Photoelectron Spectra of geminal Vinyl- and Ethynyl-Disubstituted Cyclopropane Derivatives

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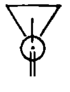
The He(I) photoelectron (PE) spectra of 1,1-divinylcyclopropane (**1**), (*Z,E*)- and (*Z,Z*)-1,1-di-1-propenylcyclopropane (**2** and **3**), 1,1-diethynylcyclopropane (**4**), 1-ethynyl-1-propynylcyclopropane (**5**), 1-ethynyl-1-vinylcyclopropane (**6**), and (Z)-1-(1-propenyl)-1-(propynyl)cyclopropane (**7**) have been recorded. The interpretation of the first bands of the PE spectra is based on the comparison with related compounds and on the results of MO calculations. For the calculations on **1**–**7** the MNDO method, and in case of **1**, **4**, and **6** an ab-initio procedure with a 3-21G basis has been applied. The investigations show that **1**, **2**, **6**, and **7** prefer the bisected conformation while in **3** the propenyl groups are strongly twisted. Our studies reveal also that the three-membered ring shows relais properties and interacts strongly with both π systems.

Studies on molecules containing a vinylcyclopropane unit in a sterically fixed conformation[1-3] have revealed that the interaction between the π unit and the cyclopropane moiety depends strongly on the dihedral angle. The maximum interaction is obtained in the bisected conformation **A**, while the minimum interaction is encountered in the perpendicular conformation **B**. These results also allow an extension of PE studies to conformationally non-rigid vinylcyclopropanes containing geminal unsaturated groups. In addition conjugative features in these compounds have been explored by microwave techniques[4] and IMO calculations[5].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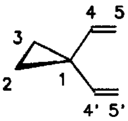
B

As a part of our continuing interest in the reactivity and electronic properties[6,7] of small ring compounds, we have undertaken a comprehensive investigation of geminal dialkenyl- and dialkynyl-substituted cyclopropanes, including the development of specific procedures for their synthesis, investigation of conformational behaviour and electronic structure. In a recent paper[8] we described several methods for their preparation starting from 1,1-diacetylcyclopropane. Here we report on results of the He(I) PE spectroscopic investigation as well as on MNDO[9] and ab initio[10] calculations.

Results and Discussion

The photoelectron spectra of compounds **1**–**3** and **4**, **6**, **7** are depicted in Figures 1 and 3, respectively, as representative examples. The measured vertical ionization energies ($I_{v,j}$) are collected in Table 1. Assuming the validity of Koopmans' approximation[11], the ionization energies are assigned to molecular orbitals. To obtain the orbital energies we employed semiempirical MNDO[9] and in the case of **1**, **4**, and **6** 3-21G[10] ab initio procedures. The latter calculations were performed for MNDO optimized geometries.



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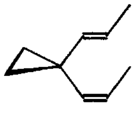
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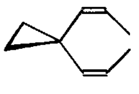
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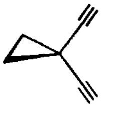
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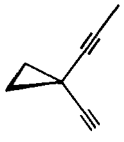
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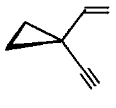
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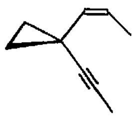
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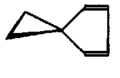
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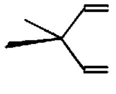
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PE Spectra of 1,1-Divinylcyclopropanes 1–3

The PE spectrum of 1,1-divinylcyclopropane (**1**) (Figure 1) shows three distinct bands below 11 eV, followed by two

Table 1. Comparison between the recorded vertical ionization energies ($I_{v,j}$) and the calculated orbital energies (ε_j). All values in eV

