

Photoelectron Spectra and Conformational Behaviour of 3-Isopropenylcyclopropene Derivatives

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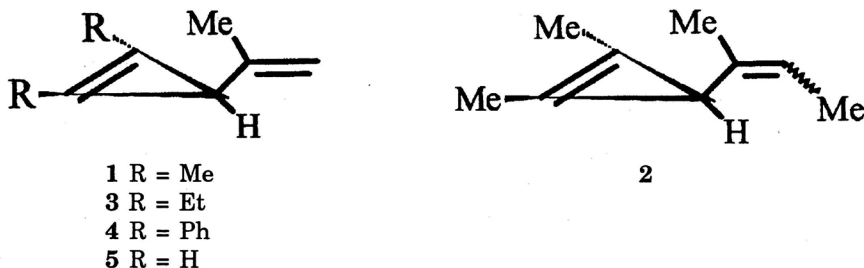
The electronic and molecular structure of a series of 1,2-dialkyl (1–3) and 1,2-diphenyl-3-isopropenylcyclopropene (4) have been investigated by means of He(I) photoelectron spectroscopy and *ab initio* MO calculations. The changes in the lowest energy ionization along the series are interpreted in terms of conformationally dependent conjugative interaction between the isopropenyl group and cyclopropenyl ring.

INTRODUCTION

Few subjects have attracted more interest of photoelectron (PE) spectroscopists than the conformational dependence of interaction between a vinyl group and an adjacent carbocyclic ring.^{1,2} Particularly intriguing in this regard are conformations of nonrigid molecules involving a vinylcyclopropane or a vinylcyclopropene unit.^{3–9} Depending on the substitution pattern, their PE spectra were found to exhibit the presence of the antiperiplanar and/or the anticlinal conformer.⁷ This holds, in particular, for geminally substituted alkenylcyclopropenes and alkenylcyclopropanes, whose PE spectra provided firm evidence on the strong dependence of the antiperiplanar-anticlinal equilibrium on the bulkiness of the alkyl moiety. On the other hand, in our recent PE study of 1,2-bis-Me₃M (M = Si, Ge, Sn)-3-methyl-3-vinylcyclo-

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propenes, we found that the sequence of the lowest ionization energies is consistent with the presence of a single conformer, which was ascribed to the antiperiplanar form.⁸ Moreover, some of the previously studied compounds, *e.g.* 3-methyl-3-vinylcyclopropene, were conclusively shown to be unstable under the conditions of PE measurements.^{8,9} Prompted by these findings, we thought it worthwhile to examine the effect of the substitution pattern on the conformational behaviour of 3-alkenylcyclopropene derivatives in more detail. Here, we present the results of the He(I) PE spectroscopic investigation of molecules 1–4, along with the *ab initio* results for rotation of the isopropenyl group in 1 and the parent molecule 5. We were primarily interested in finding if the replacement of the methyl group by hydrogen at the C(3) atom would have any appreciable effect upon the population of conformers. Another objective of the work was to investigate in more detail the effect of substituents other than the Me₃M-groups at the cyclopropene double bond on the PE spectral features of this class of compound.



RESULTS AND DISCUSSION

Computational Details

Ab initio molecular orbital calculations have been carried out using the GAMESS¹⁰ and GAUSSIAN 94¹¹ programs. Optimization of the molecular structure of 1 and 5 has been achieved at the HF/6-31G* level of theory, while the geometry of 4, due to its size, was optimized by employing the STO-3G basis set.¹² In all calculations, one of the methyl group hydrogen atoms was initially placed eclipsing the vinylic double bond. In calculating the dependence of the MO energies on the rotation of the isopropenyl group in 1, orientation of the methyl groups at the cyclopropene double bond was set to that found in the fully optimized structure of the antiperiplanar rotamer, *i.e.* with one of the hydrogen atoms within each of the methyl groups

eclipsing the cyclopropene double bond. The effect of electron correlation on the energy of individual conformers was taken into account by carrying out single point MP2(fc)/6-31G**//HF/6-31G* calculations, where (fc) stands for the frozen inner-core electrons.¹² The HF/6-31G* frequency analysis for the critical points on the potential curve for **5** showed synperiplanar-**5** and antiperiplanar-**5** structures to be minima on the potential energy surface, and a TS form to be a transition structure with one imaginary frequency. Finally, semiempirical calculations, used to derive energies of the highest occupied molecular orbitals throughout the series of the studied compounds, were carried out using the semiempirical MNDO¹³ method by employing the MOPAC 6.0¹⁴ package of programs.

