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Photoelectron Spectra of Cyclopropane and Cyclopropene Compounds

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Contents

1. Introduction

Molecular photoelectron spectroscopy (PES) is used to study the electronic structure of molecules. In this paper, the results of ultraviolet (UV) PE spectroscopic studies of compounds with cyclopropane and cyclopropene rings will be summarized. An earlier review on PES of small ring hydrocarbons (cyclopropane and cyclobutane rings), which was essentially restricted to hydrocarbons and included only a few cyclopropenes, was published by Gleiter[1] in 1979. A second review that highlighted some important PE spectroscopic aspects of a limited number of cyclopropane and cyclopropene compounds was published by Ballard in 1987.[2] Sections about cyclopropane, some polycyclics containing cyclopropane rings, and the conjugative property of the cyclopropyl group were included in a review on PE spectra of hydrocarbons of Heilbronner[3] from 1992. In the present paper derivatives with heteroatoms also are covered, but topics dealt with comprehensively by Gleiter[1] or Ballard[2] are mainly updated with more recent data. Some efforts have been made to cover “simple” derivatives of cyclopropane and cyclopropene, i.e., such compounds in which a three-membered ring is the main structural feature. But no restrictions were applied with respect to the structures of cyclopropane and cyclopropene compounds so that all compounds comprising a three-membered carbocycle, including polycycles such as tetrahedrane, are included. However, studies of compounds in which a cyclopropyl group is just a substituent and little or no information is provided with respect to this grouping are treated with lower priority.

Many of the investigations on compounds to be included in this paper have been performed in the 1970s and 1980s. Since instrumentation has made little progress in PES in more recent years, there can

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Paul Rademacher was born near Hamburg in Germany and studied chemistry at the Universities of Saarbrücken and Göttingen, where he received a Dr. rer. nat. degree (Wolfgang Lüttke, molecular structure of dimethylnitrosamine). After one year as a postdoctoral fellow at the University of Oslo/Norway (Otto Bastiansen, structure analysis by electron diffraction), he joined the University of Münster. His Habilitation, dealing with conformational analysis of aliphatic hydrazines by electron diffraction and photoelectron spectroscopy, was completed in 1974. Since 1977, he has been Professor of organic chemistry at the University of Essen. His research interests include heterocyclic chemistry, molecular spectroscopy, and pyrolysis reactions.

be no reservation to including these spectra. However, some of the theoretical methods used at that time are no longer adequate today, and therefore the corresponding results are to be considered with adequate reservation.

In the following discussion, ionization energies are given as vertical IP values if not stated otherwise. The energy unit eV is used; 1 eV = 23.060 kcal mol^{-1} = 96.485 kJ mol^{-1}.

2. Photoelectron Spectroscopy

The basic principles of PES, the experimental methods, the interpretation procedures, and the applications have been described in several books.[4−13] There are also some excellent review articles.[14−16] Extensive data collections are available, for example, refs 17 and 18. A well-documented database with IP$_1$ values is provided on the Internet.[19]

The fundamental principle of PES is the photoelectric effect. Molecules M in the gas-phase are irradiated with monochromatic light, and electrons can be ejected when their binding energy is lower than the photon energy, leaving behind radical cations M$^{\bullet+}$.

$$M \xrightarrow{h\nu} M^{\bullet+} + e \qquad (1)$$

The kinetic energy of the ejected electrons E_{kin}(e) is measured and the ionization energy IE or ionization potential IP is obtained from the energy conservation condition.

$$IP = h\nu - E_{kin}(e) \qquad (2)$$

Measuring a PE spectrum, the number of photoelectrons per time unit (e.g., counts per second, cps), is recorded as a function of the kinetic energy or IP. The radical cation may be excited to different vibrational states, and the ionization band exhibits vibrational fine structure. The adiabatic IP$_a$, i.e., transition to the vibrational ground state of M$^{\bullet+}$, can be distinguished from the vertical IP$_v$, i.e., transition with the greatest Franck−Condon factor. The latter property (IP$_v$) is of higher relevance when studying the electronic structure of a molecule because it is linked with the energy ϵ of the molecular orbital (MO), from which the electron was ejected, by the Koopmans theorem[20]

$$IP_i = -\epsilon_i^{SCF} \qquad (3)$$

stating that the vertical ionization energies are equal to the negative values of the SCF orbital energies which are obtained by quantum chemical calculations. This assumption is generally used as the basis for analysis of PE spectra. Actually, this is an approximation, which can fail and lead to the wrong interpretation of spectral data. Equation 3 assumes that M and M$^{\bullet+}$ can be described with the same MOs, and energy changes upon ionization, associated with electron reorganization and correlation, are neglected. Fortunately, these two effects have opposite signs and largely compensate each other. The correlation between MO theory and PE spectroscopy has both proved convenient and adequate provided possible deviations are born in mind. These deviations can, for example, result in different ordering of IPs and MO energies.

Quantitative characteristics of a PE spectrum, such as position and intensity of the ionization bands, vibrational fine structure, Jahn−Teller, and spin−orbital effects, are in general sufficient for reliable assignments of the IPs of simple molecules. The spectra of more complex polyatomic molecules are usually analyzed with the aid of quantum chemical calculations making use of the Koopmans approximation. Besides semiempirical methods such as MINDO/3,[21] MNDO,[22] AM1,[23] and PM3,[24] ab initio Hartree-Fock (HF) or density functional methods (DFT) methods are used with increasing frequency even for larger molecules, and in particular DFT or hybrid methods such as B3LYP[25] have proved useful since electron correlation is included. Although Kohn−Sham orbitals obtained by DFT methods[26] are not SCF molecular orbitals and their physical meaning is still debated, it has been shown that they can be used with high confidence for the interpretation of PE spectra.[27,28] Much better agreement between experimental and theoretical values can be expected for the first vertical IP (IP$_{1v}$) when the energies of the molecule and the radical cation are calculated, e.g., by the B3LYP method. For IP$_{1v}$, a single point calculation is performed for the radical cation (M$^{\bullet+}$) using the molecule's (M) geometry. Higher IP values can then easily be calculated by correcting the other ϵ^{B3LYP} values by the difference between $-\epsilon$(HOMO) and IP$_{1v}$.[27] Whereas typical energy differences between experimental IP$_i$ and $-\epsilon_i^{B3LYP}$ values are about 2 eV, experimental and calculated IP$_i$ values differ only by 0.1−0.3 eV. Furthermore, both $-\epsilon_i^{B3LYP}$ and calculated IP$_i$(calc) values are linearly correlated with the experimental IP$_i$(exp) values with correlation coefficients very close to 1.00.

In a UV photoelectron spectrometer a helium discharge lamp is used as radiation source which emits nearly monochromatic He−I radiation of 21.22 eV ($\lambda = 58.43$ nm) or He−II radiation of 40.81 eV ($\lambda = 30.38$ nm). Calibration of the energy scale is accomplished by adding compounds with known IPs to the sample. For this purpose, a mixture of the noble gases argon (15.759 and 15.937 eV) and xenon (12.130 and 13.436 eV) is frequently used. The two peaks relate to transitions to the $^2P_{3/2}$ and $^2P_{1/2}$ states of the ions. Typical uncertainties of ionization energies are about 0.01 eV.

By PES, all electrons with binding energies up to the photon energy of the radiation used for ionization, i.e., usually 21.21 eV (He−I), are accessible. The valence shell electrons of ordinary organic molecules composed of hydrogen and elements of the second or third row of the periodic table have energies between about −6 and −50 eV. Of highest interest are the upper occupied levels since they are decisive for the structural and chemical properties of the compound. Therefore, usually He−I spectra are sufficient to study the relevant electronic structure of a molecule. He−II spectra are often used in addition to the He−I spectra to assign the ionizations, because the probability that an electron will be “hit” by a photon is dependent on the shape and size of the orbital in comparison with the wavelength of the photon. Comparison of the He−I and the He−II spectra of the same compound helps to distinguish, for example, ionizations from σ- and π-type MOs.

3. PE Spectra and Electronic Structures of Cyclopropane and Cyclopropene Compounds

3.1 Cyclopropane and Cyclopropene

The molecular symmetry of cyclopropane (**1**) is D_{3h}, and its MOs have to be constructed from the orbitals of the three CH_2 groups in such a way that they belong to the irreducible representations of this point group. In this way, three π_{CH2} orbitals ($1a_1''$ and $1e''$), three orbitals with mainly σ_{CH2} character ($2a_1'$ and $1e'$), and three σ_{C-C} orbitals ($1a_1'$ and $2e'$) are obtained. (Only valence orbitals are taken into account.) Two models are common for the cyclopropane ring: the bent bond model of Förster,[29] Coulson and Moffitt,[30] and the Walsh model.[31] For the interpretation of PE spectra, the Walsh model and the related canonical SCF MOs are widely used. In particular, the two degenerate σ_{C-C} orbitals ($2e'$) are important which can be used to describe electronic interactions of the cyclopropane ring with orbitals of substituents or other neighboring groups. These orbitals are then distinguished as ω_A and ω_S. Graphical representations including the third Walsh orbital ω_O, which is characterized as an internal σ-MO, and their antibonding counterparts (ω_O*, ω_S*, ω_A*) are shown in Figure 1. In derivatives of cyclopropane with lower symmetry than that of the parent molecule, the orbitals ω_A and ω_S are no longer degenerate and usually are the highest (HOMO) and second highest (HOMO-1) occupied MOs. It has been pointed out by Gleiter et al.[1,32] and by Heilbronner et al.[33] that the antibonding Walsh orbitals have to be included if one wants to draw valid conclusions about the PE spectra of compounds containing the cyclopropane moiety. In the following sections, this is seen quite clearly for several cyclopropane derivatives for which SCF MOs termed “ω_S” or “ω_A” are depicted. These MOs, which were obtained by quantum chemical methods, are actually linear combinations of the Walsh orbitals, and usually show also contributions of π_{CH2} and σ_{CH2} orbitals. For short, such MOs are termed ω_S and ω_A which have high contributions of the “real” Walsh orbitals.

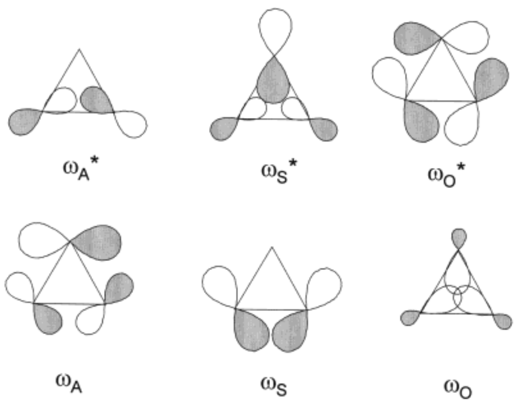


Figure 1. Walsh orbitals of cyclopropane.

1

2

Because of its molecular C_{2v} symmetry, there are no degenerate orbitals in cyclopropene (**2**), and the two Walsh orbitals ω_A ($2b_2$) and ω_S ($4a_1$) become HOMO-1 and HOMO-2 below the $\pi_{C=C}$ ($2b_1$) orbital (HOMO). Both the geometrical and the electronic structures of cyclopropane and cyclopropene have been investigated with experimental and theoretical methods,[34−37] and the chemical consequences of the special bonding properties of the three-membered ring have been reviewed.[38,39]

The PE spectra of **1** and **2** are depicted in Figures 2 and 3, respectively. The spectrum of **1** exhibits a double peak with maxima at 10.47 and 11.25 eV, a broad band at 12.96 eV, and two strongly overlapping bands with maxima at 15.77 and 16.66 eV.[40] The first two ionizations are related to the degenerate 2e′

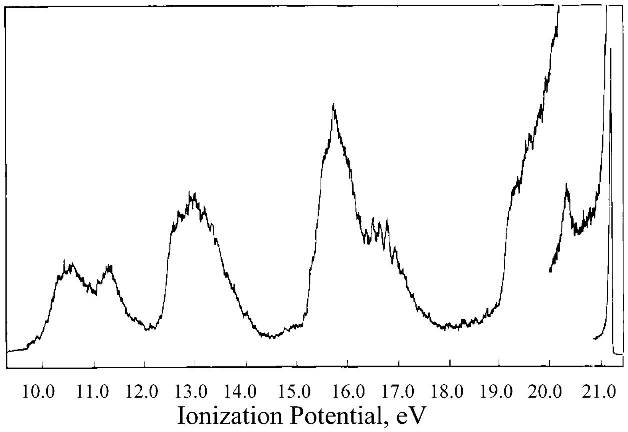


Figure 2. PE spectrum of cyclopropane (**1**). Redrawn from ref 4.