Compd.	Band	$I_{v,j}$	Assignment	$-\varepsilon_j$ (MNDO)	$-\varepsilon_j$ (3-21G)[a]
1	①	8.98	$3b_1$	9.33	8.80
	②	9.83	$2a_2$	10.12	9.96
	③	10.9	$8a_1$	11.54	11.75
	④	11.7	$6b_2$	12.46	12.33
	⑤	11.9	$2b_1$	11.91	13.30
2	①	8.40	7a′	9.20	
	②	9.16	6a″	9.95	
	③	10.5	18a′	11.53	
	④	11.3	17a′	11.95	
	⑤	11.5	5a″	12.35	
3	①	8.8		9.68[b]	
	②	9.10		10.07	
	③	10.4		11.31	
	④	11.1		11.72	
	⑤	11.4		12.43	
4	①	9.26	$3b_1$	9.85	9.46
	②	10.31	$5b_2$	10.72	10.49
	③	10.63	$7a_1$	10.79	10.86
	④		$2a_2$	10.98	10.91
	⑤	12.1	$6a_1$	12.34	13.24
	⑥	13.0	$2b_1$	13.05	14.09
5	①	8.88		9.79	
	②	9.60		10.50	
	③	10.15		10.79	
	④	10.37		10.84	
	⑤	11.8		12.32	
	⑥	12.6		12.95	
6	①	9.00	5a″	9.49	9.05
	②	10.17	4a″	10.52	10.42
	③		13a′	10.66	10.48
	④	11.5	12a′	11.96	12.45
	⑤	12.4	11a′	12.66	13.50
	⑥	12.6	3a″	12.79	13.31
7	①	8.77		9.37	
	②	9.30		10.36	
	③	9.57		10.40	
	④	10.93		11.95	
	⑤	11.70		12.44	
	⑥	12.03		12.61	

[a] Based on MNDO geometry. — [b] Calculations performed on 1 under the assumption that vinyl groups are rotated out of the symmetry plane by 60° (see text for more details).

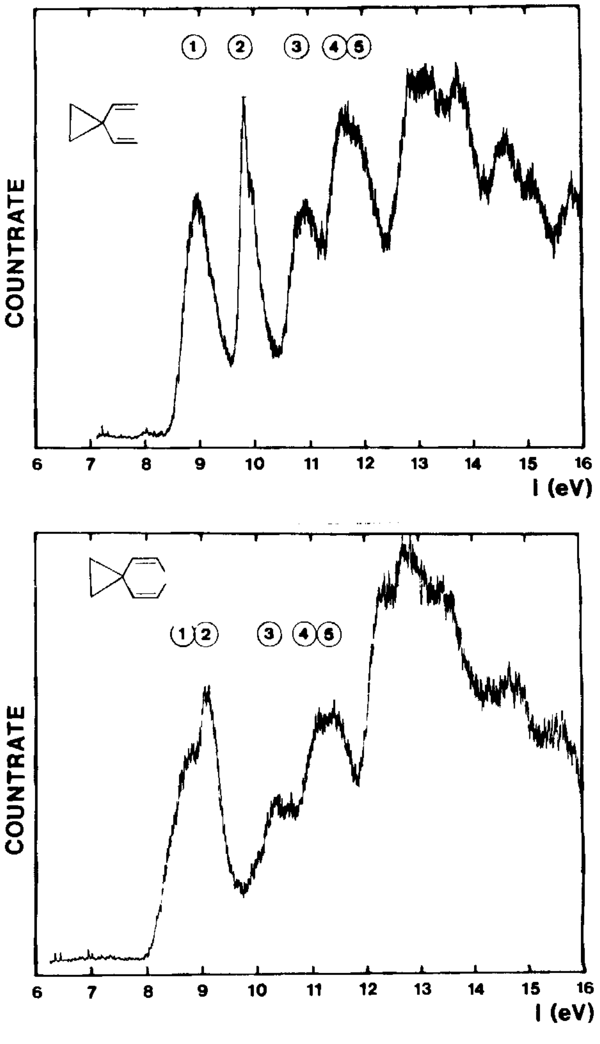

Figure 1. PE spectra of compounds 1 and 3

strongly overlapping bands with maxima at 11.7 and 11.9 eV, respectively.