*Molecular Geometry and Conformational Behaviour of
3-Isopropenylcyclopropene (5)*

The molecular structure of 3-vinylcyclopropene, which can be regarded as the simplest representative of the considered compounds, has been recently determined by X-ray measurements and studied by employing both semiempirical and *ab initio* procedures.¹⁵ The structure found in the solid state corresponds to the antiperiplanar form. The same conformation was also found in the X-ray structure of 1,2-bis(trimethylsilyl)-3-methyl-3-vinylcyclopropene.¹⁶ Hence, in studying the conformational behaviour of **5**, initial HF/6-31G* calculations were performed also on the antiperiplanar rotamer (Figure 1).¹⁷

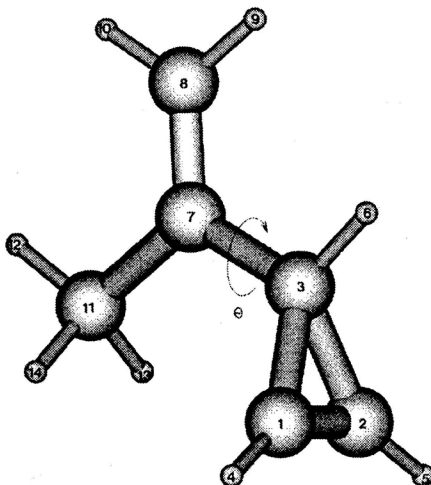


Figure 1. Atom numbering in the most stable conformer of **5**; θ denotes C(6)C(3)C(7)C(11) dihedral angle.

The optimized geometry was then used to generate the potential energy curve for the isopropenyl group rotation around the C(3)-C(7) bond within the rigid rotor approximation. Computations were performed for each 10°, with the exception of the region between 70–90°, for which steps of 1° were employed. Finally, geometries of the synperiplanar form and the transition structure (TS) were fully optimized employing the same basis set, and the total energies of all critical points were recalculated at the MP2(fc)/6-31G** level of theory. The resulting total energies, coded in the usual way,¹² are presented in Table I. Thus, »MP2(fc)/6-31G**//6-31G*« denotes a single point MP2(fc)/6-31G** run carried out on the geometries optimized at the HF/6-31G* level.

TABLE I

Calculated energies for the synperiplanar, antiperiplanar and transition state structures (TS) of **5**

	Energy/ kJ mol ⁻¹		
	synperiplanar	TS	antiperiplanar
HF/6-31G*	-608454.29	-608394.21	-608459.60
MP2/6-31G**//6-31G*	-610631.21	-610583.81	-610636.38
ZPE ⁽¹⁸⁾	70.51	70.39	70.67

The survey of the HF data reveals that the synperiplanar minimum lies 5.3 kJ mole⁻¹ above that of the antiperiplanar form. The TS for the antiperiplanar → synperiplanar rotation is predicted to lie at 86.7°, with a barrier of 65.4 and 60.1 kJ mole⁻¹ for the antiperiplanar → synperiplanar and synperiplanar → antiperiplanar interconversion, respectively. After including the MP2 corrections and zero-point vibrational energy,¹⁸ the antiperiplanar structure is 5.8 kJ mole⁻¹ more stable than the synperiplanar form at the MP2/SCF level, and a barrier for antiperiplanar → synperiplanar and synperiplanar → antiperiplanar interconversion drops to 53.8 and 48.0 kJ mole⁻¹, respectively.

The calculated geometrical parameters of the antiperiplanar-, the synperiplanar- and the transition structures are given in Table II.

We note in passing that the calculated geometry of the antiperiplanar form resembles closely the calculated structural features of the 3-methyl-3-vinylcyclopropene,^{1,5} with the exception of the C(3)-C(7) bond length, which is predicted to be longer by 0.006 Å than in the latter compound. This can be traced back to the steric hindrance between the methyl group and the

TABLE II

Structural parameters in synperiplanar-, antiperiplanar- and transition state structures of 5, as calculated by the HF/6-31G* method. Atom numbering corresponds to that given in Figure 1