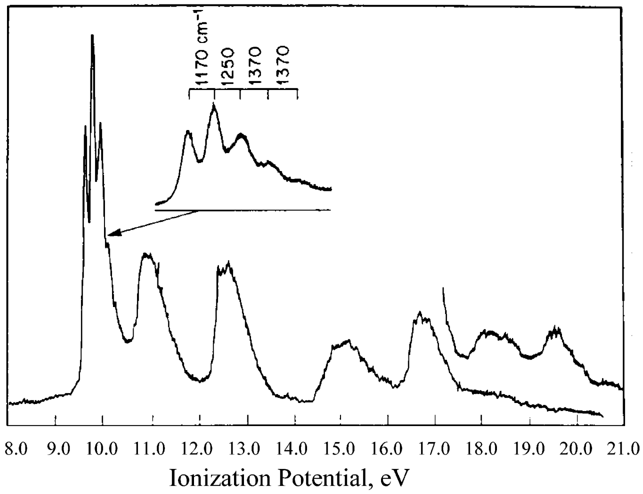
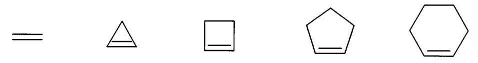


Figure 3. PE spectrum of cyclopropene (**2**). Reprinted with permission from ref 55. Copyright 1972 The American Institute of Physics. The data in the 17−21 eV region were obtained using He−II excitation.

orbitals (ω_A, ω_S) and show a Jahn−Teller split of 0.78 eV, which relates to the energy difference of the two nondegenerate states of the radical cation. This effect has been investigated by several authors.[41−46] The center of the band lies at (10.47 + 11.25)/2 = 10.86 eV, which, according to eq 3, yields $\epsilon(2e') = -10.86$ eV (cf. ref 47). The remaining three bands are related to ionizations from the orbitals 1e″ (π_{CH2}), $2a_1'$ (ω_O), and $1a_2''$ (π_{CH2}).[1,3,4,40,48−51] For the interpretation of the spectrum and assignments of the IPs besides quantum chemical calculations comparison with the spectra of related compounds such as aziridine,[48] diaziridine,[48] oxirane,[48,50] and thiirane,[50] photoionization cross sections of He−I and He−II spectra[50] as well as angle-resolved PE spectroscopy[40,51] were utilized. By the last mentioned method, the angular distribution parameter β was determined as a function of photoelectron energy for the MOs with IP values below 18 eV using dispersed polarized synchrotron radiation. $\Delta\beta$ values, defined as the difference in β at 10 and 2 eV, permit the characterization of orbitals as σ_{CC} or π_{CH2}. Vibrational fine structure of 60 meV (480 cm^{-1}) and 130 meV (1050 cm^{-1}) was observed for the first (10.47 eV) and for the fifth band (16.66 eV), respectively.[40] The first frequency corresponds to the Jahn−Teller active ν_{11} (e′) vibrational mode which has an energy of 108 meV (868 cm^{-1}) in the neutral ground state.[52] The second frequency is reasonably assigned to the ν_2 (a_1') vibrational mode which has an energy of 186 meV (1504 cm^{-1}) in **1**.[52]

The PE spectrum of **2** (Figure 3) has been studied by several authors.[53−56] It is characterized by a series of seven well-separated bands of which only the first displays a clear vibrational fine structure of 1170−1370 cm^{-1}. As for compound **1**, in the analysis of the spectrum of **2** the spectra of related compounds, diazirine and difluorodiazirine, were used.[55] Assignments are as follows:[55] 9.86 eV ($2b_2$, $\pi_{C=C}$), 10.89 eV ($2b_1$, ω_A), 12.7 eV ($4a_1$, ω_S), 15.09 eV ($1b_2$, π_{CH2}), 16.68 eV ($3a_1$, σ_{CH}), 18.3 eV ($2b_1$, σ_{CH}), and 19.6 eV ($2a_1$, σ_{CH}). The vibrational intervals of the first band show a positive anharmonicity. Since the $2b_2$ MO is largely C=C bonding, the frequency of ≈1300 cm^{-1} is assigned to the C=C stretching vibration of the radical cation, which has a frequency of 1656 cm^{-1} in the ground state of the molecule.

The $\pi_{C=C}$ ionization of **2** fits well in the sequence of homologous molecules:

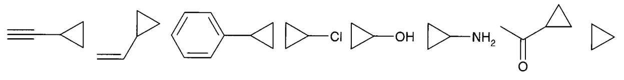


10.51 eV[53] 9.86 eV[53] 9.59 eV[56] 9.18 eV[53] 8.94 eV[53]

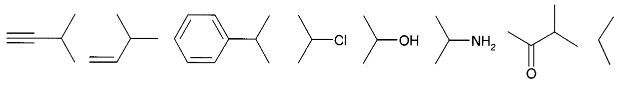
For conjugative interactions of the cyclopropane ring with substituents, orbital overlap is essential.[57,58] In particular, overlap of ω_A is conformation-dependent. Therefore, PE spectroscopy can be employed for conformational analysis, and this has been shown also for several cyclopropane derivatives.[59,60]

3.2 Derivatives of Cyclopropane

The cyclopropyl group is considerably smaller than an isopropyl group, but a better electron donor than any other alkyl group.[38,39,61] Accordingly, it is fair to suspect that cyclopropyl-substituted chromophors should have a lower IP than the corresponding isopropyl systems. That this assumption is correct becomes evident from inspection of the following data which are the IP$_1$ values, given in eV, of the respective compounds measured by PE spectroscopy:



9.58[62] 9.15[63] 8.71[63] 10.29[64] 10.24[65] 9.41[53] 9.50[66] 10.60[53]



10.05[67] 9.53[68] 8.71[69] 10.81[53] 10.36[53] 9.36[70] 9.30[71] 11.51[53]

There are only a few exceptions: The IP$_1$ values of the two benzene derivatives and those of the two amines show no significant differences, and in the ketones the sequence is inverted. For the last compounds IP$_1$ relates to removal of a lone-pair electron, and the corresponding n_O orbital is probably inductively stabilized by the cyclopropyl group. This view is supported by the fact that for the ketones with two isopropyl- or cyclopropyl groups the difference of the IP$_1$ values is even greater (0.33 eV).[66,71] For the benzene derivatives and the amines, differences in the conformational properties of the isopropyl and the cyclopropyl compounds seem to be responsible (see also section 3.2.1).

In Tables 1 and 2, PE spectroscopic data are summarized for several derivatives of cyclopropane and cyclopropene, respectively, and in Table 3 such data of polycyclic cyclopropane and cyclopropene compounds are collected. More examples of the last type are specified in Gleiter's compilation.[1] The ionic states are indicated by their spectroscopic symbols. In cases with conflicting assignments of ionizations, the most recent or most reasonable have been chosen. Occasionally, the interpretation of the original authors has been modified when comparison with

Table 1. PE Data of Cyclopropane Derivatives[a]

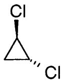
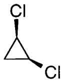
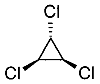
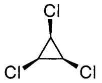
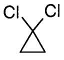
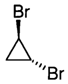
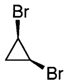
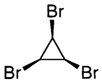
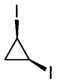
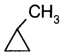
Compound		Symmetry	IP_v	Ref.
1		D_{3h}	10.47/11.25 (2e'), 12.96 (1e"), 15.77 ($2a_1$'), 16.66 ($1a_2$"), 19.63 (1e'), 26.30 ($1a_1$')	53,40
2		C_s	10.29 (4a", n_{Cl}), 10.91 (8a', n_{Cl}), 12.13 (7a', ω_S), 12.92 (3a", π_{CH2}), 13.55 (2a", ω_A), 13.85, 16.1, 17.0	64
3		C_2	10.30 (8a, n_{Cl}), 10.78 (7b, n_{Cl}), 11.84 (7a, n_{Cl}), 11.94 (6b, n_{Cl}), 13.17 (5b, ω_S), 13.75 (4b, ω_A), 14.1, 16.7, 17.0	64
4		C_s	10.29 (6a", n_{Cl}), 10.70 (9a', n_{Cl}), 11.49 (5a", n_{Cl}), 11.90 (8a', n_{Cl}), 13.06 (4a", ω_A), 13.65 (7a', ω_S), 14.0, 16.1, 17.4	64
5		C_s	10.32 (7a", 11a', n_{Cl}), 10.66 (6a", n_{Cl}), 11.72 (10a', n_{Cl}), 12.03 (9a', n_{Cl}), 12.26 (5a", n_{Cl}), 13.9 (8a', ω_S), 14.2 (4a", ω_A), 16.6, 17.2	64
6		C_{3v}	10.26 (6e, n_{Cl}), 10.60 (6e, n_{Cl}), 11.56 (5e, n_{Cl}), 11.8 ($1a_2$, n_{Cl}), 12.28 ($5a_1$, n_{Cl}), 13.89 (4e, ω_S, ω_A), 14.3 (4e, ω_S, ω_A), 16.18 ($4a_1$, $\sigma_{C\text{-}Cl}$), 17.8	64
7		C_{2v}	10.22 ($3b_1$, n_{Cl}), 11.33 ($4b_2$, $2a_2$, n_{Cl}), 11.77 ($6a_1$, n_{Cl}), 12.93 ($5a_1$, ω_s), 13.7, 13.9, 14.1, 16.4, 17.0	64
8		C_s	9.94 (n_{Br}), 10.43 (n_{Br}), 11.58 (ω_S), 12.34 (ω_A), 13.08, 13.5, 15.85, 16.8	53,64
9		C_2	9.90 (n_{Br}), 10.32 (n_{Br}), 10.90 (n_{Br}), 11.02 (n_{Br}), 11.18 (n_{Br}), 11.32 (n_{Br}), 12.40 (ω_S), 12.98, 13.3, 16.3	64
10		C_s	9.90 (n_{Br}), 10.27 (n_{Br}), 10.60 (n_{Br}), 10.91 (n_{Br}), 11.15 (n_{Br}), 12.35 (ω_S), 12.95, 13.4, 15.7, 17.2	64
11		C_{3v}	9.90 (n_{Br}), 10.27 (n_{Br}), 10.60 (n_{Br}), 10.91 (n_{Br}), 11.55 (n_{Br}), 12.85 (ω_S, ω_A), 13.1, 13.6, 14.0, 15.45 ($\sigma_{C\text{-}Br}$), 17.5	64
12		C_2	9.15 (n_I), 9.62 (n_I), 9.74 (n_I), 9.88 (n_I), 10.01 (n_I), 10.38 (n_I), 10.51 (n_I), 11.58 (ω_S), 12.10, 12.55, 13.15, 15.9	64
13		C_s	9.13 (n_I), 9.44 (n_I), 9.84 (n_I), 10.26 (n_I), 11.42 (ω_S), 12.15, 12.68, 13.14, 15.0, 16.9	64
14		C_s	10.1 (4a", ω_A), 10.9 (8a', ω_S)	78,215

Table 1 (Continued)

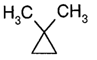
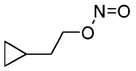
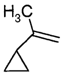
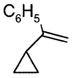
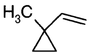
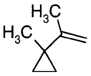
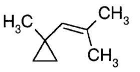
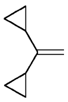
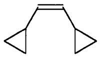
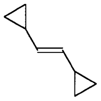
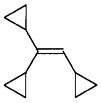
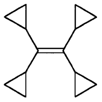
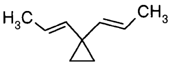
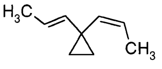
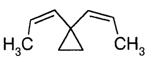
Compound	Symmetry	IP$_v$	Ref.
15 	C_{2v}	9.80 ($3b_1$, ω_A), 10.57 ($6a_1$, ω_S), 11.98 (π_{CH3}), 12.63, 13.72, 15.57	79,80, 215
16 	(C_s)	10.6	185
17 	C_s	9.15 (4a", $\pi_{C=C}$-ω_A), 10.65 (10a', ω_S), 11.7 (3a", $\pi_{C=C}$+ω_A), 12.25 (9a', π_{CH2})	63,86,87
18 	C_s	9.12 (a", $\pi_{C=C}$), 10.60 (a', ω_S), 11.31 (a", ω_A), 12.02, 12.27	92
19 	(C_s)	8.40, 9.08, 9.60	93
20 	C_1	8.92 ($\pi_{C=C}$), 10.62 (ω_S), 11.20 (ω_A), 12.00, 12.84	91
21 	C_1	9.03 ($\pi_{C=C}$), 10.14 (ω_A), 10.65 (ω_S), 11.58, 12.67	91
22 	C_1	8.61 ($\pi_{C=C}$), 9.75 (ω_A), 10.44 (ω_S), 11.31, 12.46	91
23 	C_{2v}	8.87 ($\pi_{C=C}$), 10.22, 10.61, 11.08, (11.74), 12.04	92,160
24 	C_{2v}	8.50 ($\pi_{C=C}$)	160
25 	C_{2h}	8.40 ($\pi_{C=C}$)	160
26 	C_s	8.0 ($\pi_{C=C}$)	160
27 	D_{2h}	7.90 ($\pi_{C=C}$), 9.4	160
28 	C_{2v}	8.98 ($3b_1$, ω_A-$\pi_{C=C}^+$), 9.83 ($2a_2$, $\pi_{C=C}^-$), 10.9 ($8a_1$, ω_S), 11.7 ($6b_2$, σ), 11.9 ($2b_1$, ω_A+$\pi_{C=C}^+$)	100
29 	C_{2v}	8.40 (ω_A-$\pi_{C=C}^+$), 9.16 ($\pi_{C=C}^-$), 10.60 (ω_S), 11.20 (ω_A+$\pi_{C=C}^+$)	186
30 	C_s	8.40 (7a', ω_A-$\pi_{C=C}^+$), 9.16 (6a", $\pi_{C=C}^-$), 10.5 (18a', ω_S), 11.3 (17a', σ), 11.5 (5a", ω_A+$\pi_{C=C}^+$)	100
31 	(C_2)	8.8 (ω_A-$\pi_{C=C}^+$), 9.10 ($\pi_{C=C}^-$), 10.4 (ω_S), 11.1 (σ), 11.4 (ω_A+$\pi_{C=C}^+$)	100,186

Table 1 (Continued)