The PE spectrum of (*Z*,*E*)-1,1-di-1-propenylcyclopropane (2) has, apart from a shift of all bands towards lower energy, an appearance similar to that of 1. In contrast, the PE spectrum of (*Z*,*Z*)-1,1-di-1-propenylcyclopropane (3) exhibits two close lying bands at 8.8 and 9.1 eV, followed by a series of almost equidistantly separated signals starting from ca. 10 eV.

In order to explain the differences between the PE spectra of the *Z*,*Z* and *Z*,*E* isomers we shall first consider the PE spectrum of the parent compound 1. To assign the bands we shall make use of the MNDO results and 3-21G calculations performed under the assumption that both vinyl groups are oriented *trans* with respect to the cyclopropyl ring. The MO energies obtained under this assumption correlate satisfactorily with the PE data, allowing a detailed orbital assignment of individual bands. Additional support for the given assignment is provided by the comparison of recorded $I_{v,j}$ values with the PE data for homofulvene (**8**)[1] and dimethyldivinylmethane (**9**)[12].

From the comparison of the PE data for **1** and **8** it seems reasonable to assign the band at 10.9 eV to the ionization out of the symmetric Walsh-type[13] orbital (W_S) of the three-membered ring. Comparison with the PE data for **9** suggests assignment of the band at 9.83 eV to the ionization event out of the $2a_2$ MO, which is essentially the antibonding linear combination of the π orbitals of the two double bonds. For their bonding combination we anticipate a strong destablization relative to the energy of an isolated π-MO because of its ability to enter into conjugative interaction with the antisymmetric (W_A) component of the Walsh-type orbital. Both theoretical procedures suggest assignment of the first PE-band to the $3b_1$ MO, which corresponds to the antibonding linear combination of π^+ and W_A, in accordance with the hypothesis mentioned above.

The assignment of bands ④ and ⑤ is less straightforward. Calculations suggest the assignment of band ④ to the ionization from a σ-type MO which is mainly ethylenic in character, and that of band ⑤ to the bonding counterpart of the $3b_1$ MO. However, due to their close proximity (0.2 eV) in the PE spectrum recorded, this assignment must be considered tentative.

Changes in the ionization pattern on going from **1** to **2** can be rationalized in terms of electron-donating capability of methyl groups. On the other hand, changes in ionization energies on passing from **1** to **3** can be understood only by taking into account additional factors. The fact that the PE spectra of **1** and **2** are somewhat better resolved than the PE spectrum of **3** indicates that the structure of the latter compound is less rigid. Moreover, significant reduction of the energy gap between bands related to ionization from π^+/W_A mixed MOs (Figure 2) leads to the conclusion that the isopropenyl groups in **3** are displaced out of the symmetry plane passing through C-1 and bisecting the C-2—C-3 bond of the cyclopropyl ring. To check this assumption we performed MNDO calculations for various conformers of **1** by rotating the vinyl groups around the C-1—C-4 and C-1—C-4′ bonds in a disrotatory fashion. Fairly good agreement between experimental and calculated data was achieved for the torsional angles of 60°[18]. It should be kept in mind, however, that in the case of **3** the same effect can be achieved by even smaller distortions, due to the cooperative action of the inductive/hyperconjugative effect of the methyl groups.

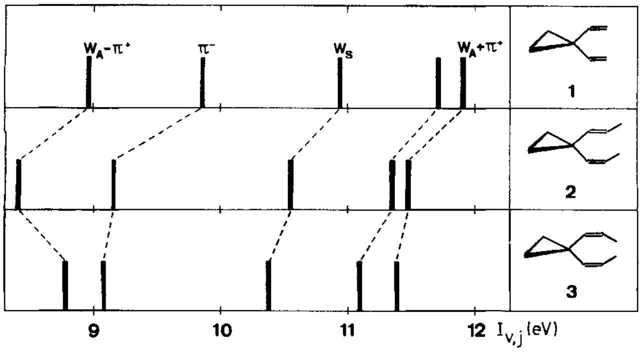

Figure 2. Correlation of the observed first five ionization energies in the series **1**, **2**, **3**

