheme, types of interactions, etc. Thus, a detailed analysis of the MO wave functions provides an interpretation of the observed substituent effects, and allows an independent means of assignment of the observed PE bands to specific MO ionizations. The magnitude of the interactions of a methyl group with the MO's will be proportional to the sums of the products of the coefficients of the AO's on the methyl and ring carbon atoms. Table III lists such sums for the six highest energy MO's, as calculated from the CNDO wave functions for **4** along with average changes in MO energy per methyl attached to the three-membered ring (see Figure 5 for a graphical summary of the MO energies and identities for **1–5**, **14**, and **15**). In the right-hand column are listed the observed changes in the IP's of the MO's per methyl, which are matched in relative magnitude to the calculated changes (the associated PE band number is indicated in parentheses). The correlation between $\Delta eV/CH_3$ is very good. Not surprisingly, for the deeper lying MO's, the ordering with respect to energy differs from the experimental IP's. (The ordering of the fourth and lower MO's as calculated by the CNDO method depends somewhat on the degree of substitution on the ring; see Figure 5.) The three highest en-

Table III. Comparison of Calculated and Observed Methyl Substituent Shifts for 4

	Calculated		Observed
MO type	ΣC_3C_4 occ.	Methyl shift, eV/CH_3	Methyl shift, eV/CH_3[a]
B_1 Walsh	0.0282	~0.15	~0.12 (1)
B_2 π	0.0161	~0.03	0.08–0.12 (2)
A_1 Walsh	0.1225	0.5–0.6	~0.33 (3)
A_1 p_y allene	0.0166	~0.05	
A_2 p_z π-type	0.1613	0.4–0.5	~0.3–0.42 (5)
B_1 Walsh	0.0500	~0.12	0.12–0.17 (4)

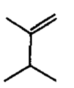
[a] Band number assignments given in parentheses.

ergy MO's agree with the observed ordering, but the PE spectra indicate that bands **4** and **5** must arise from the Walsh B_1 and A_2 π-type MO's.

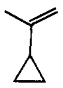
Phenyl-Substituted Alkenylidenecyclopropanes. The presence of a phenyl group attached to the three-membered ring results in very little change in the IP of the HOMO relative to the dimethyl compounds (compare **3** with **9**, and **4** with **8** in Table I). An additional band appears in these spectra as expected, since benzene has an IP of 9.2 eV. This band results from ionization of a doubly degenerate MO which is expected to be split upon substitution (e.g., toluene, IP $\simeq$ 9.0, IP_2 = 9.3 eV).[2] Therefore, we assign the band at 8.8 eV (relative area 1) to one of the phenyl ionizations, and the band at 9.16 eV (relative area 2.5) to the other phenyl ionization and the C_1–C_4 π ionization (band 2 in the previous notation). The lack of significant changes in the energies of the HOMO of the alkenylidenecyclopropane and the phenyl bands indicates that little conjugation exists between the π MO's of the aromatic ring and the Walsh orbital of the three-membered ring. This observation is consistent with the recent rationalization of the inability of the cyclopropane ring to transmit or propagate resonance effects owing to the small coefficients of the appropriate AO's on the *ipso* and ring carbon atoms.[16] The lack of a significant resonance interaction between the aromatic and three-membered ring **7**, **8**, and **9** has also been deduced from the rates of reaction of these compounds with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).[17]

A comparison of the other low-energy IP bands of **7**, **8**, and **9** with **3** and **4** shows that the presence of the phenyl group leads to a lowering of the energy of the MO's, i.e., shifts to higher IP's. This again indicates little or no conjugative interaction, and that the phenyl group is acting predominantly as an electron-withdrawing group. Although $\Delta_{1,2}$ is not well determined in these compounds, both it and $\Delta_{3,4}$ are approximately equal to the values deduced for the unsubstituted alkenylidenecyclopropane above.

Comparison of Alkenylidenecyclopropanes with Vinylcyclopropanes. Chemical, physical, and theoretical studies indicate that the C_4–C_5 double bond of alkenylidenecyclopropanes interacts more strongly with the three-membered ring than does the double bond in vinylcyclopropanes. For example, vinylcyclopropanes fail to undergo facile cycloaddition reactions with PTAD as does the alkenylidenecyclopropanes.[18] The difference (0.26 eV) in IP's of the HOMO's of **16** (9.18 eV)[19] and **17** (8.92 eV)[19] is less than that between tetramethylallene (taken as the average of the Jahn–Teller split bands, 8.72 eV) and isobutenylidenecyclopropane (estimated to be 8.39 eV) of 0.33 eV. This difference must be due to basic differences in the geometrics of the two systems, i.e., differences in bond lengths of the C_1–C_4 bond and in the orientation of the π-bond with respect to the ring, both of which reduce the overlap between the necessary AO's on the ring and attached carbon atoms.



16



17

Experimental Section

The photoelectron spectrometer used in these studies was constructed using information published by other workers.[20] Spectra were obtained using He(I) radiation only. The resolution of the instrument was 25 mV (full width at half-height) at 5 eV electron energy. Calibration was carried out using an internal standard consisting of the mixture of argon and xenon.

The bond lengths used in the CNDO calculations are: C_1–C_2, C_2–C_3, C_1–C_3, 1.524 Å; C_1–C_4, 1.309 Å; C_4–C_5, 1.309 Å; C_2 (or C_3)–CH_3, 1.515 Å; C_5–CH_3, 1.500 Å; C_2 (or C_3)–H, 1.010 Å; C_5–H, 1.061 Å; $-CH_2-H$, 1.110 Å. Bond angles are: H–C_2–H (or H–C_3–H), H–C_2–CH_3, H_3C–C_2–CH_3, H_3C–C_5–CH_3, H–C_5–H, 120°; C_1–C_2–C_3, C_2–C_3–C_2, C_2–C_1–C_3, 60°.

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(1) Supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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