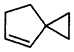
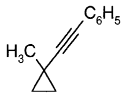
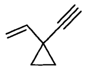
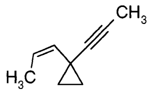
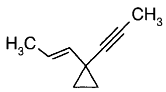
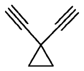
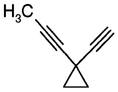
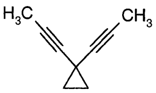
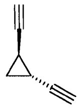
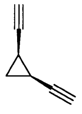
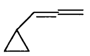
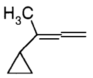
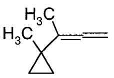
Compound	Symmetry	IP_v	Ref.
32 	C_s	8.48 ($\pi_{C=C}$), 10.3 (ω_S), 11.05 (ω_A), 11.6	63
33 	C_s	9.58 (4a", $\pi_{C\equiv C}$-ω_A), 10.09 (9a', $\pi_{C\equiv C}$-ω_S), 11.58 (8a', ω_S+$\pi_{C\equiv C}$), 12.2 (3a", ω_A+$\pi_{C\equiv C}$)	62
34 	C_s	8.34 (π_{Ph}), 9.26 (ω_S), 9.35 (π_{Ph}), 10.32 (ω_A), 11.02, 11.70	99
35 	C_s	9.00 (5a", $\pi_{C=C}$-ω_A), 10.17 (4a", $\pi_{C\equiv C}$-$\pi_{C=C}$; 13a', $\pi_{C\equiv C}$-ω_S), 11.5 (12a', $\pi_{C\equiv C}$+ω_S), 12.4 (11a'), 12.6 (3a")	100,186
36 	(C_s)	8.77 ($\pi_{C=C}$-ω_A-$\pi_{C\equiv C}$), 9.30 (ω_S-$\pi_{C\equiv C}$), 9.57 (ω_A), 10.93 ($\pi_{C\equiv C}{}^+$), 11.70 ($\pi_{C\equiv C}{}^-$), 12.03	100,186
37 	(C_s)	8.30 ($\pi_{C=C}$-ω_A-$\pi_{C\equiv C}$), 8.50 (ω_S-$\pi_{C\equiv C}$), 9.40 (ω_A), 10.22 ($\pi_{C\equiv C}{}^+$), 10.82 ($\pi_{C\equiv C}{}^-$), 11.40	186
38 	C_{2v}	9.26 (3b$_1$, $\pi_{C\equiv C}{}^+$-ω_A), 10.31 (5b$_2$, $\pi_{C\equiv C}{}^-$), 10.63 (7a$_1$, $\pi_{C\equiv C}{}^+$-ω_S; 2a$_2$, $\pi_{C\equiv C}{}^-$), 12.1 (6a$_1$, $\pi_{C\equiv C}{}^+$+ω_S), 13.0 (2b$_1$, $\pi_{C\equiv C}{}^+$+ω_A)	100,186
39 	C_s	8.88 ($\pi_{C\equiv C}{}^+$-ω_A), 9.60 ($\pi_{C\equiv C}{}^-$), 10.15 ($\pi_{C\equiv C}{}^+$-ω_S), 10.37 ($\pi_{C\equiv C}{}^-$), 11.8 ($\pi_{C\equiv C}{}^+$+ω_S), 12.6 ($\pi_{C\equiv C}{}^+$+ω_A)	100,186
40 	C_{2v}	8.56 ($\pi_{C\equiv C}{}^+$-ω_A), 9.40 ($\pi_{C\equiv C}{}^-$), 9.70 ($\pi_{C\equiv C}{}^+$-ω_S), 11.60, 12.28	186
41 	C_2	9.84 (9a, π), 10.03 (8b, π), 10.54 (8a, π), 10.59 (7b, π), 12.04 (6b, ω_A), 12.24 (7a, ω_S), 13.28 (5b), 13.75 (6a), 15.66 (5a), 16.09 (4b), 16.67 (4a), 17.32 (3b)	188
42 	C_s	9.83 (10a', π), 9.98 (7a", π), 10.43 (6a", π), 10.49 (9a', π), 12.05 (5a", ω_A), 12.28 (8a', ω_S), 13.22 (7a'), 13.83 (4a"), 15.63 (6a'), 16.25 (5a'), 16.28 (3a"), 17.40 (4a')	188
43 	C_s	8.6 (a", π), 9.5 (a', π), 10.3 (a', σ), 11.25 (a", π)	1
44 	C_s	8.83 (a", π), 9.75 (a', π), 10.54, 11.21, 12.49, 13.60, 14.16	92
45 	C_s	8.81 (a", π), 9.67 (a', π), 10.25, 10.81, 12.17, 12.65, 13.80	92

Table 1 (Continued)

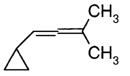
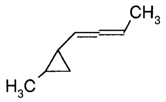
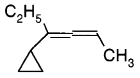
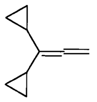
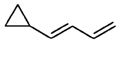
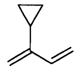
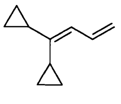
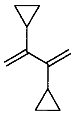
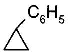
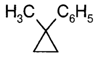
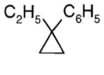
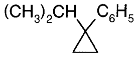
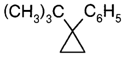
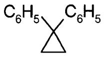
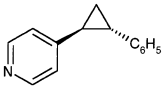
Compound	Symmetry	IP$_v$	Ref.
46 	C$_s$	8.78 (a", π), 8.98 (a', π), 10.63, 11.47, 12.70, 13.05, 14.49	92
47 	C$_s$	8.96 (a", π), 9.29 (a', π), 10.25, 11.05, 12.68, 13.76	92
48 	(C$_s$)	8.60 (a", π), 9.15 (a', π), 10.41, 11.04, 12.05, 12.64, 13.68., 14.61	92
49 	C$_{2v}$	8.62 (b$_1$, π), 9.68 (b$_2$, π), 10.19, 10.65, 11.11, 11.74, 12.62, 15.12	92
50 	C$_s$	8.57 (π_2-ω_A), 10.61 (π_2+ω_A-π_1), 11.13 (ω_S), 11.77, 12.96 (ω_A+π_1)	163
51 	C$_s$	8.85 (π_2-ω_A), 10.21 (π_2+ω_A-π_1), 10.88 (ω_S), 11.60, 12.93 (ω_A+π_1)	163
52 	C$_s$	8.15 [π_2-(ω_A'-ω_A")], 10.38 [π_2+(ω_A'+ω_A")-π_1], 10.97 (ω_S), 11.56, 12.69 [(ω_A'+ω_A")+π_1]	163
53 	C$_{2h}$	8.65 [π_2-(ω_A'-ω_A")], 9.57 [(ω_A'+ω_A")-π_1], 10.90 (ω_S), 11.37, 12.63 [(ω_A'+ω_A")+π_1]	163
54 	C$_s$	8.74 (14a', π_{Ph}-ω_S), 9.18 (9a", π_{Ph}), 10.50 (8a", ω_A), 11.0 (13a', ω_S+π_{Ph}), 11.6 (σ), 12.1	63,94,95,164
55 	C$_s$	8.75 (a', π_{Ph}-ω_s-π_{CH3}), 9.25 (a", π_{Ph}), 10.09 (a", ω_A-π_{CH3}), 10.67 (a', ω_s+π_{Ph}), 11.43, 11.94	80,95,164
56 	C$_s$	8.70 (a', π_{Ph}), 9.17 (a", π_{Ph}), 9.95 (a", ω_A), 10.50 (a', ω_S)	95
57 	C$_s$	8.63 (a', π_{Ph}), 9.12 (a", π_{Ph}), 9.74 (a", ω_A), 10.38 (a', ω_S)	95
58 	C$_s$	8.63 (a', π_{Ph}), 9.15 (a", π_{Ph}), 9.63 (a", ω_A), 10.33 (a', ω_S) (a', ω_S)	95
59 	C$_{2v}$	8.50 (π_{Ph}), 9.00 (π_{Ph}-ω_s), 9.24 (π_{Ph}), 10.42 (ω_A), 10.90 (π_{Ph}+ω_s), 11.88	80
60 	C$_1$	8.69 (π_{Ph}), 9.35 (π_{Ph}, π_{Py}, n$_N$), 10.8 (ω_A), 11.5 (ω_S)	168

Table 1 (Continued)

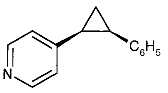
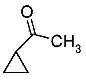
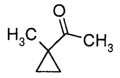
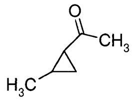
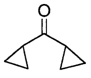
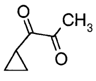
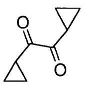
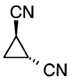
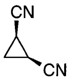
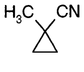
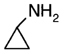
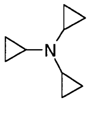
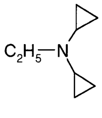
Compound	Symmetry	IP$_v$	Ref.
61 	C_1	8.75 (π_{Ph}), 9.35 (π_{Ph}, π_{Py}, n_N), 10.6 (ω_A), 11.5 (ω_S)	168
62 	C_s	9.50 (n_O-ω_S), 10.62 (ω_A), 11.40 (n_O+ω_S), 12.64	66,83
63 	C_s	9.3 (n_O-ω_S), 10.13 (ω_A), 11.13 (n_O+ω_S), 12.4	83
64 	C_s	9.38 (n_O-ω_S), 10.28 (ω_A), 11.05 (n_O+ω_S), 12.26	83
65 	(C_{2v})	9.28 (n_O), 10.43 (ω_A), 11.5 (ω_S)	66
66 	(C_s)	9.33 (n_O), 10.78 (ω_A), 11.35 (ω_S, n_O)	66
67 	(C_{2h})	9.09 (n_O), 10.40 (ω_A), 11 - 12 (ω_S, n_O)	66
68 	C_s	10.91 (4a'', ω_A-π_{CN}), 11.54 (9a', ω_S-π_{CN}), 12.54 (8a', π_{CN}+ω_S), 13.00 (7a', n_N), 13.37 (3a'', π_{CN}+ω_A), 13.94 (2a'', π_{CH2}), 14.75 (6a'), 17.08 (5a'), 18.15 (4a')	4,74
69 	C_2	11.45 (9a, ω_S-π_{CN}), 11.95 (8b, ω_A-π_{CN}), 12.92 (8a, n_N), 13.10 (7b, n_N), 13.38 (7a, π_{CN}), 14.16, 14.5, 15.2, 16.0, 18.3	64
70 	C_s	11.34 (10a', ω_S-π_{CN}), 11.85 (7a'', ω_A-π_{CN}), 12.83 (6a'', n_N), 12.97 (9a', n_N),13.23 (8a', 5a'', π_{CN}), 14.15, 14.6, 16.1, 18.3	64
71 	C_s	10.53 (ω_A-π_{CN}), 11.47 (ω_S-π_{CN}), 12.33 (π_{CN}+ω_S), 12.77 (n_N), 13.72, 14.32	102
72 	C_s	9.41 (8a', n_N), 10.65 (4a'', ω_A), 11.41 (7a', ω_S), 12.86 (π_{CH2}), 13.69 (σ), 15.59, 16.91	53
73 	C_{3v}	8.44 (n_N), 9.95, 10.52, 10.82, 11.8, 13.0, 14.7, 15.3, 16.3	169
74 	(C_s)	8.39 (n_N), 9.9, 10.5, 11.3, 12.7, 14.4, 15.6, 16.4	169

Table 1 (Continued)

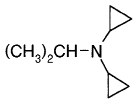
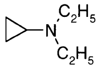
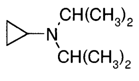
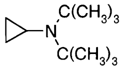
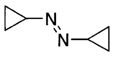
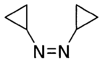
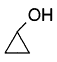
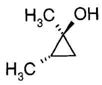
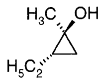
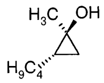
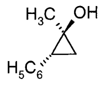
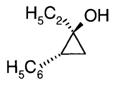
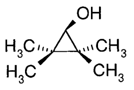
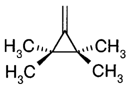
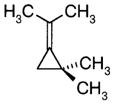
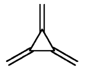
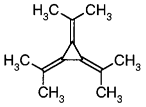
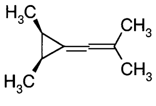
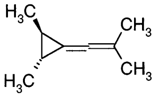
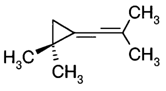
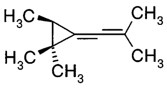
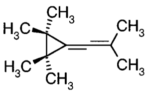
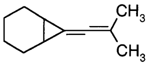
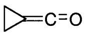
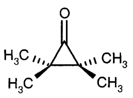
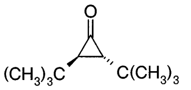
Compound	Symmetry	IP_v	Ref.
75 	(C_s)	8.14 (n_N)	169
76 	(C_s)	8.23 (n_N), 10.13, 10.78, 10.7, 12.7, 14.1, 15.1, 16.1, 18.1, 19.2	169
77 	(C_s)	7.79 (n_N), 9.97, 10.7, 11.3, 12.6	169
78 	(C_s)	7.76 (n_N), 9.9, 10.6, 11.2, 12.7, 14.4, 15.6, 16.4	169
79 	C_i	8.84 (n_N), 9.57, 10.84	189
80 	C_2	8.47 (n_N), 10.02, 10.60	189
81 	C_1	10.24 (12a, ω_S-n_π(O)], 10.85 [11a, ω_A-n_σ(O)], 12.44 (10a, π_{CH2}), 13.10 [9a, n_σ(O)+ω_S], 13.80 [8a, n_σ(O)-π_{CH2}], 15.20 [7a, ω_A+n_σ(O)], 16.45 (6a)	65
82 	C_1	9.58 [ω_S-n_π(O)], 10.21 (ω_A), 11.63 [n_π(O), π_{CH3}]	65
83 	C_1	9.47 [ω_S-n_π(O)], 10.12 (ω_A), 11.46 (π_{CH3}, π_{CH2})	65
84 	C_1	9.37 [ω_S-n_π(O)], 10.08 (ω_A), 11.27 (π_{CH3}, π_{CH2})	65
85 	C_1	8.70 (π_{Ph}), 9.26 (π_{Ph}), 9.85 [ω_S-n_π(O)], 10.44 (ω_A), 11.52 (π_{CH3}, π_{CH2}), 12.08 (π_{CH2})	65
86 	C_1	8.69 (π_{Ph}), 9.28 (π_{Ph}), 9.79 [ω_S-n_π(O)], 10.36 (ω_A), 11.46 (π_{CH3}, π_{CH2}), 12.17 (π_{CH2})	65
87 	C_s	9.00 [ω_S-n_π(O)], 9.60 (ω_A), 11.3 (π_{CH3}), 11.5 [n_π(O), π_{CH3}, ω_S]	65,190
88 	C_{2v}	9.57 ($2b_1$, $\pi_{C=C}$), 10.47 ($3b_2$, ω_A), 11.35 ($5a_1$, ω_S), 13.08 ($1a_2$, π_{CH2}), 14.52 ($2b_2$), 15.75 ($4a_1$, $1b_1$), 17.45 ($3a_1$), 19.72 ($1b_2$), 22.20 ($2a_1$)	4,56,67
89 	C_{2v}	9.22 ($\pi_{C=C}$), 9.44 (ω_S), 9.92 (ω_A), 11.28 (π_{CMe2}), 12.6, 13.4, 14.9, 15.7, 16.6	191
90 	C_s	8.46 ($\pi_{C=C}$), 9.53 (ω_S), 10.20 (ω_A), 11.84 (π_{CMe2}), 12.00, 12.92, 13.32, 15.34, 16.1	191

Table 1 (Continued)