PE Spectra of 1,1-Diethynylcyclopropane (4) and 1-Ethynyl-1-(1-propynyl)cyclopropane (5)

As is evident from Figure 3, the PE spectrum of 1,1-diethynylcyclopropane (**4**) displays one Gaussian-type band at 9.26 eV separated from two sharp, but overlapping bands with maxima at 10.31 and 10.63 eV. The latter two bands are followed by a series of broad bands starting at ca. 11.0 eV. The relative areas of the first three bands suggest assignment of bands ① and ② to one transition each, whilst the third peak is assigned to two transitions. This is corroborated by the changes in the PE spectra on going from **4** to **5**, as well as by the spacing of the uppermost occupied MOs predicted by calculations (Table 1). The shape of the second band and of one of the bands in the third ionization feature (presumably band ④) indicates that these bands result from an almost pure π ionization event[19]. In line with this expectation both theoretical procedures suggest assignment of the second (10.31 eV) and the fourth (10.63 eV) band to the ionization from an antibonding linear combination of the in-plane (π_i^-) and out-of-plane (π_o^-) MOs of the two

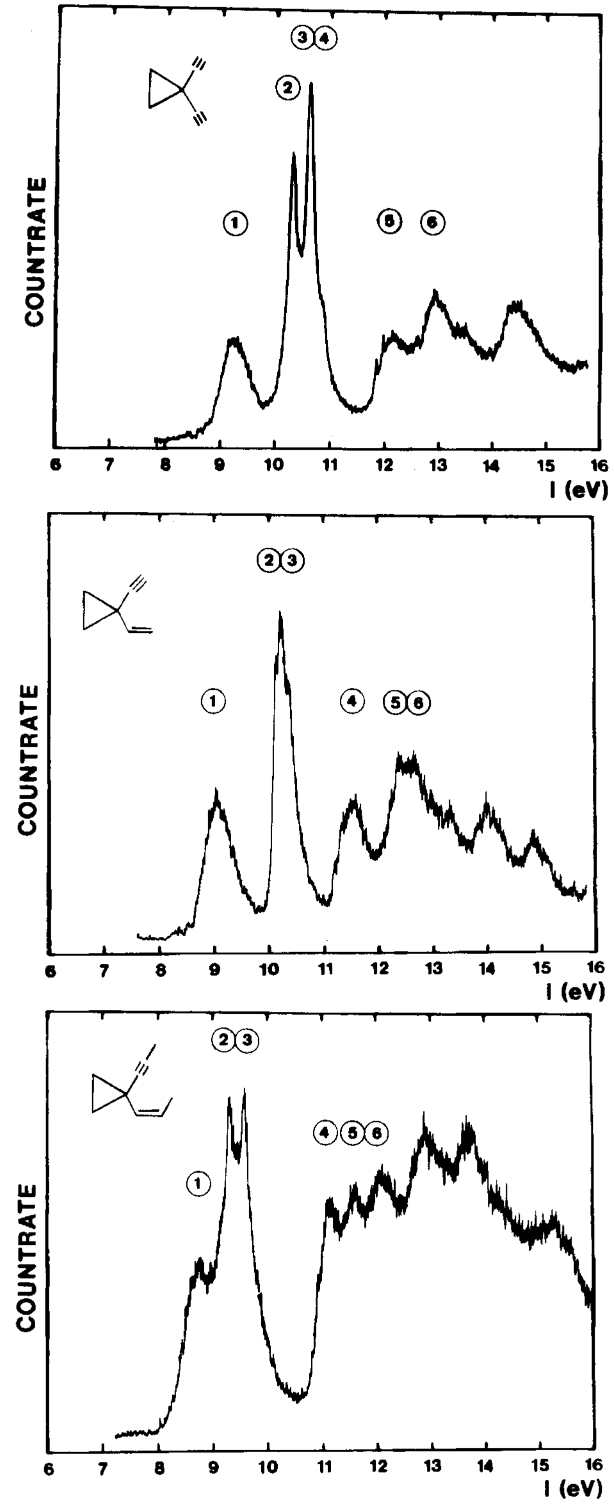

Figure 3. PE spectra of **4**, **6**, and **7**

acetylenic moieties, respectively. These are pure π linear combinations, for symmetry reasons.