Parameters	synperiplanar	antiperiplanar	transition state
bond length/ Å			
C(1)-C(2)	1.275	1.276	1.275
C(1)-C(3)	1.496	1.500	1.499
C(2)-C(3)	1.496	1.500	1.503
C(3)-C(7)	1.508	1.501	1.517
C(7)-C(8)	1.323	1.323	1.324
C(7)-C(11)	1.508	1.508	1.503
C(1)-H(4)	1.068	1.068	1.068
C(2)-H(5)	1.068	1.068	1.068
C(3)-H(6)	1.083	1.083	1.082
C(8)-H(10)	1.076	1.076	1.077
C(11)-H(12)	1.083	1.083	1.084
C(11)-H(13)	1.086	1.087	1.084
bond angle/ deg			
C(1)-C(2)-C(3)	64.8	64.8	64.5
C(3)-C(7)-C(8)	123.3	120.2	120.8
C(11)-C(7)-C(8)	122.0	122.0	123.3
H(4)-C(1)-C(2)	150.8	150.2	150.3
H(5)-C(2)-C(1)	150.8	150.2	150.1
H(6)-C(3)-C(7)	112.6	112.1	119.2
H(9)-C(8)-C(7)	122.0	121.6	121.7
H(10)-C(8)-C(7)	121.5	122.0	121.9
H(12)-C(11)-C(7)	111.8	111.0	112.9
H(14)-C(11)-C(12)	108.3	108.3	107.5
torsion angle/ deg			
H(4)-C(1)-C(2)-C(3)	175.2	179.4	180.0
H(5)-C(1)-C(2)-C(3)	175.2	179.3	180.0
C(8)-C(7)-C(3)-H(6)	180.0	0.0	93.3
H(10)-C(8)-C(7)-C(3)	180.0	180.0	151.4
H(9)-C(8)-C(7)-C(3)	0.0	0.0	331.4
C(11)-C(7)-C(8)-C(3)	180.0	180.0	208.6
H(12)-C(11)-C(7)-C(3)	180.0	180.0	197.3
H(14)-C(11)-H(12)-C(7)	122.2	122.2	123.3

ring hydrogen atoms, which might be expected to be relatively important in the antiperiplanar form. Comparison of the calculated parameters with the crystal structure of 3-methyl-3-vinylcyclopropene¹⁵ reveals, however, only a qualitative agreement, as pointed out already by Boese and coworkers for the latter compound. In particular, the C(3)-C(7) bond distance is found to

be considerably longer (by 0.025 Å), while the cyclopropene C-C single bonds are found to be shorter by 0.015 Å. The survey of the data presented in Table II uncovers several interesting features. We notice, for instance, that the central C(3)-C(7) bond is calculated to be longer by 0.007 Å in the synperiplanar than in the antiperiplanar form. A similar trend has been observed in the related studies on vinylcyclopropane¹⁹ and 1,3-butadiene²⁰ derivatives, described previously. Its origin is rationalized in terms of a larger steric hindrance between the hydrogen atoms of the ring and the isopropenyl group in the synperiplanar form, compared to the steric effects between the ring and the methyl groups in the antiperiplanar rotamer. This is also apparent from the calculated variation of the C(8)=C(7)-C(3) bond angle on rotation from the antiperiplanar (120.2°) to the synperiplanar (123.3°) structure. Again, the same phenomenon has been observed in earlier theoretical studies of vinylcyclopropanes, as well as in 1,3-butadiene and their derivatives.^{19,20} Finally, a slight pyramidalization of the olefinic atoms C(1) and C(2) found in the periplanar structure (Table II) probably reflects the same phenomena.

Turning to the transition state, we observe a considerable lengthening of the bond joining the ring and the isopropenyl group, as it might be expected due to the loss of conjugation between the double bond and the cyclopropene ring. Another point of interest is asymmetry in the cyclopropene bonds adjacent to the site of attachment of the isopropenyl group. Furthermore, the C(11)H₃ group appears to be rotated by *ca.* 8° relative to its position in either the synperiplanar or the antiperiplanar conformer.

Photoelectron Spectra

The He(I) PE spectra of **1** and **2**, as representatives of 1,2-dialkyl substituted cyclopropenes, are shown in Figure 2.

The measured vertical ionization energies are listed in Table III, as well as their assignment to molecular orbitals. For **1** and **4**, MO energies calculated by employing *ab initio* (HF/6-31G* (**1**) and HF/STO-3G (**4**)), and semiempirical MNDO approaches are included. For molecules **2** and **3**, for the reason given above, only MNDO derived MO energies are presented. The proposed assignment is based on the assumed validity of the Koopmans approximation.²¹

The photoelectron spectroscopic features of 1,2-dialkyl-3-isopropenylcyclopropenes **1-3** will be considered first, together with the *ab initio* results on the influence of the isopropenyl group rotation on the sequence of the highest occupied MOs in **1**. The energies of the latter were calculated by employing the HF/6-31G* model, in steps of 30°. The relevant data are summarized in Table IV, together with the relative energies of the pertinent conformers.