Compound	Symmetry	IP_v	Ref.
 91	D_{3h}	8.94 (1e", $\pi_{C=C}$), 10.7/11.5 (4e', ω_s, ω_A), 13.0 (1a_2", $\pi_{C=C}$), 14.1 (1a_2', π_{CH2})	113
 92	D_{3h}	7.49 (e", $\pi_{C=C}$), 9.71/10.45 (e', ω_s, ω_A), 11.50 (a_2", $\pi_{C=C}$)	114
 93	C_s	8.16 (a", π), 9.00 (a', π), 10.05 (a', ω_S), 11.09 (a"), 11.75	117
 94	C_2	8.13 (a"), 8.98 (a'), 10.10 (a'), 11.08 (a"), ~11.9	117
 95	C_s	8.08 (a"), 8.96 (a'), 10.07 (a'), 11.24 (a"), 11.95	117
 96	C_1	8.00 (π), 8.90 (π), 9.72, 10.96, 11.63	117
 97	C_{2v}	7.87 (b_1), 8.78 (b_2), 9.42 (a_1), 10.78 (b_1), 11.21	117
 98	(C_{2v})	8.01 (b_1), 8.88 (b_2), 9.79 (a_1), 10.84 (b_1), 11.72	117
 99	C_{2v}	8.78 (3b_1, π), 10.7 (3b_2, ω_A-n_O), 11.3, 12.7	121
 100	C_s	9.97 (8a', n_N-ω_A), 10.78 (3a", $\pi_{C=N}$), 12.9 (7a', ω_S), 13.0 (2a", π_{CH2}), 13.5 (6a', n_N+ω_A), 14.5 (1a", π_{CH2}), 16.5 (5a', σ), 18.0 (4a', σ)	120
 101	C_{2v}	9.63 (3b_2, n_O-ω_A), 11.88 (5a_1, ω_S), 12.9 (2b_1, $\pi_{C=O}$; or 1a_2, π_{CH2}), 13.7 (1a_2, π_{CH2}; or 2b_1, $\pi_{C=O}$), 14.4 (2b_2, n_O+ω_A), 15.9 (4a_1), 17.0 (1b_1)	118
 102	C_{2v}	8.2 (n_O), 9.76	191
 103	C_2	8.45 (n_O)	125

[a] Molecular symmetry point group. Vertical ionization energies IP_v (eV) and their orbital assignment.

closely related compounds suggested this. For the labeling of MOs the core orbitals (i.e., 1s orbital except for hydrogen, 2s and 2p for third-row elements, etc.) were neglected and only valence orbitals were taken into account. For the choice of the coordinate system the Mulliken convention[72] was used. Many assignments provided in the original publications were based on MO calculations with methods such as MINDO/3,[21] MNDO,[22] AM1,[23] and PM3,[4] which are notorious for giving too high energies for σ orbitals in comparison with π and n orbitals. For some molecules, PM3 results have been used to visualize the shape of orbitals that have been plotted with a recent version of the program PERGRA.[73]

Table 2. PE Data of Cyclopropene Derivatives[a]

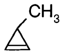
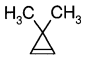
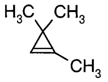
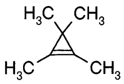
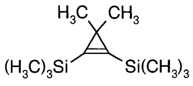
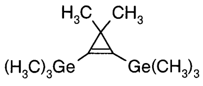
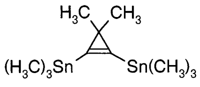
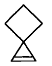
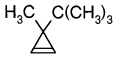
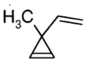
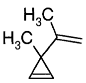
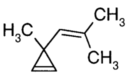
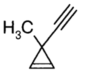
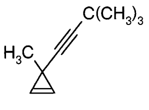
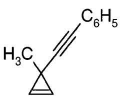
Compound		Symmetry	IP_v	Ref.
1		C_{2v}	9.86 ($2b_1$, $\pi_{C=C}$), 10.89 ($2b_2$, ω_A), 12.7 ($4a_1$, ω_S), 15.09 ($1b_1$, π_{CH2}), 16.68 ($3a_1$, σ_{CH}), 18.3 ($1b_2$, σ_{CH}), 19.6 ($2a_1$, σ_{CH})	53,55,56
2		C_s	9.60 (8a', $\pi_{C=C}$), 10.50 (3a", ω_A)	103,192
3		C_{2v}	9.42 ($4b_2$, $\pi_{C=C}$), 10.02 ($3b_1$, ω_A), 11.60 ($6a_1$, ω_S-π_{CH3}), 12.25 ($3b_2$, π_{CH3}), 13.27, 14.50	79,80
4		C_s	9.00 ($\pi_{C=C}$), 9.63 (ω_A), 11.22 (ω_S-π_{CH3}), 12.10 (π_{CH3}), 13.33, 13.96	79
5		C_{2v}	8.58 ($5b_1$, $\pi_{C=C}$), 9.30 ($5b_2$, ω_A), 10.76 ($8a_1$, ω_S-π_{CH3}), 11.85 ($4b_1$, π_{CH3})	79,193
6		C_{2v}	8.4 ($9b_1$, $\pi_{C=C}$), 8.66 ($10b_2$, ω_A), 10.05 ($13a_1$, $\sigma_{Si\text{-}C}$), 10.1-11.3 ($\sigma_{Si\text{-}C}$), 11.86 ($12a_1$, ω_S)	194
7		C_{2v}	8.15 ($9b_1$, $\pi_{C=C}$), 8.59.($10b_2$, ω_A), 9.66 ($13a_1$, $\sigma_{Ge\text{-}C}$), 9.7-11.0 ($\sigma_{Ge\text{-}C}$), 11.69 ($12a_1$, ω_S)	194
8		C_{2v}	7.88 ($9b_1$, $\pi_{C=C}$), 8.45 ($10b_2$, ω_A), 9.3 ($13a_1$, $\sigma_{Sn\text{-}C}$), 9.4-10.7 ($\sigma_{Sn\text{-}C}$), 11.46 ($12a_1$, ω_S), 12.30 ($7b_1$)	194
9		C_{2v}	9.30 ($\pi_{C=C}$), 9.92 (ω_A), 10.86, 11.53, 12.39 (ω_S), 13.30	79
10		C_s	9.20 ($\pi_{C=C}$+π_{CH3}+π_{tBu}), 9.73 (ω_A-π_{tBu}-π_{CH3}), 10.85 (ω_S-π_{tBu}-π_{CH3}), 11.35 (π_{tBu}-π_{CH3}-ω_A)	108,192
11		C_s	8.18 ($\pi_{C=C(vinyl)}$-ω_A+π_{CH3}), 10.20 ($\pi_{C=C}$+π_{CH3}+ $\pi_{C=C(vinyl)}$), 11.57 (ω_A+ $\pi_{C=C(vinyl)}$-π_{CH3})	91,107–109
12		C_1	7.84 ($\pi_{C=C(vinyl)}$+$\pi_{C=C}$), 10.00 (ω_A), 11.44 ($\pi_{C=C}$+ $\pi_{C=C(vinyl)}$), 11.78, 12.28, 13.02	91,107
13		C_1	8.08 ($\pi_{C=C(vinyl)}$+$\pi_{C=C}$), 10.20 (ω_A), 11.44 ($\pi_{C=C}$+ $\pi_{C=C(vinyl)}$), 12.30, 13.10	91,107
14		C_s	9.19 (4a", ω_A-$\pi_{C\equiv C}$-π_{CH3}), 10.02 (11a', $\pi_{C=C}$-π_{CH3}), 10.37 (10a', $\pi_{C\equiv C}$-ω_S), 11.41 (3a", $\pi_{C\equiv C}$+ω_A+π_{CH3})	108,192
15		C_s	8.60 (ω_A-$\pi_{C\equiv C}$-π_{tBu}+π_{CH3}), 9.13 ($\pi_{C\equiv C}$+$\pi_{C=C}$-ω_S-π_{CH3}- π_{tBu}), 9.74 ($\pi_{C=C}$-$\pi_{C\equiv C}$-π_{tBu}+π_{CH3}), 11.04 ($\pi_{C\equiv C}$+ω_A+π_{tBu}-π_{CH3}), 11.64, 12.48	108,192
16		C_s	8.28 (π_{Ph}), 9.20 ($\pi_{C=C}$), 9.30 (π_{Ph}), 9.90 (σ), 10.44 (ω_A), 11.12	99

Table 2 (Continued)

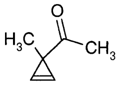
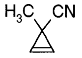
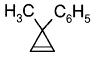
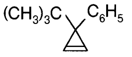
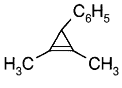
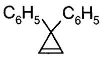
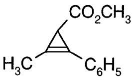
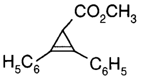
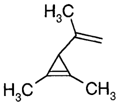
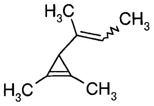
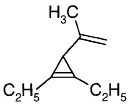
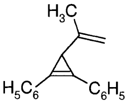
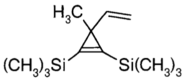
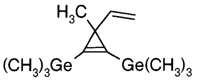
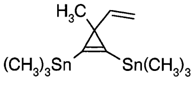
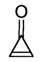
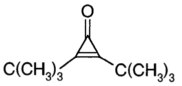
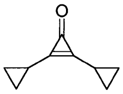
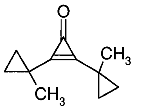
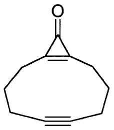
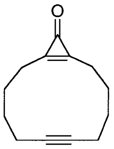
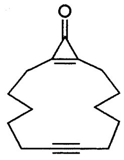
Compound	Symmetry	IP$_v$	Ref.
17 	C_1	8.14 $(\pi_{C=C}-n_O)$, 9.64 (ω_A), 11.52 $(\pi_{C=C}+n_O)$	108
18 	C_s	10.71 $(\pi_{C=C})$, 11.01 (ω_A), 11.78 (π_{CN}), 12.60 (π_{CN}), 13.43 (n_N), 14.55	102
19 	C_s	8.51 $(\pi_{Ph}-\omega_A)$, 9.07 $(\pi_{Ph}-\pi_{C=C}+\pi_{CH3})$, 9.50 $(\pi_{C=C}+\pi_{Ph}+\pi_{CH3})$, 10.40 $(\omega_A+\pi_{Ph}-\pi_{CH3})$, 11.40	108,195,196
20 	C_1	8.76 (π_{Ph}), 9.13 (π_{Ph}), 9.3 $(\pi_{C=C})$, 9.91 (ω_A)	195
21 	C_s	8.17 (π_{Ph}), 8.85 $(\pi_{Ph}, \pi_{C=C})$, 10.32 (ω_A), 11.08, 11.53	195,196
22 	C_{2v}	8.00 $(\pi_{Ph}-\pi_{C=C})$, 9.20 (π_{Ph}), 9.44 $(\pi_{Ph}-\omega_s)$, 10.25 $(\pi_{Ph}+\pi_{C=C})$, 11.0 (ω_A), 12.05	80
23 	C_1	8.28, 9.32, 9.76, 10.60, 11.62	196
24 	C_1	7.82, 9.23, 9.68, 10.63	196
25 	C_s	8.50 (5a", $\omega_A-\pi_{C=C(vinyl)}$), 8.71 $(\omega_A-\pi_{C=C(vinyl)})^{*)}$, 8.93 (17a', $\pi_{C=C}$), 10.6 (4a", $\omega_A+\pi_{C=C(vinyl)}$), 11.16 (16a', ω_S), 12.04 (15a') $^{*)}$second conformer	110
26 	C_s	8.33 $(\omega_A-\pi_{C=C(vinyl)})$, 8.50 $(\omega_A-\pi_{C=C(vinyl)})^{*)}$, 8.76 $(\pi_{C=C})$, 10.38 $(\omega_A+\pi_{C=C(vinyl)})$, 10.88 (ω_S), 11.55 $^{*)}$second conformer	110
27 	C_s	8.10 $(\omega_A-\pi_{C=C(vinyl)})$, 8.44 $(\omega_A-\pi_{C=C(vinyl)})^{*)}$, 8.66 $(\pi_{C=C})$, 10.42 $(\omega_A+\pi_{C=C(vinyl)})$, 11.25 (ω_S), 11.60 $^{*)}$second conformer	110
28 	C_s	7.52 (26a', $\pi_{Ph}-\omega_A$), 8.57 (18a", $\pi_{C=C(vinyl)}$), 9.1 (17a", 25a', π_{Ph}), 9.5 (16a", π_{Ph}), 10.02 (24a', π_{Ph}), 10.59 (15a", $\omega_A+\pi_{Ph}$)	110
29 	C_s	8.1 $(\omega_A-\pi_{C=C(vinyl)})$, 8.9 $(\pi_{C=C})$, 10.0-11.5 $(\sigma_{Si-C}, \omega_A+\pi_{C=C(vinyl)})$, 11.7 (ω_S)	109
30 	C_s	7.9 $(\omega_A-\pi_{C=C(vinyl)})$, 8.6 $(\pi_{C=C})$, 9.5-11.2 $(\sigma_{Ge-C}, \omega_A+\pi_{C=C(vinyl)})$, 11.5 (ω_S)	109
31 	C_s	7.6 $(\omega_A-\pi_{C=C(vinyl)})$, 8.5 $(\pi_{C=C})$, 9.7-11.0 $(\sigma_{Sn-C}, \omega_A+\pi_{C=C(vinyl)})$, 11.6 (ω_S)	109

Table 2 (Continued)

Compound	Symmetry	IP_v	Ref.
32 	C_{2v}	8.41 ($2b_1$, $\pi_{C=C(vinyl)}$), 10.95 ($3b_2$, ω_A), 13.1 ($1b_1$, π; $5a_1$, ω_S), 14.3 ($2b_2$), 15.9 ($4a_1$), 18.1 ($3a_1$)	122
33 	C_{2v}	9.57 ($3b_2$, n_O), 11.19 ($2b_1$, $\pi_{C=C}$), 13.63 ($5a_1$, ω_S), 14.70 ($1b_1$,$\pi_{C=C}$; $2b_2$, ω_A), 16.11 ($4a_1$), 19.35 ($3a_1$, $1b_2$)	124
34 	(C_{2v})	8.36 (n_O), 9.67 ($\pi_{C=C}$)	125,197
35 	(C_{2v})	8.55 (n_O), 9.15 ($\pi_{C=C}$)	197
36 	C_s	8.44 (n_O), 9.04 ($\pi_{C=C}$)	197
37 	C_s	8.42 (n_O), 9.33 ($\pi_{C=C}$-$\pi_{(C\equiv C)i}$), 9.64 ($\pi_{(C\equiv C)o}$), 10.14 ($\pi_{C=C}$+$\pi_{(C\equiv C)i}$), 11.4 (ω)	126
38 		8.45 (n_O), 9.53-9.8 ($\pi_{C=C}$-$\pi_{(C\equiv C)i}$, $\pi_{(C\equiv C)o}$, $\pi_{C=C}$+$\pi_{(C\equiv C)i}$, ω)	126
39 		8.48 (n_O), 9.47-9.69 ($\pi_{(C\equiv C)i}$, $\pi_{C=C}$+$\pi_{(C\equiv C)o}$, $\pi_{C=C}$-$\pi_{(C\equiv C)o}$, ω)	126

[a] Molecular symmetry point group. Vertical ionization energies IP_v (eV) and their orbital assignment.