On the other hand, for both of their bonding counterparts (π_o^+ and π_i^+, resp.), which are associated with the first and third ionization event, the calculations predict significant admixtures of the Walsh-type orbitals from the cyclopropane subunit. More precisely, the first band is found to correspond to the ionization out of the $3b_1$ MO, which can be described as the antibonding linear combination of the π_o^+ and antisymmetric Walsh-type orbital, whereas the third band corresponds to the ionization process from the antibonding linear combination of the π_i^+ and symmetric (W_S) Walsh orbital. Their bonding counterparts are predicted at 12.1 ($W_S + \pi_i^+$) and 13.0 eV ($W_A + \pi_o^+$), respectively.

The energy differences between the π-dominated bands (① – ④) is in excellent agreement with the energy interval predicted for the highest occupied MOs by the 3-21G procedure. For instance, the experimental separation between the 1st and 4th band, of 1.37 eV, is close to the calculated energy difference between $3b_1$ and $2a_2$ MOs, which is found to be 1.42 eV. Similarly, the computed split between π_i^- and π_i^+ MOs $\varepsilon(5b_2) - \varepsilon(7a_1)$ is 0.37 eV. This again compares well with the respective experimental value of 0.32 eV.

MNDO calculated values, particularly those related to the splitting of the in-plane linear combinations of the acetylenic π-orbitals, are much less accurate (see Table 1). In contrast, the energy gap between the set of π-dominated MOs and the lower lying MOs, which are characterized by more pronounced σ character, appears to be better reproduced at the semiempirical level of theory.

Replacing one of the acetylenic hydrogens in **4** with the CH_3 group leads, as expected, to a more pronounced mixing of σ and π levels due to the overall lowering of symmetry[19] (from C_{2v} in **4** to C_s in **5**). Destabilization of all occupied levels as a consequence of electron donating characteristics of the methyl group takes place as well. Comparison of the PE data for the two compounds in question shows that there is a shift of the first six bands toward lower energy within the range of 0.15 – 0.7 eV in **5**. The largest change is found in the bond corresponding to ionization out of π_i^- orbital.

PE Spectra of 1-Ethynyl-1-vinylcyclopropane (6) and (*Z*)-1-1(1-propenyl)-1-(1-propynyl)cyclopropane (7)

Before discussing the PE spectra of 1-ethynyl-1-vinyl-cyclopropane (**6**) and its methylated congener **7**, we shall briefly examine the influence of the vinyl group rotation around the C-1 – C-4 bond on the sequence of the highest occupied MOs of **6**. For this purpose the orbital energies of the six highest occupied MOs of **6** obtained by MNDO calculations are shown in Figure 4 as a function of the torsional angle (Θ). Inspection of Figure 4 indicates that for torsional angles close to 0° (180°) the PE spectrum should be characterized by two distinct sets of bands. Each of them starts with a single band well separated from two closely spaced bands at higher energies. Rotation of the vinyl group out of the C-1 – C-4 – C-5 plane (0° < Θ < 90° and 90° < Θ < 180°, resp.) leads to the stabilization of the first and the fourth level, while the energy of the second and fifth bands changes in the opposite direction.