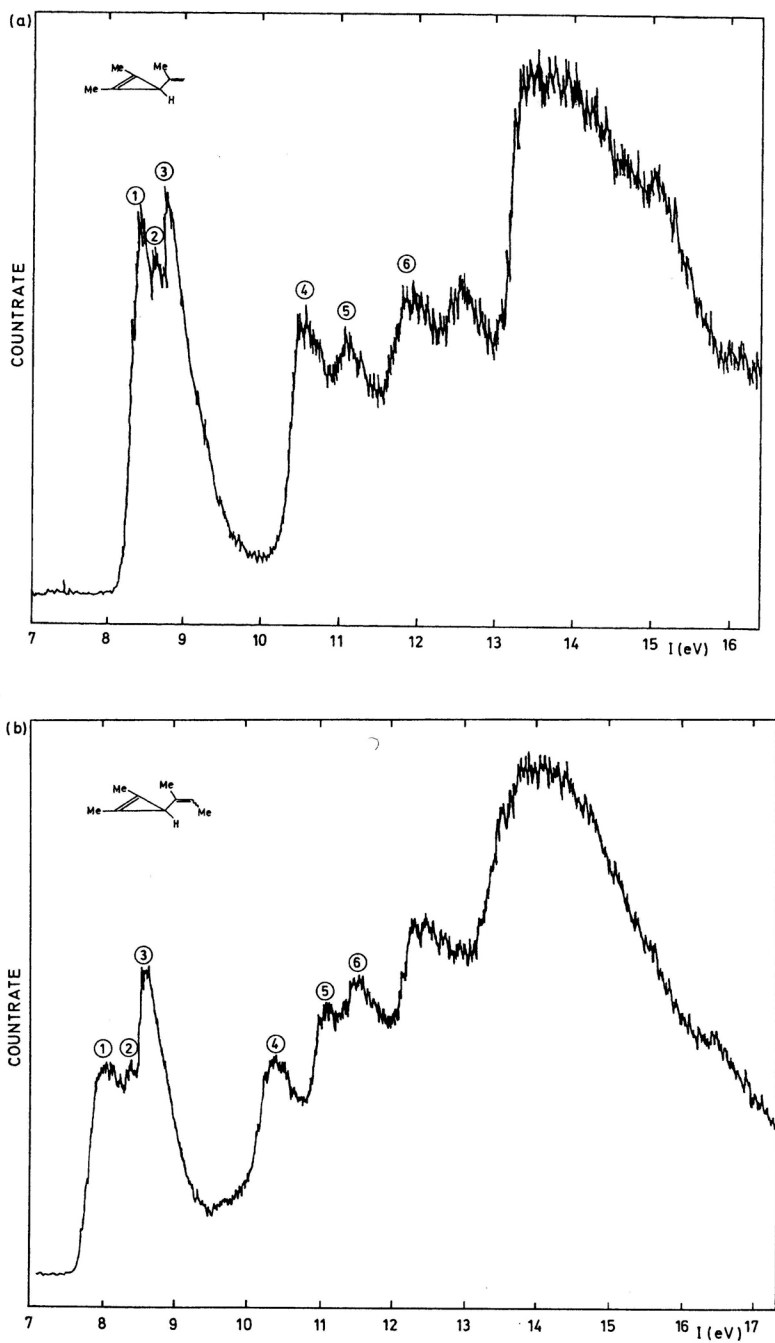


Figure 2. PE spectra of 1 (a) and 2 (b).

TABLE III

Measured vertical ionization energies (I_{vj}) and calculated orbital energies (ϵ_j) of **1-4**

Compd.	band	I_{vj}	Assign.	$-\epsilon_j/\text{eV}$	
				MNDO	6-31G*
1	①	8.50	5a'' ($W_A - \pi_V$)	9.44	8.61
	②	8.71 ^(a)			
	③	8.93	17a' (π_c^-)	9.62	9.15
	④	10.6	4a'' ($W_A + \pi_V$)	11.59	11.58
	⑤	11.16	16a' (W_S)	11.87	12.20
	⑥	12.04	15a' (π_c^+)	12.61	13.15
2	①	8.33	$W_A - \pi_V$	9.47	
	②	8.50 ^(a)			
	③	8.76	π_c^-	9.58	
	④	10.38	$W_A + \pi_V$	11.54	
	⑤	10.88	W_S	11.67	
	⑥	11.55	π_c^+	12.75	
3	①	8.10	$W_A - \pi_V$	9.32	
	②	8.44 ^(a)			
	③	8.66	π_c^-	9.63	
	④	10.42	$W_A + \pi_V$	11.53	
	⑤	11.25	W_S	11.71	
	⑥	11.60	π_c^+	12.59	
4	①	7.52	26a' ($\pi_1 - W_A$) ^(b)	8.32	6.06 ^(c)
	②	8.57	18a'' (π_V^-)	9.46	7.47
	③, ④	9.1	17a'', 25a' (π_2, π_3)	9.48, 9.50	7.89; 7.90
	⑤	9.5	16a'' (π_4)	9.73	
	⑥	10.02	24a' (π_5)	10.82	
	⑦	10.59	15a'' $W_a + \pi_1$	11.63	

^(a) Band 2 is tentatively assigned to ionization event from $W_A - \pi_V$ linear combination in the second conformer (see p. 1529 for more detailed discussion).