3.2.1 Monosubstituted Cyclopropanes

The characteristic orbitals of the cyclopropane ring are perturbed by substituents, but in general also in the derivatives there are orbitals that still can be classified as ω_A and ω_S. However, in most cases they are no longer degenerate when the symmetry is lowered from D_{3h} of the parent compound. This applies for all monosubstituted derivatives which have C_s or even no symmetry (point group C_1). With C_s symmetry, there is a symmetry plane bisecting the three-membered ring with C^1 lying in this plane. Accordingly, in such cyclopropane derivatives ω_S can obtain a contribution on C^1 that is directed toward the center of the ring. When internal rotation of the substituent against the cyclopropane ring is possible, the type of interaction can be decisive for the stability of the conformers, and the actual conformation is reflected in the electronic structure. Such interactions of the ω_A and the ω_S orbitals with a $\pi_{C=C}$ and a $\pi^*_{C=C}$ orbital are illustrated in Figure 4.

Depending on the substituent, the effect on the structures and energies of cyclopropane orbitals can be quite large. In general, the influence of a substituent can be ascribed to an inductive effect that is independent of conformational changes, and a conjugative or hyperconjugative effect that varies with conformation. In Figure 5 a correlation diagram is shown for the IPs of a representative number of monosubstituted cyclopropanes. The highest first IP is found for cyanocyclopropane ($IP_1 = 10.91$ eV).[74,75] And of all compounds listed in Table 1 this value is only beaten by those of *cis*- and *trans*-1,2-dicyanocyclopropane (11.34 and 11.45 eV).[64] The nitrile group can thus be identified as the most effective group to stabilize the Walsh orbitals. An even larger effect would be expected for the nitro group; however, no PE spectrum of a nitrocyclopropane seems to be available. On the other hand, the opposite holds for the ethynyl group by which these orbitals are most effectively destabilized. While the effect of the latter substituent can be explained—as we will see—nearly entirely by conjugative interaction, the former group exerts a large inductive effect that is partially compensated by conjugation.

Table 3. PE Data of Polycyclic Cyclopropane and Cyclopropene Compounds[a]

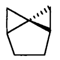
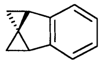
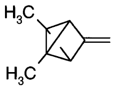
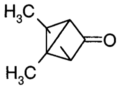
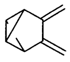
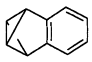
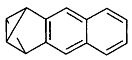
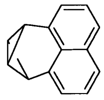
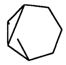
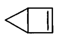
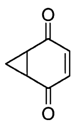
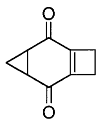
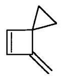
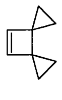
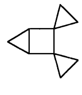
Compound	Symmetry	IP_v	Ref.
1 	D_{2d}	9.73 ($3b_2$), 10.4/10.9 (3e), 12.25 ($1a_2$), 12.85 ($3a_1$), 13.1 ($1b_1$), 15.8/16.0 (2e), 16.2 ($2b_2$)	129
2 	C_2	9.15 (10a), 9.7 (9b), 10.3 (8b), 11.3 (9a), 11.7 (7b), 12.0 (8a), 13.0 (7a)	129
3 	C_2	8.2 (13b, π_{Ph}), 8.8 (14a, π_{Ph}), 9.6 (13a, σ), 10.4 (12b, σ), 10.7 (11b, σ)	129
4 	C_{2v}	9.39 ($7a_1$), 11.30 ($1a_2$), 11.70 ($3b_1$), 12.99 ($4b_2$), 14.51 ($6a_1$), 14.99 ($3b_2$), 17.0 ($5a_1$)	1,198
5 	C_{2v}	8.54 ($9a_1$, σ), 8.96 ($5b_2$, π), 9.53 ($2a_2$, σ), 11.1 ($5b_1$, σ)	199
6 	C_{2v}	9.38 ($9a_1$, σ), 9.6 ($5b_1$, n_O), 10.1 ($2a_2$, σ), 11.17 ($5b_2$, σ)	199
7 	C_{2v}	8.55 ($3b_2$, π), 9.8 ($7a_1$, σ), 10.8 ($1a_2$), 12.2 ($4b_1$)	130
8 	C_{2v}	8.27 ($2a_2$ (π), 9.5 ($9a_1$, σ), 10.0 ($3b_1$, π), 11.2 ($1a_2$, σ), 11.75 ($6b_2$, σ)	131
9 	C_{2v}	8.14 ($4b_2$, π), 8.79 ($2a_2$, π), 9.7 ($11a_1$, σ), 11.1 ($10a_1$)	130
10 	C_{2v}	7.71 ($3a_2$, π), 8.1 ($5b_2$, π), ~9.4 ($15a_1$, σ), 9.7 ($2a_2$, π), 10.2 ($4b_2$, π; $14a_1$)	130
11 	C_{2v}	7.55 ($3a_2$, π), 8.47 ($5b_2$, π), ~8.9 ($14a_1$, σ), ~9.2 ($4b_2$, π), 10.2 ($11b_1$; $2a_2$, π)	130
12 	C_1	8.71	200
13 	C_s	8.6 (9a', π-ω_S), 10.8 (8a', π+ω_S), 11.2 (4a", ω_A), 11.9, 12.6, 14.7	201
14 	C_s	9.64 (9a", n^-), 10.0 (14a', n^+), 10.77 (12a', π), 10.96, 11.2 (13a', ω_S), 11.9 (8a", ω_A)	167
15 	C_s	9.38 (11a", n^-), 9.65 (17a', n^+), 10.0 (16a', π), 11.0 (15a', ω_S)	167
16 	C_s	8.74 (5a"), 9.55 (4a"), 10.46 (13a'), 11.65 (12a'), 12.7 (11a', 3a", 2a"), 13.9 (10a'), 14.5 (9a'), 16.1 (8a', 7a', 6a')	144
17 	C_{2v}	8.73 ($4b_1$), 9.86 ($3a_2$), 10.39 ($6b_2$), 10.7 ($8a_1$), 11.81 ($7a_1$), 12.9 ($3b_1$, $5b_2$, $2b_1$, $4b_2$), 14.1 ($6a_1$), 15.3 ($3b_2$), 16.5 ($5a_1$, $4a_1$, $2b_2$)	144
18 	C_s	8.86 (10a"), 9.2 (14a'), 10.03 (9a"), 10.62 (13a'), 11.5 (12a', 8a"), 12.3 (11a', 7a", 10a', 6a"), 12.9 (9a'), 13.8 (5a", 8a'), 15.2 (7a', 6a', 4a")	144

Table 3 (Continued)

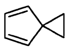
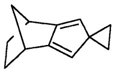
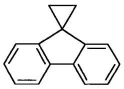
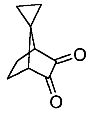
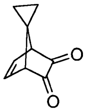
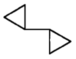
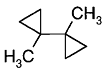
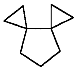
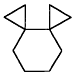
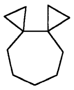
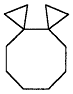
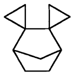
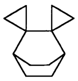
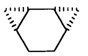
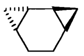
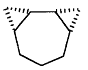
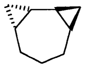
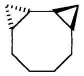
Compound	Symmetry	IP_v	Ref.
19 	C_{2v}	8.14 ($2a_2$, $\pi_{C=C}$), 9.46 ($4b_1$, $\pi_{C=C}$-ω_A), 10.9 ($8a_1$, ω_S), 11.89 ($4b_2$, σ), 12.7 ($3b_1$, ω_A +$\pi_{C=C}$)	187
20 	C_s	7.83 ($\pi_{C=C}^-$), 8.91 ($\pi_{C=C}^+$-ω_A), 10.07 (σ)	202
21 	C_{2v}	7.84 (π)	183
22 	C_s	8.75 (a', n_O^+), 10.7 (a'', n_O^-; a', ω_A), 11.7 (a'', π_{CO}^-)	203
23 	C_s	8.50 (a', n_O^+), 10.20 (a', $\pi_{C=C}$), 10.95 (a'', n_O^-; a', ω_A), 11.7 (a'', π_{CO}^-)	203
24 	C_2	9.5 (9a, ω_A^-), 10.1 (8b, ω_s^-), 11.0 (8a, ω_S^+), 11.7 (7b, ω_A^+)	137,143
25 	C_2	9.3 (12a, ω_A^-), 9.9 (11b, ω_s^-), 10.45 (11a, ω_S^+), 10.9 (10b, ω_A^+)	137
26 	C_2	9.05 (ω_A^-), 10.0	137
27 	C_2	9.2 (ω_A^-), 9.7 (ω_s^-), 10.2 (ω_S^+), 10.8 (ω_A^+)	137
28 	C_2	~9.2, ~9.7	137
29 	C_2	9.1, 9.6	137
30 	C_s	8.76 (ω_A^-), 9.82 (ω_s^-), ~10.3 (ω_S^+), ~10.6 (ω_A^+), 11.02 (σ)	204
31 	C_{2v}	8.67 (ω_A^-), 9.58 (ω_s^-), 9.99 (ω_S^+), 10.61 (ω_A^+), 10.86 (σ)	204
32 	C_s	8.95 (10a'', ω_A^-), 9.66 (12a'), 10.14 (9a''), 11.34 (11a')	137,205
33 	C_2	9.39 (10b, ω_s^-), 9.82 (12a), 10.14 (9b), 11.24 (11a)	137,205
34 	C_s	8.95, 9.70, 10.0	137
35 	C_2	9.00, 9.45, ~10.5	137
36 	C_2	9.10, 9.55, 10.25, 10.60	137

Table 3 (Continued)

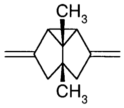
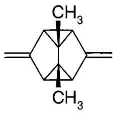
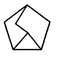
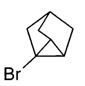
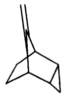
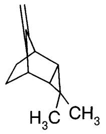
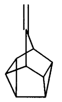
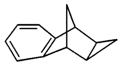
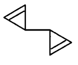
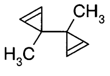
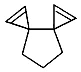
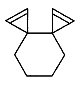
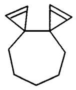
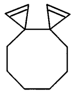
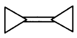
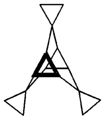
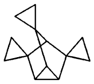
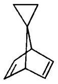
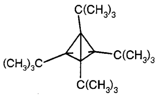
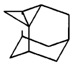
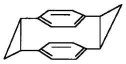
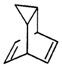
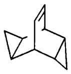
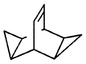
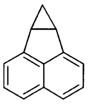
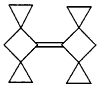
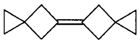
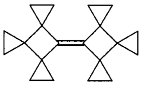
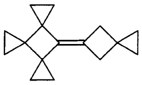
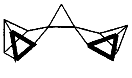
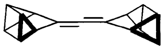
Compound	Symmetry	IP_v	Ref.
 37	C_s	8.36 (a', π^+), 8.77 (a'', π^-), 9.60 (a'', ω)	145,146
 38	C_{2v}	7.89 (a_1, π^+), 8.93 (a_2, ω), 9.15 (b_1, π^-), 9.93 (b_2, ω)	145,146
 39	C_{3v}	9.37/10.03 (6e), 10.95/11.4 (5e), 12.1-12.9 ($6a_1$, 4e, $1a_2$), 14.2 ($5a_1$), 15.1 (3e), 16.94 ($4a_1$), 17.4 (2e)	158,206
 40	C_s	9.22 (8a''), 9.75 (14a'), 10.68 (13a'), 11.3 (7a''), 11.4 (12a'), 11.5 (6a''), 12.4-13.1 (11a', 10a', 5a'', 4a''), 14.33 (9a'), 15.3 (8a'), 15.6 (3a''), 16.6 (7a'), 17.6 (6a'), 18.5 (2a'')	206
 41	C_s	9.10 (π), 9.60 (ω_S), 10.30 (ω_A), 10.65	182
 42	C_s	8.80 (π), 9.30 (ω_S)	207
 43	C_{2v}	9.00 ($7b_2$, π), 9.40 ($3a_2$), 10.00 ($10a_1$), 10.15 ($6b_2$), 10.65 ($6b_1$)	182,208
 44	C_s	8.40 (π_{Ph}), 8.95 (π_{Ph}), 9.57 (ω_S), 10.19 (ω_A)	209
 45	C_{2h}	9.05 ($6a_g$, π^+), 9.70 ($2b_g$, $\omega_A{}^+$), 10.22 ($5b_u$, π^-), 11.46 (6b, $\omega_A{}^+$)$^{*)}$, 12.22 ($5a_g$, $\omega_S{}^+$; $2a_u$, $\omega_A{}^-$), 12.8 (6a, $\omega_S{}^+$)$^{*)}$, 13.0 (5b, $\omega_S{}^-$)$^{*)}$ $^{*)}$sc conformer (C_2 symmetry)	148
 46	C_2	8.84 (11a, π^+), 9.5 (10a, $\omega_A{}^-$), ~10.0 (10b, $\omega_A{}^+$), ~10.3 (9b, π^-), 11.5 (9a, $\omega_S{}^+$), 12.2 (8b, $\omega_S{}^-$)	149
 47	C_2	8.63 (12a, π^+), 9.13 (11a, $\omega_A{}^-$), 9.78 (11b, π^-), 10.51 (10b, $\omega_A{}^+$), 11.4 (10a, $\omega_S{}^+$), 11.7 (9b, $\omega_S{}^-$; 8b, σ)	149
 48	C_2	8.73 (14a, π^+), 9.2 (13a, $\omega_A{}^-$), ~9.7 (12b, $\omega_A{}^+$), ~10.0 (11b, π^-), 10.92 (12a, $\omega_S{}^+$-σ), 11.6 (11a, σ+$\omega_S{}^+$, 10b, $\omega_S{}^-$; 10a, σ)	149
 49	C_2	8.66 (π^+), 9.20 ($\omega_A{}^-$), 9.64 (π^-), ~10.2 ($\omega_A{}^+$), 10.7	149
 50	C_2	8.66 (π^+), 9.14 ($\omega_A{}^-$), ~9.6 ($\omega_A{}^+$), ~10.8 (π^-), 11.2	149
 51	D_{2h}	8.93 ($2b_{1u}$, $\pi_{C=C}$), 9.63 ($2b_{1g}$, $\omega_A{}^-$), 10.58 ($4a_g$, $\omega_S{}^+$), 11.48 ($3b_{2u}$, $\omega_S{}^-$), 12.48 ($2b_{3u}$, $\omega_A{}^+$)	153