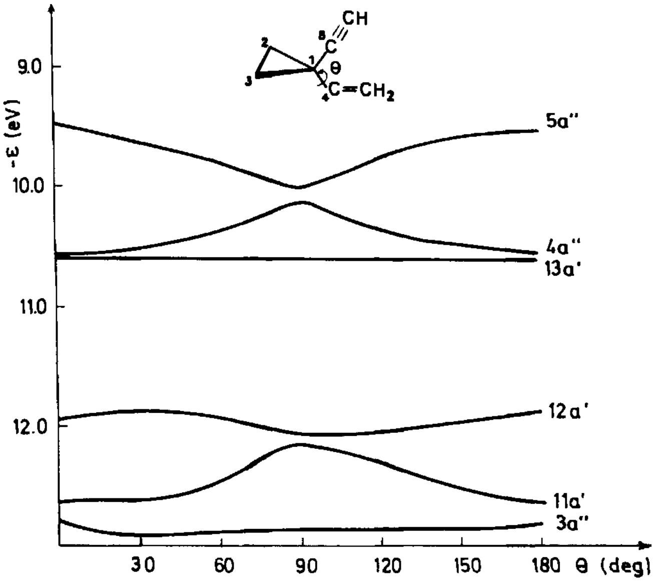

Figure 4. Orbital energies of **6** as a function of torsional angle according to MNDO

It follows from Figure 3 that the PE spectrum of **6** features three distinct peaks with intensity ratio 1:2:1 followed by an ionization feature consisting of two highly overlapping bands. Assignment of the second peak to two overlapping transitions (bands ② and ③) is corroborated by comparison with the PE spectrum of **7** in which the second ionization event is clearly split into two components. According to the diagram in Figure 4, this level pattern is strongly indicative of a torsional angle close to 0° (180°). The NMR spectra of **6** and **7** were interpreted in terms of a *trans* conformer (Θ = 0°)[8]. We shall assume therefore that this conformation also predominates in the gas phase[20]. Good resolution of the recorded PE spectrum indicates furthermore that the molecule is fairly rigid under the measurement conditions.

The wave functions that correspond to the six highest occupied MOs are shown schematically in Figure 5. As expected, the three uppermost MOs are dominated by contributions from the vinylic and ethynylic π orbitals, while 12a′ – 3a″ show strong participation of the Walsh-type MO's. An analysis of the calculated wave functions shows that 5a″ has the largest amplitudes at the vinylic carbons, whilst the 4a″ MO is more evenly distributed over both π units. The 13a′ and 12a′ MOs correspond to the antibonding and bonding linear combinations of the in-plane acetylenic π-MO and symmetric Walsh orbital, respectively. The corresponding bands are found at 10.17 (13a′) and 11.5 eV (12a′). Strong support for this assignment comes from the comparison between the PE data for **6** and ethynylcyclopropane[21] whose related bands are found at 10.09 and 11.58 eV, respectively (see also Figure 6).

For the fifth and sixth band, calculations predict ionization out of σ-type orbitals 11a″ and 3a″. Further indications in favour of such an assignment come from comparison of