^(b) π_1 - π_5 refer to MOs depicted in Figure 5.

^(c) Calculations were performed at the STO-3G level.

1,2-Dialkyl-3-isopropenylcyclopropenes

Inspection of the calculated MO sequences shows that in each of the considered conformers of **1** (Table IV), the highest occupied MO corresponds to the antibonding linear combination of vinylic, (π_V), and antisymmetric Walsh-type, (W_A), MO of the cyclopropene fragment, as expected. It is followed by the cyclopropene π -MO (π_c^-), while the two lower lying MOs correspond to the ($W_A + \pi_V$), linear combination and W_S type MO, respectively.

TABLE IV

6-31G* orbital energies for the highest occupied MOs/ eV and relative energies/ (kJ/mol) of **1** as a function of torsional angle Θ

MO	Θ / deg						
	1	30	60	90	120	150	180
HOMO	8.57	8.69	8.91	8.95	8.94	8.68	8.61
HOMO-1	9.13	9.10	9.12	9.20	9.04	9.12	9.15
HOMO-2	11.52	11.25	10.79	10.53	10.79	11.29	11.58
HOMO-3	11.98	12.10	12.22	12.28	12.31	12.27	12.20
HOMO-4	13.45	13.47	13.48	13.42	13.31	13.20	13.15
$-\Delta E$ / (kJ/mol)	4.19	5.00	9.09	14.23	13.81	6.28	–

^(a) $E_{\text{tot}}(\text{antiperiplanar}) = -309.83366$ a.u.

The first and the third MOs reveal a pronounced change in energy upon isopropenyl group rotation. In contrast, the energy of the second level remains nearly constant, indicating that influence of direct π_v, π_c -interaction in the non-bisected conformers,^{7(b),9} if any, is minute. Similarly, the W_S -type cyclopropene MO, except for the torsion angles close to zero, remains of similar energy.

Another feature worth noting is the appearance of a substantial energy gap between the second and the third MOs throughout the series. Contrary to that, the PE spectrum of **1** exhibits three close lying ionization events separated by a large energy gap between a series of Gaussian-type bands starting at *ca.* 10.5 eV. The PE spectra of **2** and **3**, apart from a shift of all bands toward lower energy and a change in the intensity ratio of the first three ionization events, have an appearance similar to that of **1** (Figure 3).

The observed spectral pattern is not easy to rationalize unless rotational isomerism in the considered molecules, under the conditions of the measurements, is assumed. Based on the comparison with the calculated MO energies (Table IV), one is tempted to ascribe the first two signals in all three spectra to the ($W_A - \pi_v$), MOs in two different conformers (Table III), implying that the rest of the lower energy part of the spectra should be interpreted under assumption that the bands ③ – ⑤ correspond to two individual transitions each. Starting from this assumption, the third band is attributed to the superposition of bands arising from the ejection of an electron from the cyclopropene π -MO (π_c^-) in both conformers and the band ⑥ to the ionization from its in-phase (π_c^+) counterpart. This is fully corroborated by the results of the HF/6-31G* calculations for **1**, (Table IV), which predict a negligible effect of the isopropenyl group rotation on the corresponding energy level. Additional support comes from the intensity ratio of the first three sig-

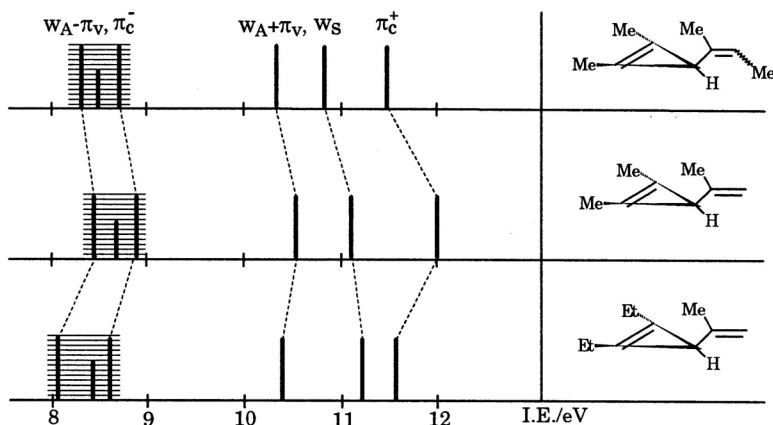


Figure 3. Correlation of the six lowest ionization energies for 1, 2, and 3.

