Photoelectron Spectra of Molecules. Part VII.[1] Cyclopropylallenes

By **M. J. S. Dewar,* G. J. Fonken, T. B. Jones, and David E. Minter,** Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

A series of alkyl-substituted cyclopropylallenes have been investigated by p.e. spectroscopy using the He^{I} resonance line and the MINDO/3 method. In all cases studied the highest occupied MO is thought to be the π-MO adjacent to the three-membered ring. Comparison of the allenes with the corresponding vinylcyclopropanes indicates little, if any, interaction occurs between MOs of the cyclopropyl ring and the nonadjacent double bond. MINDO/3 calculations of the dicyclopropyl compounds, assuming the known bisected conformation, led to accurate predictions of splittings between the double bond and the MO of the cyclopropane possessing π-type symmetry.

THE electronic structure of cyclopropane has been extensively studied both theoretically, by molecular orbital methods,[2] and experimentally, by measurements of ionization potentials (IPs).[3] The results support the description advanced by Walsh,[4] that the σ framework[5] consists of two degenerate orbitals of *e* type symmetry and one orbital of *a* type symmetry (Figure 1). The symmetries of the two *e* MOs are such that overlap with adjacent π orbitals is possible in the 'bisected' conformation of Figure 2a but not in the 'perpendicular' one of Figure 2b. That the bisected conformation is more stable than the perpendicular has been confirmed by n.m.r. for cyclopropyl carbonium ions[6] and for uncharged species both by n.m.r.[7] and by electron diffraction.[8]

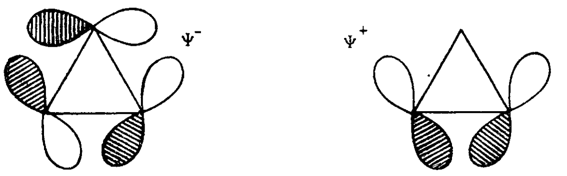

FIGURE 1 Degenerate *e* levels of cyclopropane

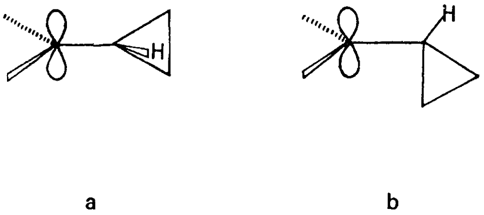

FIGURE 2 a, Bisected and b, perpendicular conformations of a cyclopropyl group adjacent to a *p* orbital

The magnitude of the interaction resonance integral, as indicated by the orbital splitting, between a cyclopropane ring and an adjacent olefin is of the order 2.5 eV for vinylcyclopropane.[9] It is difficult to compare the splittings in vinylcyclopropane and butadiene because of the ambiguity of assignments in the diene spectrum.[10]

Allene, like cyclopropane, has also been studied in some detail by p.e. spectroscopy[11] but no one as yet has examined the interactions between these two systems when they are linked together. Here we report the results of such a study.

EXPERIMENTAL

The He^{I} photoelectron spectra were measured on an instrument similar to that described by Turner.[12] The operating resolution (argon peak width at half height) was 30—60 mV. Samples[13] were thoroughly degassed and internally calibrated. The IPs reported are the averages of reproducible runs. Ionization energies were calculated using the latest version (MINDO/3)[14] of the MINDO[15] semiempirical SCFMO method. The geometry of each molecule was calculated by minimizing the energy with respect to all geometrical variables, no assumptions of any kind being made, by means of a rapidly convergent minimization procedure based on the Davidon–Fletcher–Powell