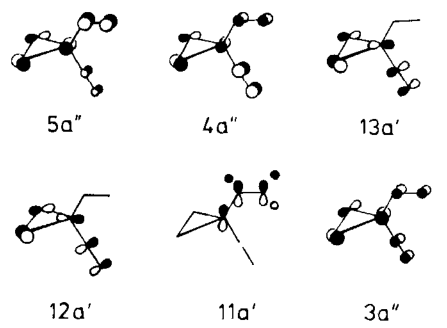

Figure 5. Approximate shape of the highest occupied MOs of **6**

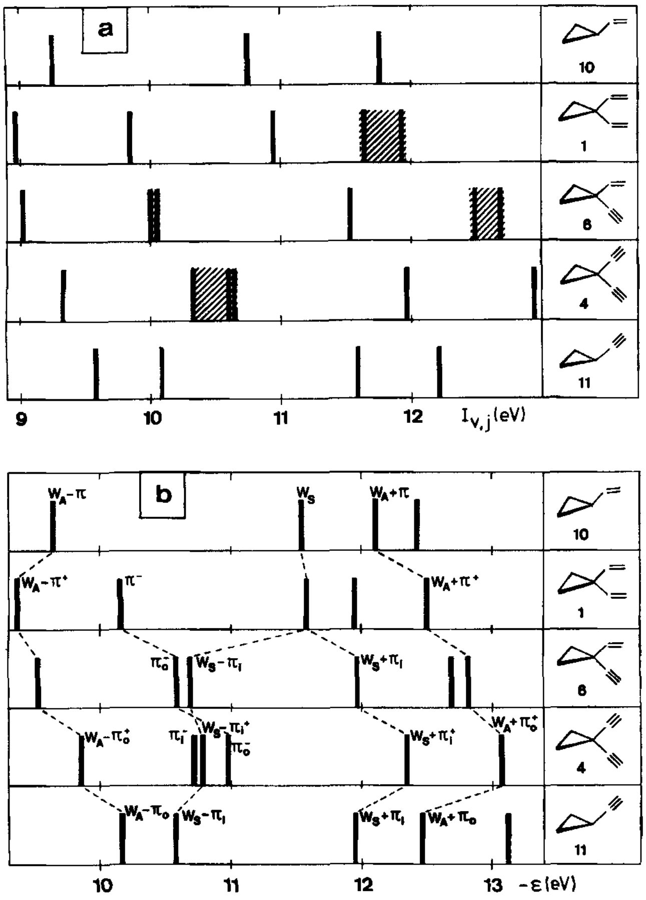

Figure 6. Comparison of the first bands of the PE spectra of **10**, **1**, **6**, **4**, **11** (Figure 6a, top) with the results of MNDO calculations (Figure 6b, bottom)

their positions in the PE spectra of **6** and **7**. This comparison reveals that band ⑤ undergoes a more pronounced shift toward lower energy than band ⑥, as anticipated from the comparison of their wave function coefficients at the site of substitution.

Bands ①—② in the PE spectrum of 7 are found at lower energies relative to the positions of corresponding bands in the PE spectrum of **6**. Most of the encountered shifts are consistent with a pattern expected on the basis of discussion presented in the two preceding sections.

Concluding Remarks

The most significant results of this investigation can be summarized as follows:

(a) The PE spectra of 1,1-divinylcyclopropane and its *Z*,*E*-dimethylated analogue **2** are best understood under the assumption that the observed maxima correspond to the bisected conformation, whereas the PE spectrum of (*Z*,*Z*)-1,1-di-1-propenylcyclopropane (**3**) indicates that in this compound the vinyl groups are significantly displaced from the symmetry plane bisecting the cyclopropane ring.

(b) PE spectral data for both 1-ethynyl-1-vinylcyclopropane derivatives are consistent with the ionization pattern expected for bisected conformers.

(c) Comparison of the PE spectra presented with the PE spectral data for divinyl-[12,22] and diethynylmethane[14] derivatives fully confirms the conclusion from previous studies about pronounced efficacy of the three-membered ring in transmitting the electronic effect between two π bonds[1-3].

(d) Comparison of the PE spectral data of **1**, **4**, and **6** with their monosubstituted congeners vinylcyclopropane[1,23,24] (**10**) and ethynylcyclopropane[16] (**11**) as displayed in Figure 6a unequivocally shows that the introduction of the second unsaturated group into the geminal position leads to significant destabilization of the highest occupied levels. The magnitude of the destabilization is approximately the same for vinylic and acetylenic groups. The same trend is evident from Figure 6b, which shows the correlation of the highest occupied MOs for the same series of compounds calculated by the MNDO procedure, indicating good performance of this approach in describing the most salient features of the electronic structure of gem-substituted cyclopropanes.

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Experimental

Preparation of compounds **1**—**7** was described in detail in ref.[8]. — He(I) PE spectra: Perkin-Elmer Ltd. Model P18 instrument, calibrated with Xe and Ar. A resolution of 20 meV at the $^2P_{3/2}$ Ar line was obtained.

CAS Registry Numbers

1: 17085-84-6 / **2**: 105961-71-5 / **3**: 105961-70-4 / **4**: 72323-66-1 / **5**: 105961-79-3 / **6**: 105961-74-8 / **7**: 129217-86-3

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