nals in the PE spectrum of 2, which obviously indicates a more uniform population of the conformers involved than in 1 and 3. Using similar arguments, the band systems ④ and ⑤ are related to ionizations from the ($W_A + \pi_v$) linear MO combination and the cyclopropene W_S MO in both conformers. This again seems to be plausible in view of the broadness of the observed PE bands and it is in fact fully corroborated by the changes in ionization energies across the series 1–2–3 and results of the MNDO calculations. This conjecture holds, in particular, for the changes in energies of the fourth and fifth ionization events across the series, which is easily understood in terms of the perturbation theory.^{22, 23} We notice, for instance, that the fifth ionization band (associated with the W_S MO) appears at approximately the same energy in the PE spectrum of 1 and 2, while the PE spectrum of their diethyl congener 3 shows the same signal at a considerably lower energy, as expected due to the larger size of the alkyl groups.

However, in view of the assumptions involved, the assignments given in Table III should be considered as tentative only. In particular, the presented data do not allow a definite conclusion about the conformers involved. For instance, *ab initio* calculations predict synperiplanar and antiperiplanar conformers as the only minima of the potential energy curve for the rotation of the isopropenyl group in both 1 and 5. On the other hand, the comparison of the measured ionization energies and the calculated MO energies, presented in Figure 3, indicates that in one of the conformers of 1–3, present under the conditions of the measurements, the isopropenyl group deviates significantly from the plane bisecting the cyclopropene ring. Moreover, it should be strongly emphasized that the ionization features ① and ② taken together might be considered as a composite band system, which is strongly

reminiscent of the »double-band« structures observed earlier in the PE spectra of molecules with free internal rotation.²⁴ Hence, it appears that the recorded spectra of molecules 1–3 could be equally well interpreted in terms of practically unrestricted rotation of the isopropenyl group around the central C-C bond. This ambiguity will not, however, affect the general conclusions drawn above concerning the interaction pattern of the fragment orbitals involved. By the same token, the nature of the highest occupied MO in the considered compounds should remain unaffected too.

1,2-Diphenyl-3-isopropenylcyclopropene

Replacement of the alkyl groups in 1 or 3 with the phenyl groups leading to 4 is expected to cause a significant change in the low energy part of the PE spectrum which is presented in Figure 4, due to the possibility of conjugative interaction between the cyclopropene double bond and the aromatic π -systems.

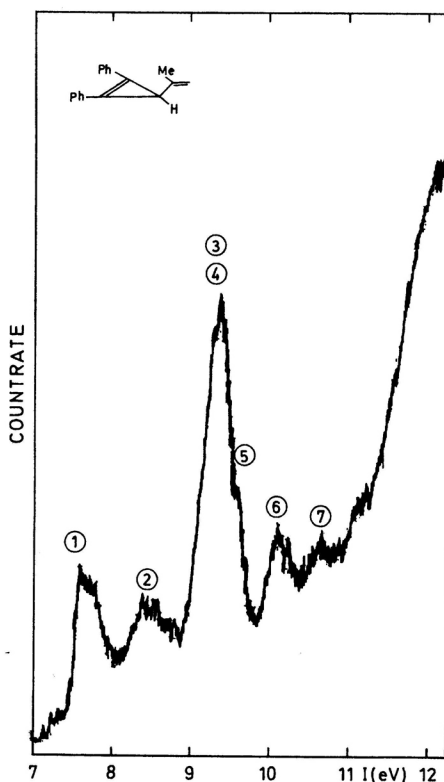


Figure 4. PE spectrum of 4.

In this regard, it is instructive to commence discussion by considering the PE spectrum of the parent 1,2-diphenylcyclopropene (**6**), which has been discussed in detail by Schweig's²⁵ group, and subsequently by Hohlneicher and coworkers.²⁶ Both research groups ascribed five out of six low energy transitions to the π -MOs, with the lowest (π_1) and the highest (π_5) energy among them corresponding to the antibonding- and bonding linear combination of the cyclopropene π -MO and the benzene π -MOs of the appropriate symmetries, respectively. It should be mentioned in passing that the ionization energy from π_5 could not be deduced due to the overlapping with the transition from the cyclopropene W_A MO. Further, π_2 and π_3 MOs correspond to two nearly unperturbed benzene π -orbitals, while π_4 , in addition to the coefficients in the benzene rings, exhibits an admixture of the unoccupied antibonding π orbital of the cyclopropene double bond. The approximate shape of the orbitals involved is shown in Figure 5.¹⁷