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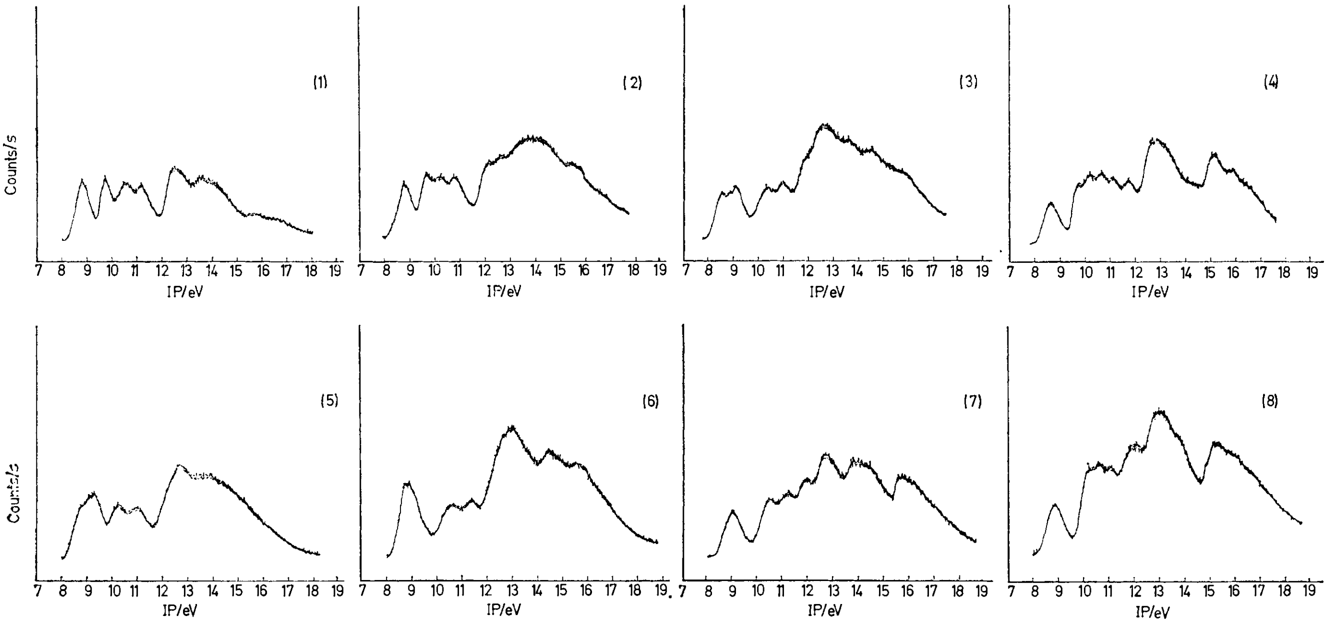


FIGURE 3 He^{I} photoelectron spectra of some cyclopropylallenes and vinylcyclopropanes

algorithm (see ref. 14). Calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

RESULTS AND DISCUSSION

The photoelectron spectra of the substituted cyclopropylallenes (1)—(6) are shown in Figure 3 and the corresponding ionization energies in Table 1. An asterisk denotes those compounds for which MINDO/3 calculations were carried out. The ionization energies are correlated in Figure 4.

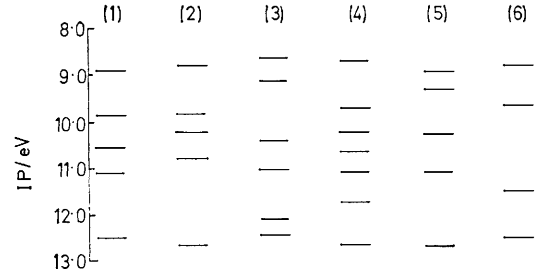


FIGURE 4 Correlation diagram for substituted cyclopropylallenes

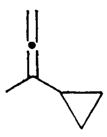
The first two bands in each spectrum (Figure 3) clearly correspond to π-MOs. The ionization potentials of allene are 10.0 and 10.6 eV, corresponding to a Jahn–Teller distortion [3] of the ion following electron removal from one of two degenerate π-orbitals,[5a] whereas the ionization potentials of cyclopropane are 10.5 and 11.3 eV.[3] Again, two values arise from a Jahn–Teller distortion of the ion produced by loss of an electron from one of the degenerate orbitals of *e* type symmetry. The highest occupied MO can be unambiguously assigned to the π-MO adjacent to the cyclopropane ring, the one

TABLE 1

Ionization energies of cyclopropylallenes and vinyl cyclopropanes

Molecule	Ionization energy (eV)
(1)	8.83, 9.75, 10.54, 11.21, 12.49, 13.60, 14.16
(2)	8.81, 9.67, 10.25, 10.81, 12.17, 12.65, 13.80
(3)	8.60, 9.15, 10.41, 11.04, 12.05, 12.64, 13.68, 14.61
(4)	8.62, 9.68, 10.19, 10.65, 11.11, 11.74, 12.62, 15.12
(5)	8.96, 9.29, 10.25, 11.05, 12.68, 13.76
(6)	8.78, 8.98, 10.63, 11.47, 12.70, 13.05, 14.49
(7)	9.12 (9.17),[a] 10.60, 11.31, 12.02, 12.27
(8)	8.87 (8.94),[a] 10.22, 10.61, 11.08, (11.74),[b] 12.04