Table 3 (Continued)

Compound	Symmetry	IP_v	Ref.
52 	D_{3h}	7.9/8.2 (8e', ω), [10.1, 10.4, 10.9 ($2a'_2$, ω; 5e", ω; $6a_1$, ω; 7e', ω; 4e", ω)], 12.5 (6e', ω)	157
53 	C_{3v}	8.6/9.0 (11e, ω), [9.5, 9.8, 10.2 (10e, ω; $3a_2$, ω)], 10.9 ($9a_1$, ω), 11.3 (9e, ω)	157
54 	C_{2v}	8.37 (b_2, π^--ω_A), 9.26 (a_1, π^--ω_S), 10.05 (b_2, ω_A+π^-), 10.8, 11.1, 12.5	210
55 	T_d	7.50/8.20 (e)	133
56 	D_{3h}	9.74 ($3a_1'$), 11.35 (1e"), 12.60 (3e'), (13.45) ($1a_2'$), 15.7 (16.1) (2e')	134
57 	C_s	7.9 (19a'), 10.0-11.5	136
58 	C_{2h}	7.9 (π, b_u), 8.1, 9.5	166
59 	C_s	8.50 (15a', π), 9.28 (14a', π), 9.70 (13a', ω_S), 10.17 (8a", ω_A)	159
60 	C_s	8.64 (17a', π), 9.3 (16a', ω_S(exo)), 9.7 (9a", $\omega_A{}^+$), 10.1 (8a", $\omega_A{}^-$)	159
61 	C_{2v}	9.0 ($7b_1$, π; $6b_1$, $\omega_s{}^-$, $10a_1$, $\omega_S{}^+$), 9.9 ($6b_2$, $\omega_A{}^+$; $3a_2$, $\omega_A{}^-$)	159
62 	C_{3h}	8.8 (7a', $\omega_S{}^-$), 9.7 (6e'), 10.1 (3e")	159
63 	C_s	7.68 (13a", π), 8.61 (18a', π), 9.12 (17a', ω_S), 10.39 (12a", ω_A)	211
64 	D_{2h}	7.4 (π), 9.0	160
65 	D_{2h}	8.16 (π), 9.5	160
66 	D_{2h}	7.3 (π), 9.0	160,212
67 	C_{2v}	7.6 (π), 9.2	160
68 	C_{2v}	8.4, 9.6, 11.3	213
69 	D_{2d}	7.80, 8.15, 8.95, 9.75, 11.25	213

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[a] Molecular symmetry point group. Vertical ionization energies IP_v (eV) and their orbital assignment.

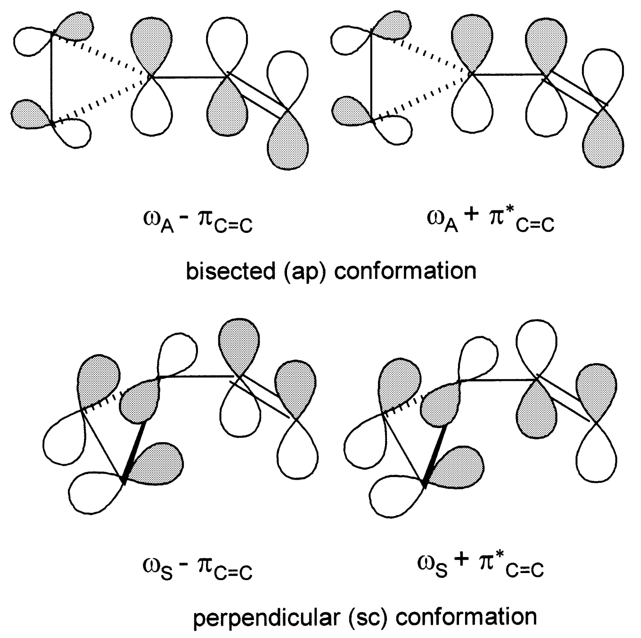


Figure 4. Interactions of the Walsh orbitals ω_A and ω_S with the π and π^* orbitals of a C=C double bond.

As has been outlined by Plemenkov[76] in some detail, the interactions important for the electronic structure of monosubstituted cyclopropanes may be classified in a similar manner as for the FMO description of pericyclic cycloaddition reactions.[77] In X:-substituents a heteroatom such as Hal, O, or N is directly linked to the ring. Here interactions of ω_S and ω_A with n_X orbitals are most important. Alkyl groups behave similarly, and interactions are described using their pseudo π orbitals. All these groups are conjugative electron donors but can be either inductive donors or acceptors. Z-substituents are strong conjugative acceptors; the most important are acyl, nitrile, and nitro groups. And finally, C-substituents are unsaturated groups such as alkenyl, alkynyl, and aryl groups. Compared with the MO energies of alkenes[77] the situation in cyclopropanes is somewhat more complicated because of the intermediate energy of the Walsh orbitals (2e′) so that the substituent's interacting orbital can be higher or lower in energy leading to stabilization or destabilization of ω_A and ω_S.

It seems to be appropriate to study a few examples in more detail. The orbital structures of methyl- and chlorocyclopropane illustrate the interaction of orbitals of the fragments in the molecules of X:-substituted cyclopropanes. Methyl and chloro groups are interesting because they have two degenerate occupied orbitals each as valence orbitals, n_{Cl} in a chlorine atom and π_{CH3} in a methyl group, which provide interaction of these substituents with both 2e′ orbitals. Methylcyclopropane represents an example where the orbitals of the substituent are lower than those of cyclopropane, and with chlorocyclopropane the situation is opposite.

Methylcyclopropane. According to their PE spectra, in methylcyclopropane[78] (**3**) and 1,1-dimethylcyclopropane[79,80] (**4**) the highest occupied orbital (HOMO, ω_A) is destabilized by 0.85 and 1.05 eV, respectively, compared to the initial 2e′ state in cyclopropane (**1**) (Table 1, entries 1, 14, and 15). On the other hand, the second highest occupied orbital (HOMO-1, ω_S) is destabilized in the dimethyl derivative while in the monomethyl compound it has the same energy as in **1**. The separation of the two Walsh orbitals is thus the same ($\Delta IP_\omega = IP(\omega_S) - IP(\omega_A) = 0.8$ eV) for both methyl derivatives. Calculations for these molecules show that their HOMOs correspond to an antibonding combination of ω_A and π_{CH3} with only a small contribution of the orbital fragment of the

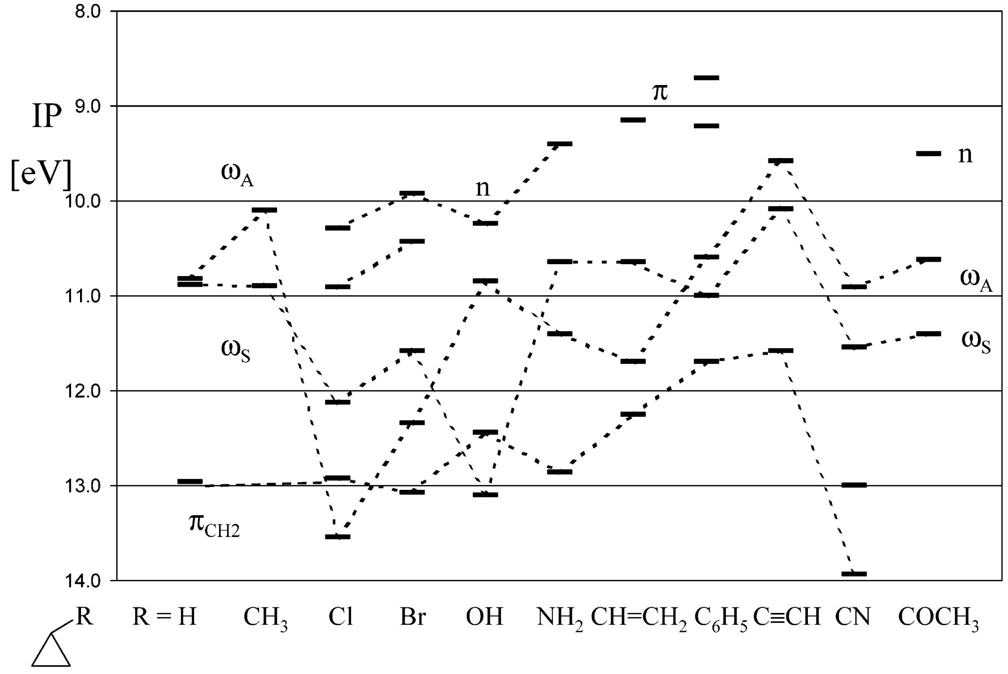
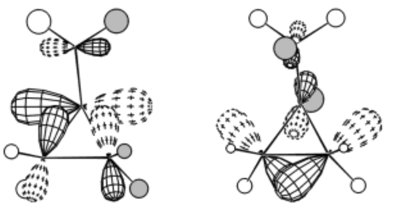


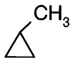
Figure 5. IPs of monosubstituted cyclopropanes.



4a“ (ω_A) 8a‘ (ω_S)

Figure 6. HOMO and HOMO-1 of methylcyclopropane (**3**).

substituent. The two Walsh orbitals of **3** are depicted in Figure 6.[215]



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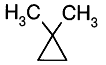
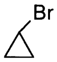


4

Chloro- and Bromocyclopropane. In chlorocyclopropane[64] (**5**; Table 1, entry 2) both Walsh orbitals are stabilized to a large extent relative to their position in **1**, owing to interactions with higher lying n_{Cl} orbitals, and as expected, ω_A is again shifted more than ω_S. This leads to $\Delta IP_\omega = -1.4$ eV, and according to the different interactions of the n_{Cl} orbitals, the first two IPs indicate an energy difference $\Delta IP_{n(Cl)} = 0.6$ eV. As far as the analysis of their PE spectra has been possible until now, it can be concluded that in polychlorocyclopropanes ω_A and ω_S are further stabilized with varying ΔIP_ω values (cf. section 3.2.2).

5



6

The PE spectroscopic data of bromocyclopropane[53,64] (**6**; Table 1, entry 8) and polybromocyclopropanes (see below) show a similar picture of interactions with the 2e′ orbitals of the three-membered ring with the n_{Br} orbitals as for the chloro derivatives, although the effects are less pronounced. For **6** $\Delta IP_\omega = -0.7$ eV and $\Delta IP_{n(Br)} = 0.5$ eV are found.

Cylopropylamine and Cyclopropanol. These compounds differ from the preceding cases in the conformational flexibility of the molecules, and this difference leads to essentially different orbital structures for these isoelectronic molecules. The lone-pair orbitals of both nitrogen (n_N) and oxygen (n_O) are close in energy to the degenerate 2e′ orbitals of cyclopropane. For the corresponding n orbitals the following IP values should be considered: NH_3 (10.85 eV), CH_3NH_2 (9.64 eV), H_2O (12.62 and 14.74 eV), CH_3OH (10.94 and 12.68 eV).[53] Effective interactions are possible by which the energy of the Walsh orbital is lowered and that of the respective n orbital is raised. However, these interactions are destabilizing for the corresponding conformer since only occupied orbitals are involved.[57,58] The destabilization is most effective in case of the ω_A orbital, and this leads to conformations of the molecules in which the n orbital of the heteroatom is orthogonal to ω_A. The PES data for cyclopropylamine[53] (**7**; Table 1, entry 72) and cyclopropanol[65] (**8**; Table 1, entry 81) confirm this picture of the orbital structures: IP_1 of the amine is lower than that of the alcohol, and IP_2 of both molecules is close to the energy of the 2e′ orbital of **1**. The avoided n_N/ω_A interaction is thus the explanation for the fact that the first IP of cyclopropylamine is not significantly lower than that of isopropylamine, as we have seen in the beginning of section 3.2.

antiperiplanar (ap) synclinal (sc)

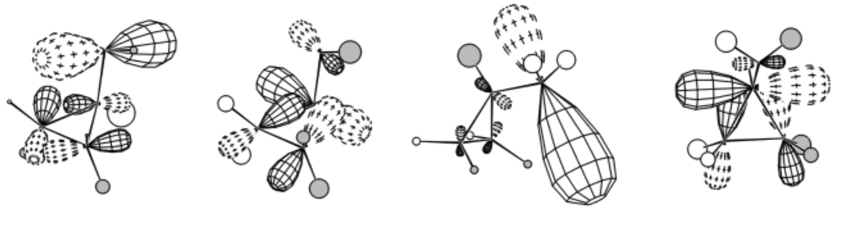
7

antiperiplanar (ap) synclinal (sc)

8

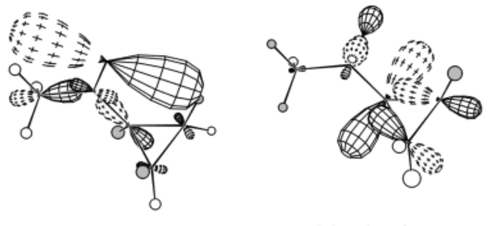
The two highest occupied MOs of cyclopropanol (**7**) and cyclopropylamine (**8**) are depicted in Figure 7. The splitting ΔIP_ω of the two Walsh orbitals amounts to 0.8 eV (**7**) and -0.6 eV (**8**). It is noteworthy that in **8** the above-mentioned n_O/ω_A interaction destabilizes the antiperiplanar (ap) conformation[214] and, therefore, the molecule prefers the synclinal (sc) conformation. However, also in this conformer there is an n_O/ω_A interaction. But now the $n_\sigma(O)$ and not the $n_\pi(O)$ is involved, which is less destabilizing since $n_\sigma(O)$ is energetically farther separated from ω_A. Experimental observations for cyclopropylamine[81] (**7**) and cyclopropanol[82] (**8**) confirm that in the former compound the ap conformation and in the latter the sc form is most stable. For **7**, the second conformer may contribute a few percent to the conformational equilibrium at room temperature.