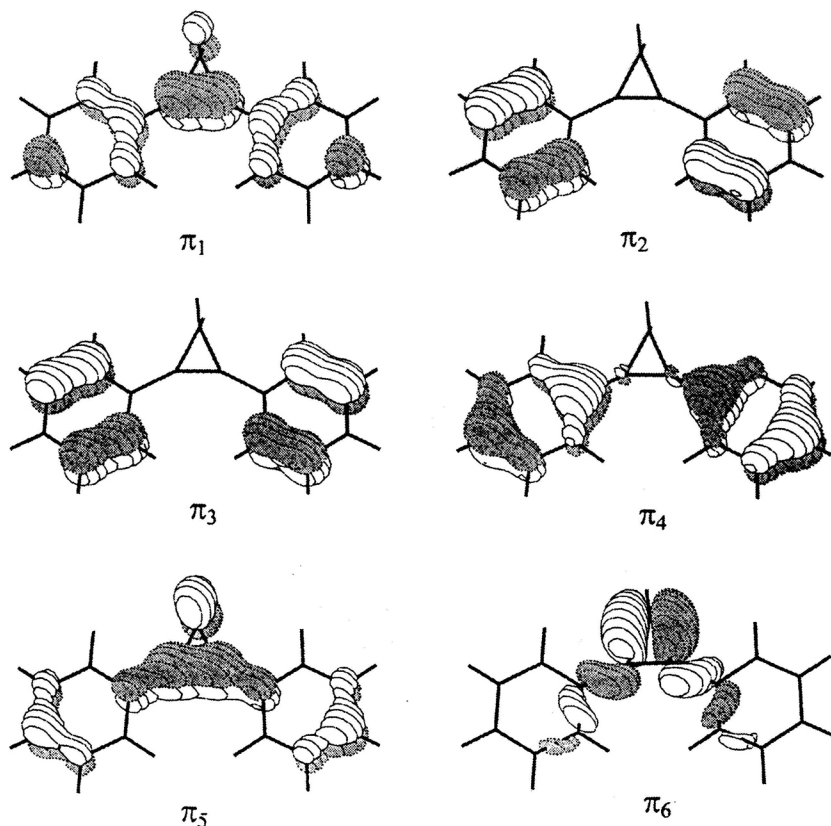


Figure 5. Graphic illustrations of the highest occupied MOs of **6**, as calculated using the STO-3G procedure.

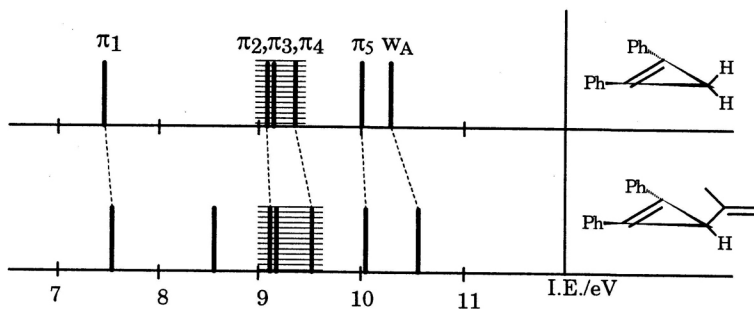


Figure 6. Correlation of the six lowest ionization energies for **4** and **6**.

Replacement of one of the hydrogen atoms at C(3) by the isopropenyl group is expected to affect the first (π_1) and fifth (π_5) levels at most, while the π_2 to π_4 ionizations should be practically of the same energy as in **6**.²² The magnitude of the effect could be evaluated by comparing the first IE of **1** (8.93 eV) with the corresponding value for 1,2-dimethylcyclopropene, which was estimated as 8.7 eV from the comparison of the ionization energies of 1,2,3,3-tetramethyl.²⁷ and 3,3-dimethylcyclopropene.²⁸ This in turn, suggests that the first IE of **4** should be slightly higher than in the parent 1,2-diphenylcyclopropene. It seems therefore logical to assign the first signal at 7.52 eV to the MO related to π_1 in **6**. Similarly, the comparison of the lower energy part of the PE spectrum of **4** with that of **6** (Figure 6) suggests assigning the third and the fourth peaks at 9.1 eV to the MOs related to the π_2 and π_3 MOs in **6**, while the signals at 9.5 and 10.02 eV are obviously related to the π_4 and π_5 MOs. This leaves the assignment of the second band in the PE spectrum of **4** to the ionization from the π -MO localized mainly on the vinylic fragment. Its energy is by *ca.* 0.9 eV lower than in 2-methylpropene²⁹ due to the inductive perturbation by the three-membered ring and the conjugative interaction with the W_A cyclopropene MO. Its bonding counterpart is found at 10.59 eV, *i.e.* roughly at the same position as in the PE spectrum of **1**. Assuming that the difference in IEs of this MO on passing from **4** to **6** roughly corresponds to the change in energy of the respective MOs between **1** (10.6 eV) and 1,2-dimethylcyclopropene (estimated value 10.2 eV), we can conclude with confidence that W_A in **6** appears below π_5 , *i.e.* at *ca.* 10.2 eV. The proposed assignment is fully corroborated by the results of MNDO, as well as STO-3G calculations (Table III), at least as far as the sequence of the bands is concerned.