[a] Calculated (MINDO/3) first ionization potential. [b] This value corresponds to the fourth of the four ionizations from the cyclopropyl groups; it is not resolved in our p.e. spectrum.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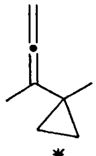
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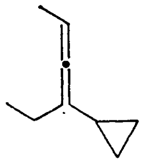
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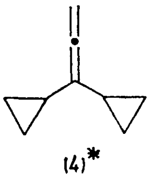
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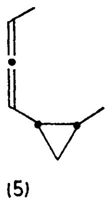
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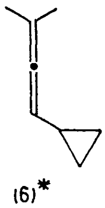
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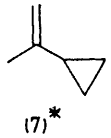
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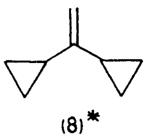
(8)*

uncertainty being (6). The inductive and hyperconjugative interactions between alkyl or cyclopropyl groups and the double bond both result in destabilization. Moreover the first bands of compounds (1)—(5) are somewhat broadened, indicating appreciable interaction with other portions of the molecule. The second ionization energies of (1), (2), and (4) are close enough to 10.3 eV to be attributed to the unsubstituted allenic double bonds, β to the cyclopropane ring.

The attachment of an sp^3 hybridized group to a double bond reduces the ionization energy by 0.7—0.8 eV; for example ethylene, propylene, and but-2-ene have IPs of 10.5,[16] 9.7,[16] and 9.1 eV,[16] respectively. Therefore the first ionization potential of (6) corresponds to the double bond β to the cyclopropyl group since (*ca.* 10.3 — *ca.*1.4) eV = *ca.* 8.9 eV. This value is slightly closer to I_2 than I_1 indicating that the double bond adjacent to the three-membered ring is I_1. MINDO/3 Calculations support this; the agreement for the calculated π-ionization energies of the other molecules is also good (Table 2). The trend of the observed differences between the second and first ionizations is reproduced in the calculations. The agreement ranges from fair [(2)] to excellent [(6)].

TABLE 2

Calculated and observed π-ionization potentials

	I_1 (eV)		I_2 (eV)		$(I_2 - I_1)$	
Molecule	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
(1)	8.83	8.57	9.75	9.18	0.92	0.61
(2)	8.81	8.80	9.67	9.18	0.86	0.38
(4)	8.62	8.38	9.68	9.09	1.08	0.71
(6)	8.78	8.52	8.98	8.70	0.20	0.18

The next two ionizations (I_3 and I_4) of compounds (1)—(3), (5), and (6) are from MOs of *e* type symmetry of the cyclopropane ring.[3,17] The magnitudes $(I_4 - I_3)$ and arithmetic mean $[(I_4 + I_3)/2]$ of the Jahn–Teller distortions are given in Table 3. The magnitude of the splitting is proportional to the amount of orbital interaction between the *e* levels in the resultant ion, which, in turn, is proportional to the overlap of electron density. The mean indicates roughly the energy of the degenerate levels in the absence of the Jahn–Teller effect. Perhaps the most interesting feature of the splittings is the abnormal size of the values obtained for (5) and (6). This can be attributed to the lack in each case of an alkyl group at the carbon atom α to the ring. The consequent absence of hyperconjugative delocalization increases the density of the two relevant MOs in the cyclopropane ring and so increases the interaction between them; consequently an increased splitting is observed. Allenes (2) and (5) have higher arithmetic mean IPs due to the effect of the alkyl substituents on the rings. The same arguments concerning destabilization of π-MOs by alkyl groups apply equally here.

TABLE 3

Magnitudes and arithmetic means of Jahn–Teller distortions in cyclopropylallenes

Molecule	Magnitude	Mean
(1)	0.67	10.87
(2)	0.56	10.53
(3)	0.63	10.72
(4)	0.46, 0.63	10.42, 11.48
(5)	0.80	10.65
(6)	0.84	11.05

Dicyclopropylallene represents a special case. Prior to interaction with other orbitals in the molecule, there are four degenerate cyclopropyl MOs (Figure 5; the rings have been rotated 90° in a disrotatory mode toward the observer from a symmetrical C_{2v} bisected conformation) formed by linear combinations of ψ^+ and ψ^- (Figure 1) with ϕ^+ and ϕ^-. Only one of these MOs $(\psi^- + \phi^-)$ has π-type symmetry (in a bisected conformation) and will interact with the olefinic π-system. The degeneracy of the remaining three orbitals should be removed by interaction with orbitals of σ-type, as indeed is indicated by MINDO/3 calculations. The calculated interaction between the double bond and the $(\psi^- + \phi^-)$ combination is 3.52 eV, whereas the observed splitting is 3.12 eV. The remaining cyclopropyl MOs have effectively no interaction with the double bond.