Acetylcyclopropane. Acetylcyclopropane (cyclopropylmethyl ketone, **9**; Table 1, entry 62) is a derivative of cyclopropane with a conformationally flexible Z-type substituent. Another feature of this substituent is the presence of two lone-pairs on the oxygen atom, of which one has a higher energy than all other occupied orbitals of the carbonyl group. The PE spectrum[66,83] and MO calculations show that as in most carbonyl compounds, n_O is the HOMO. It is delocalized owing to interaction with ω_S of the three-



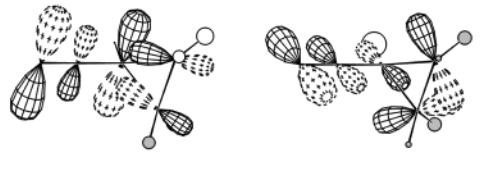
12a (ω_S-n_O) 11a (ω_A) 11a‘ (n_N) 5a“ (ω_A)

Figure 7. HOMO and HOMO-1 of cyclopropanol (**8**) and cyclopropylamine (**7**).



12a (n_O) 11a (ω_A)

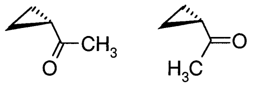
Figure 8. HOMO and HOMO-1 of acetylcyclopropane (**9**).



4a“ (ω_A–$\pi_{C\equiv C}$) 9a‘ (ω_S-$\pi_{C\equiv C}$)

Figure 9. HOMO and HOMO-1 of cyclopropylacetylene (**10**).

membered ring thus resulting in C^1-C^4 bonding. The HOMO-1 corresponds to a practically unperturbed ω_A. These two MOs are shown in Figure 8. ΔIP_ω has a value of 0.8 eV. Conformational analysis of **9** indicates that the predominant rotamer has the bisected synperiplanar (sp) conformation.[84] A second form, having a “near” antiperiplanar (ap) structure, has a larger total dipole moment than the sp form, which accounts for its increased abundance in the liquid compared to that in the gas. The stabilization of the bisected forms can be explained with interaction of ω_A with the unoccupied $\pi^*_{C=O}$ orbital.



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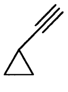
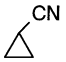
Cyclopropylacetylene. Cyclopropylacetylene (**10**; Table 1, entry 33) is an almost ideal system for the analysis of interactions of the π orbitals of a C-type substituent with the 2e′ orbitals of the three-membered ring. The presence of two mutually orthogonal π orbitals in the acetylene group and conformational rigidity of the molecule favor such interactions. The PE spectrum of **10** has been measured by Bruckmann and Klessinger.[62] Since the acetylene π orbitals (IP = 11.40 eV)[53] are energetically lower (by 0.45 eV) than cyclopropane’s 2e′, they destabilize these orbitals (cf. Figure 5). Therefore, the HOMO and HOMO-1 of **10** are represented by antisymmetrical combinations ($\omega_A-\pi_{C\equiv C}$, $\omega_S-\pi_{C\equiv C}$). By these interactions, ω_A is again more destabilized than ω_S ($\Delta IP_\omega = 0.5$ eV). The orbitals are depicted in Figure 9.



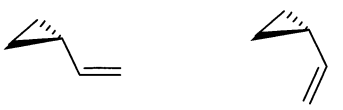
10

Cyanocyclopropane. The nitrile group is a Z-type substituent that is both inductively electron withdrawing and π conjugative. Both effects have been roughly estimated by Houk and Munchausen,[85] and it has been found that the net effect is a lowering of both the HOMO and LUMO energies. The orbital interactions in cyanocyclopropane[74,75] (cyclopropanecarbonitrile, **11**; Table 1, entry 68) are similar to those in the isoelectronic cyclopropylacetylene (**10**). However, the destabilization of the Walsh orbitals is much smaller because the π orbitals of the nitrile group (IP of HCN: 13.60 eV) are lower in energy than those of acetylene (see above). In addition, the negative inductive effect overcompensates the conjugative effect. As a consequence, ω_A and ω_S are both shifted to lower energies by 0.3 and 0.9 eV, respectively, with $\Delta IP_\omega = 0.63$ eV.



11

Alkenylcyclopropanes. The at first glance simple interaction scheme of the olefinic π orbital with the 2e′ system of the cyclopropane ring (cf. Figure 4) is complicated by conformational flexibility of such molecules with C-type substituents. Therefore, this interaction is analyzed more easily in molecules with a fixed orientation of the substituent. This is fulfilled in spiro[2.4]hept-4-ene (**12**), where the C=C double bond has a rigid ap conformation with respect to the ring. This molecular geometry provides effective overlap of the π with the ω_A orbital and its orthogonality to the ω_S orbital. It follows from their PE spectra that in going from cyclopentene (IP = 9.18 eV,[53] its HOMO is much higher in energy than those of cyclopropane and dimethylcyclopropane) to spiro[2.4]hept-4-ene[63] (**12**) the π orbital is destabilized by 0.72 eV. This value may be taken as a measure for the interaction of the alkenyl π orbital with ω_A in a conformation of maximum conjugation, that is, in the ap form. Since the separation of the first three IPs of vinylcyclopropane[63,86,87] (**13**; Table 1, entry 17) and the spiro compound (**12**; Table 1, entry 32) show a quite similar pattern, it can be concluded that the interacting groups are in the same relative positions, i.e., that **13** prefers the ap conformation. This is in accord with theoretical investigations[88] and a structure analysis by gas-phase electron diffraction that revealed a mixture of ap and sc conformers, with the former being the more stable.[89] Structural aspects of cyclopropyl conjugation have been studied by X-ray crystal structure analysis.[90] By additional substituents, the ap conformer can be destabilized so that the sc form predominates.[91] HOMO and HOMO-1 of **13** are depicted in Figure 10. From the IP values related to the orbitals with the greatest ω_S and ω_A character (IP_2, IP_3), $\Delta IP_\omega = -1.05$ eV is obtained for **13**.



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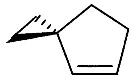

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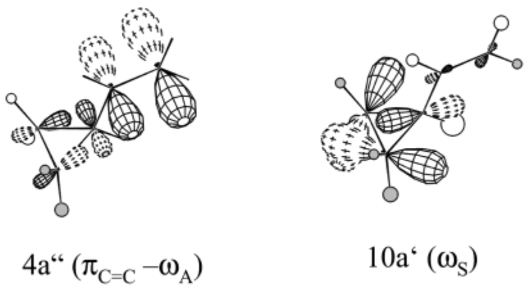
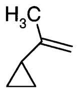

4a“ ($\pi_{C=C}$ −ω_A) 10a‘ (ω_S)

Figure 10. HOMO and HOMO-1 of vinylcyclopropane (**13**).

With a second substituents on C^1 of the C═C double bond, the energy of the two bisected conformers is modified and the sc form will be favored, as is probably the case in the methyl (**14**; Table 1, entry 18) and the phenyl derivative (**15**; Table 1, entry 19) that have been studied by PE spectroscopy.[92,93]



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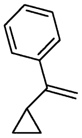
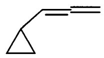


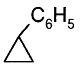
15

Cyclopropylallenes. Cyclopropylallene[1] (**16**) and a number of alkyl derivatives[92] (Table 1, entries 43−49) have been investigated. These compounds show essentially the same interaction between the cyclopropane ring and the adjacent double bond as in vinylcyclopropane, but nearly no interaction with the nonadjacent double bond.



16

Phenylcyclopropane. Arylcyclopropanes behave quite similarly to alkenylcyclopropanes since both have C-type substituents. The two highest occupied orbitals of phenylcyclopropanes are always dominated by the π orbitals of the phenyl group, with the main contribution of the b_1 orbital to the HOMO, while the next occupied orbital (HOMO-1) has nearly pure π (a_2) character. From the PE spectra of phenylcyclopropane[63,94] (**17**) and l-methyl-l-phenylcyclopropane[80,95] (**18**), it is actually seen that their IP_1 differs from that of benzene ($IP_1 = 9.25$ eV)[53] by about 0.5 eV, while their IP_2 remains unchanged. IP_3 of **17** is assigned to a nearly unperturbed ω_A orbital, and IP_4 to a stabilized ω_S. From the data (Table 1, entries 54 and 55), $\Delta IP_\omega = -0.4$ eV is obtained for this compound and $\Delta IP_\omega = -0.6$ eV for the methyl derivative.



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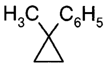

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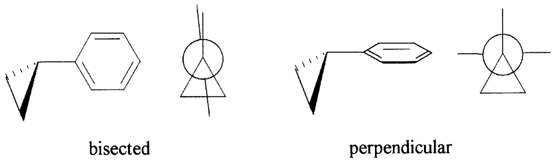
Structure analyses by different methods and quantum-chemical calculations have shown that phenylcyclopropane (**17**) has its global minimum in the bisected conformation.[96] In l-alkyl-substituted 1-phenylcyclopropanes such as **18** the global minimum corresponds to the perpendicular form.[95] The IP_1 values of the compounds are in accord with these findings. In the former molecule, the HOMO is obtained by mixing π (b_1) with ω_A, in the latter by mixing it with ω_S.



17

The bisected form of **17** maximizes the donor−acceptor interaction between the HOMO of the cyclopropyl group and the LUMO of the phenyl π system. The consequence of this interaction (donation of electron density from the cyclopropyl group to the π system) is the lengthening of the vicinal C−C bonds relative to the distal C−C bond in the three-membered ring.[57] The perpendicular conformation of **17** would enhance the interactions of the cyclopropyl LUMO and the HOMO of the π system and result in the donation of electron density from the π system to the cyclopropyl group, which incidentally is a weak π acceptor.

Conclusion. In the preceding sections we have considered ΔIP_ω values as a measure of a substituent’s effect on the electronic structure of the cyclopropane ring. These values cover a range from −1.42 eV (Cl) to +2.25 eV (OH). It seems, however, to be unlikely that a simple relation might exist between ΔIP_ω and an electronic substituent parameter like σ_R or σ_I,[97] because different interaction types are involved in the individual compounds, as we have seem in the examples.[216]

With regard to conformational preferences, it can be concluded that in X:-substituted cyclopropanes such rotamers are favored in which n_X/ω_A interaction is avoided. Typical examples are cyclopropanol (**8**, sc) and cyclopropylamine (**7**, ap). In simple C- and Z-substituted cyclopropanes, bisected conformers prevail because the destabilizing π/ω_A interaction is overcompensated by stabilizing π^*/ω_A interaction. This is the case in vinyl- (**13**) and phenyl-cyclopropane (**17**) and in acetylcyclopropane (**9**). Steric effects may prevent conformers with maximal electronic stabilization.

3.2.2 Polysubstituted Cyclopropanes

The effect of several substituents on the characteristic cyclopropane orbitals (ω_A, ω_S) should be expected to be additive if no mutual distortions between substituents occur. Such interactions can for example be sterical, inducing conformational changes and thus alter conjugative contributions. But also direct electronic interchange between substituents is possible. Since a three-membered ring is a small molecular unity, such interactions generally cannot be excluded. In addition, it is not uncommon that PE spectra of polysubstituted cyclopropanes are too complex to assign IP values to the relevant orbitals with high confidence.

Alkylcyclopropanes. Apparently, there are no PE data except for the two methylcyclopropanes (**3**[78] and **4**[79,80]) mentioned in section 3.2.1, and for the former compound only the first two IPs are known (Table 1, entries 14 and 15).

Halogenocyclopropanes. A literature search did not reveal PE spectra of simple fluorocyclopropanes. The only spectra of fluorocyclopropane derivatives are those in which a CF_2 group is present in cyclopropabenzene, -naphthalene, and -anthracene[98] (see section 3.6). Only a few PE spectra of simple chloro- and bromocyclopropanes could be found in the literature. However, spectra of several more compounds were measured.[64] The data of these compounds are summarized in Table 1 (entries 2−13). The spectra are dominated by strong ionizations of electrons from the halogens. The first IP of all chloro derivatives has a rather constant value of 10.22−10.32 eV. The same holds for the bromo derivatives (IP_1: 9.90−9.94 eV) and the iodo derivatives (IP_1: 9.13−9.15 eV).

As examples the PE spectra of *cis*-1,2,3-trichloro- (**19**) and *cis*-1,2,3-tribromocyclopropane (**20**) are depicted in Figure 11. The spectrum of the trichloro compound **19** exhibits a remarkable and astonishing feature: the ionization band centered at 16.18 eV shows vibrational fine structure in which about eight peaks, separated by 0.07 eV (≈ 550 cm^{-1}), are discernible. This frequency corresponds most likely to a C−Cl stretching vibration of the radical cation, and accordingly this ionization is assigned to $4a_1$ which is mainly C−Cl bonding. In the *cis*-1,2,3-tribromo compound **20** the corresponding ionization is observed at 15.45 eV, but the vibrational transitions do not appear as separate peaks but as shoulders on the envelope band. The corresponding frequency is about 400 cm^{-1} and is assigned to a C−Br stretching vibration. A similar feature is not found in the spectra of other halogenocyclopropanes so that it seems to be likely that C_{3v} symmetry is essential for this phenomenon.