CONCLUSIONS

The present work provides an additional piece of evidence that a combination of He(I) PE measurements and *ab initio* calculations offers an interesting insight into the electronic structure and conformational behaviour

of floppy molecules like the derivatives of 3-isopropenyl cyclopropene. The most interesting finding is related to the changes in the nature of the highest occupied MOs on passing from 1,2-dialkyl- to 1,2-diphenyl derivatives. Whereas in the former molecules the HOMO is largely localized in the olefinic double bond, the latter compound exhibits HOMO localization in the cyclopropene double bond. Thus, we expect differences in reactivity of compounds 1–3 relative to 4 in all those chemical reactions where selectivity is governed by the HOMO. Another point of interest is provided by the PE evidence on the presence of rotational isomerism in the PE spectra of 1–3. It should be, however, stressed that the presented data do not allow a definite conclusion about the composition of the rotamers involved. In particular, they do not allow distinction between two different modes of behaviour: the presence of a mixture of two »frozen« conformers and the practically unrestricted rotation of the isopropenyl group. Perhaps, higher level calculations and variable temperature PES of thermally stable congeners of the considered molecules, accompanied with detailed band shape analysis, will help resolve this problem in the future.

EXPERIMENTAL

The He(I) PE spectra of 1–3 were measured on a PS18 (Perkin Elmer, Ltd, England), while the PE spectrum of 4 was recorded on a UVG3 (Vacuum Generator) instrument. The PE spectra of 1–3 were measured at room temperature, while 4 had to be heated at 130 °C. The PE spectra were calibrated with Ar and Xe; a resolution of ca. 20 meV on the Ar-line was achieved. The vertical ionization energies listed in Table III were generally estimated from the maximum of the PE bands. ^1H - and ^{13}C -NMR spectra were recorded on the JEOL FX 90 FT instrument.

The preparation of compounds 1 and 2 has been reported in Ref. 30. 3 and 4 were prepared by the Wittig reaction of the corresponding ketones³¹ in 47% and 50.4% yield, respectively. Analytically pure 3 was obtained by vacuum distillation. IR(KBr) ν/cm^{-1} : 1875 (C=C)_c, 1630 (C=C)_v. ^1H -NMR (CDCl_3) δ/ppm : 1.14 (t, 6H, CH_2CH_3), 1.43–1.46 (dd, 3H, CH_3); 2.12 (s, 1H, CH), 2.39 (q, 4H, CH_2CH_3); 4.59–4.75 (m, 2H, = CH_2). ^{13}C -NMR (CDCl_3) δ/ppm : 12.30 (CH_2CH_3), 19.07 (CH_2CH_3), 19.64 (CH_3), 28.16 (CH), 105.8 (=CH₂), 114.67 (C=C), 151.63 (C=CH₂). Purification of 4 was accomplished by column chromatography (silicagel, ether-pentane as eluent). IR(KBr) ν/cm^{-1} : 1820 (C=C)_c. ^1H -NMR (CDCl_3) δ/ppm : 1.46–1.47 (dd, 3H, CH_3), 2.88 (s, 1H, CH), 4.80–5.08 (m, 2H, =CH₂), 7.25–7.73 (m, 10 H, C_6H_5). ^{13}C -NMR (CDCl_3) δ/ppm : 19.19 (CH_3), 27.31 (CH), 108.36 (=CH₂), 115.24 (C=C), 128.50, 128.73, 129.40, 129.57 (C₆H₅), 148.42 (C=CH₂).

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SAŽETAK

Fotoelektronski spektri i konformacijsko ponašanje 3-izopropenil derivata ciklopropena

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Primjenom He(I) fotoelektronske spektroskopije i *ab initio* kvantno-kemijskih računa istražena je elektronska i molekulska struktura 1,2-dialkil- (1-3) kao i 1,2-difenil-3-izopropenil (4) ciklopropena. U interpretaciji rezultata posebna je pažnja posvećena konjugativnoj interakciji ciklopropenskog prstena i π -sustava izopropenilne skupine i njihovoj ovisnosti o konformaciji molekule.