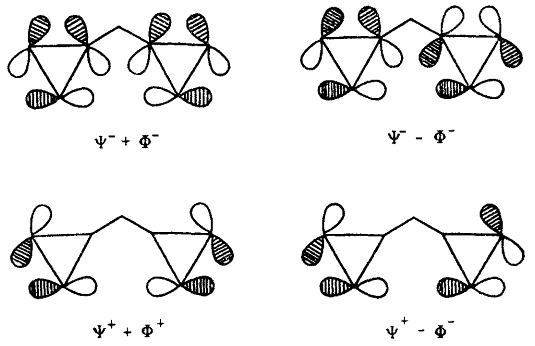

FIGURE 5 Degenerate linear combinations of cyclopropyl molecular orbitals

To compare the magnitudes of cyclopropane–allene interactions with cyclopropane–ethylene ones, two model compounds (7) and (8) were subject to calculations and analysed by p.e. spectroscopy (Figure 3, Table 2). The agreement between the experimental and calculated first ionisation potentials (Table 2) suggests that MINDO/3 can be relied on here in assigning the observed IPs.

The geometries calculated for the vinylcyclopropanes and for the analogous cyclopropylallenes show strong similarities (Figure 6). Only small changes in bond lengths and twist angles, ϕ, occur on passing from an ethylene to an allene.

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The calculated geometries do not agree perfectly with those observed[8,18] for cyclopropyl groups attached to sp^2 hybridized carbon. In the geometry predicted by MINDO/3 one of the cyclopropane bonds is eclipsed with the plane of the π-bond. A comparison of the calculated geometries of dicyclopropylethylene with C_{2v} symmetry and without symmetry restrictions reveals an increase in interatomic distance of *ca.* 0.5 Å (2.043 $\longrightarrow$ 2.583 Å) between the hydrogen atoms attached to the cyclopropyl carbons α to the double bond. Presumably eclipsing the bonds of the cyclopropyl ring with the plane of the double bond relieves the steric repulsion between the hydrogen atoms. The net effect is a reduction of the symmetry of the molecule from C_{2v} to approximately C_2. Enforcement of C_{2v} symmetry raises the heat of formation by only 0.85 kcal mol^{-1}. Moreover the calculated splitting between the double bond, and the linear combination of cyclopropyl MOs with π-type symmetry, is 2.87 compared with 2.19 eV obtained without symmetry restrictions. The observed value (2.77 eV) indicates the MINDO method can give reasonable estimates of such interactions. The differences between the first ionizations of the allenes and the corresponding vinylcyclopropanes must then be due to electronic redistribution rather than changes in overlap integrals as a result of differences in geometry. The effect of changing the hybridization of a carbon from sp^2 to sp is reduction in ionization potential of *ca.* 0.2 eV [$\mathrm{IP}_{\mathrm{ethylene}} - \mathrm{IP}_{\mathrm{allene}}$ (mean of Jahn–Teller distortion)]. The reductions in first ionization potential of (7) and (8) upon conversion into (1) and (4) respectively are 0.29 and 0.25 eV, indicating that the double bonds of the vinylcyclopropanes are responding ' normally ' to the change in hybridization. The absence of shifts in the bands corresponding to cyclopropane MOs in dicyclopropylethylene on passing to dicyclopropylallene shows that there can be little if any interaction between the rings and the terminal allenic double bond.

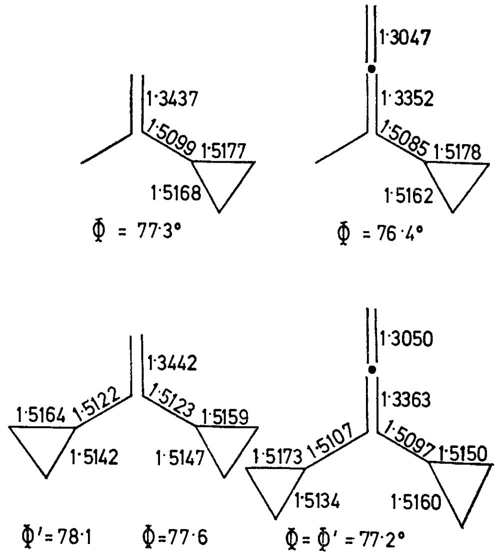

FIGURE 6 Calculated geometries of cyclopropylallenes

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