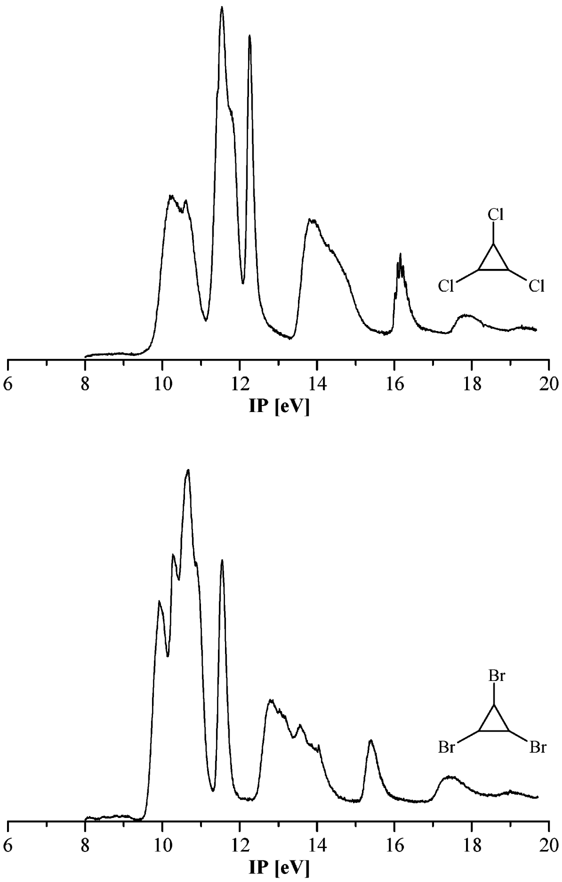
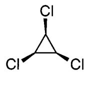


Figure 11. PE spectra of *cis*-trichloro- (**19**) and *cis*-1,2,3-tribromocyclopropane (**20**).



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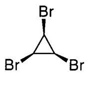

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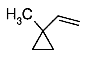
1,1-Disubstituted Cyclopropanes. A series of methyl-substituted vinylcyclopropanes (Table 1, entries 20−22) have been studied by Plemenkov et al.[91] From the smaller separation of the first IPs, it was concluded that these compounds have orthogonal (sc) and not ap conformations as the parent compound (**13**, see above).



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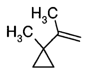

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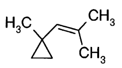

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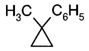

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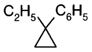

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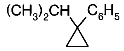

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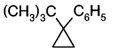

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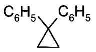

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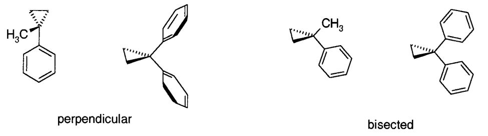
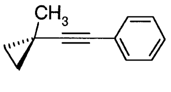


Also phenylcyclopropanes with a geminal substituent such as **18**, **24**−**27** (Table 1, entries 55−59) cannot adopt the favorable bisected conformation. This has been shown for a number of compounds.[95] In the diphenyl derivative[80] (**27**) both aromatic rings occupy a perpendicular orientation. If, however, the phenyl group is moved farther away from the cyclopropyl ring without removing the conjugation by placing a C≡C triple bond between the two groups, then the bisected conformation remains the most stable. This has been shown by Plemenkov et al.[99] for 1-methyl-1-(phenylethynyl)-cyclopropane (**28**; Table 1, entry 34).



28

PE spectra of several geminal alkenyl- and alkynyl-disubstituted cyclopropane derivatives (**29**−**36**) have been investigated by Eckert-Maksic, Gleiter, and co-workers.[100] The observed IP values are included in Table 1 (entries 28−40). Changes in the ionization pattern on going from **29** to **30** can be

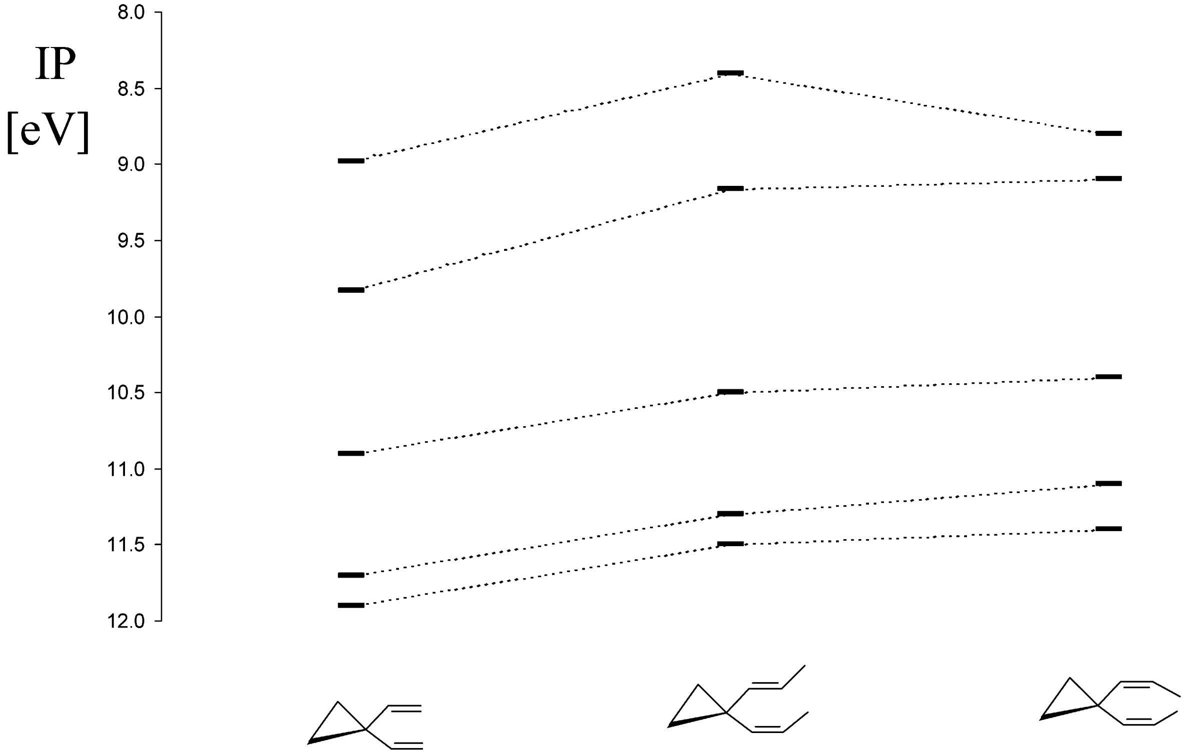
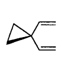
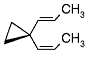


Figure 12. Correlation between the observed first five ionization energies in the series **29**−**31**.

rationalized in terms of the electron donating capability of the methyl groups. On the other hand, changes in the ionization energies on passing from **29** to **31** can be understood only by taking into account additional factors. The fact that the PE spectra of **29** and **30** are somewhat better resolved than that of **31** indicates that the structure of the latter molecule is less rigid. Moreover, significant reduction of the energy gap between bands related to ionization from the $\pi_{C=C}{}^{+}/\omega_A$ mixed MOs (Figure 12) leads to the conclusion that the propenyl groups in **31** are displaced out of the symmetry plane passing through C^1 and bisecting the C^2-C^3 bond of the cyclopropyl ring.



29



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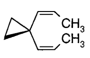

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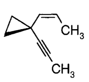

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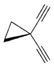

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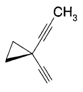

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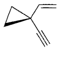
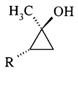


35

36

Alkyl- and Aryl-Substituted Cyclopropanols. Besides the parent cyclopropanol (**8**, see section 3.2.1), several alkyl- and phenyl-substituted derivatives (**37**−**42**) have been investigated.[65] The relevant data are summarized in Table 1 (entries 81−87). These compounds offer the possibility to study the combined effect of several substituents on the electronic structure of cyclopropanes. It has, however, to be taken into account that already **8** has no symmetry and the unsymmetrical substitution pattern in most of the derivatives renders the distinction of ω_A and ω_S more or less arbitrary. In all compounds, except for those with phenyl groups (**40**, **41**), two orbitals with high ω_S and ω_A character are the HOMO and the HOMO-1, respectively. Both orbitals are affected nearly quantitatively in the same way by the additional substituents. The energy difference $\Delta IP_\omega = IP(\omega_S) - IP(\omega_A)$ varies only between −0.51 and −0.65 eV. This indicates that the splitting of the two Walsh orbitals is caused nearly exclusively by the interaction of ω_S with $n_\pi(O)$ as in the unsubstituted cyclopropanol (**8**) and that in all derivatives the hydroxy group must have rather the same sc orientation. A comparison of the IP data for **8** and those for its methyl derivatives **37** and **42** indicates that the destabilizing effect of the methyl groups on the two highest occupied MOs is additive (0.31−0.33 eV per CH_3 group). Substitution of a methyl group by an ethyl or butyl group (compounds **37**−**39**, or **40** and **41**) has a much smaller effect. This additivity of the substituent effects on the energies of the two Walsh MOs is an indication that compounds **8**−**42** have the same configurations and also rather similar conformations.



R = CH_3, C_2H_5, C_4H_9

37 38 39

The phenyl group on C^2 (**40**, **41**) induces a stabilization of both Walsh orbitals by about 0.2 eV. It is remarkable that in these compounds the first two IPs, which are related to the aromatic π electrons, are very close to their values in cyclopropylbenzene (**17**) indicating that also in the cyclopropanols **40** and

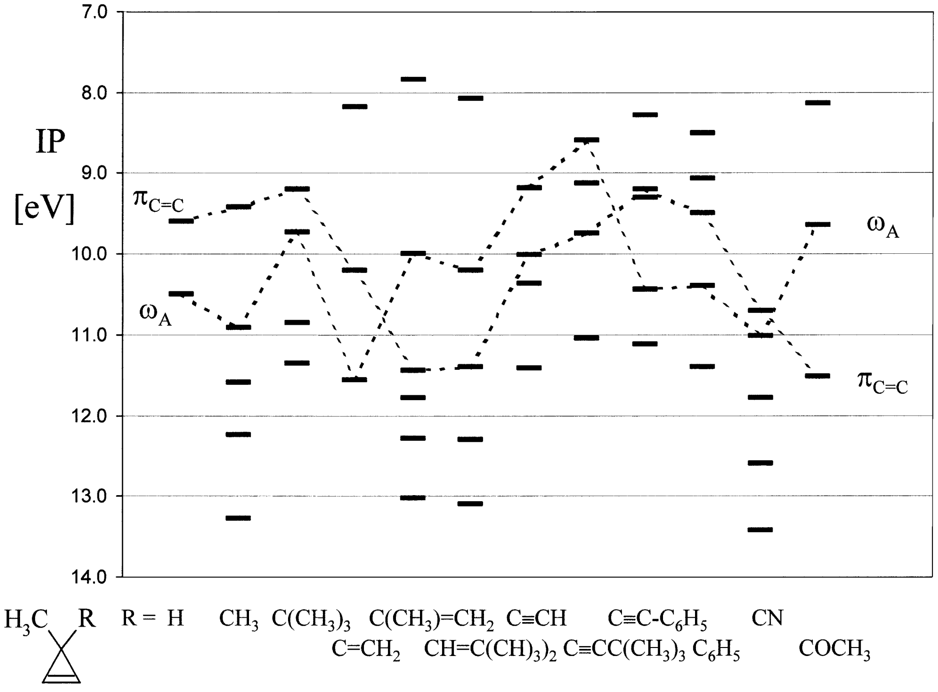
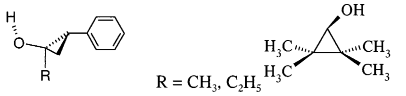


Figure 13. IPs of 3-substituted 3-methylcyclopropenes.

41 the phenyl groups occupy the bisected conformation.



40 **41** **42**

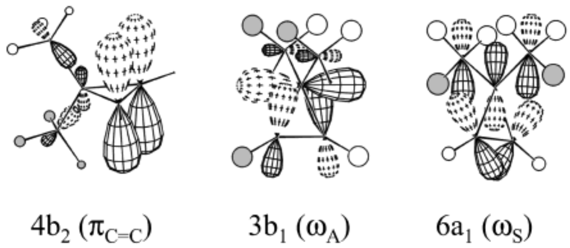
Conclusion. Valuable information can be obtained by comparing spectra of closely related molecules. As we have seen for cyclopropanols, inspection of the data may provide, probably only in fortunate cases, indication of conformational properties even for more than one substituent.

With respect to spectroscopic and structural effects, cyclopropane derivatives with exceptional high- or low-lying Walsh orbitals (ω_A, ω_S) would be of great interest. As an example, 1,1-dicyanocyclopropane is mentioned. This compound should have a rather high IP_1, short vicinal and a long distal C−C bond length (cf. ref 101), in accordance with its high reactivity in nucleophilic ring-opening reactions. To our knowledge, a PE spectrum of this compound has not been reported. Also the effect of fluoro atoms on the energy of the Walsh orbitals remains to be investigated. Considering the vast number of known PE spectra of rather complex cyclopropane compounds, it is surprising that many "simple" derivatives that are even commercially available, e.g., cyclopropanecarbaldehyde and cyclopropanecarboxylic acid, have not yet been studied by PES.[216]

3.3 Derivatives of cyclopropene

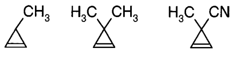
3.3.1 3,3-Disubstituted Cyclopropenes

It is not possible to discuss the PE data of "simple" substituted cyclopropenes in a similar way as those of cyclopropanes (section 3.2.1) since the database is much more limited (Table 2). The largest series seems to be that of 3-substituted 3-methylcyclopropenes. The IP values of such compounds are visualized in Figure 13. Only for the $\pi_{C=C}$ and the ω_A ionizations of the three-membered ring there are rather safe assignments for nearly all members of the series. Both orbitals are shifted appreciably. The energy of $\pi_{C=C}$ varies by about 2.3 eV and that of ω_A by about 3.0 eV. As has already been observed for cyclopropane derivatives, also for the cyclopropenes the nitrile group is most efficient in increasing the IP values. IP_1 of 3-cyano-3-methylcyclopropene (**43**) has a value of 10.71 eV[102] that is 1.0 eV larger than that of 3-methylcyclopropene (**44**).[103] Also the second observation made for cyclopropane derivatives seems to apply for the unsaturated compounds: The $\pi_{C=C}$ orbital of the ring is most effectively destabilized by an ethynyl group. As an example for the interplay of ring- and substituent-orbitals, the three characteristic MOs of 3,3-dimethylcyclopropene (**45**) are depicted in Figure 14.



$4b_2$ ($\pi_{C=C}$) $3b_1$ (ω_A) $6a_1$ (ω_S)

Figure 14. Three MOs of 3,3-dimethylcyclopropene (**45**).



44 **45** **43**

As for cyclopropanes, interactions of the cyclopropene orbitals with substituent orbitals can be con-

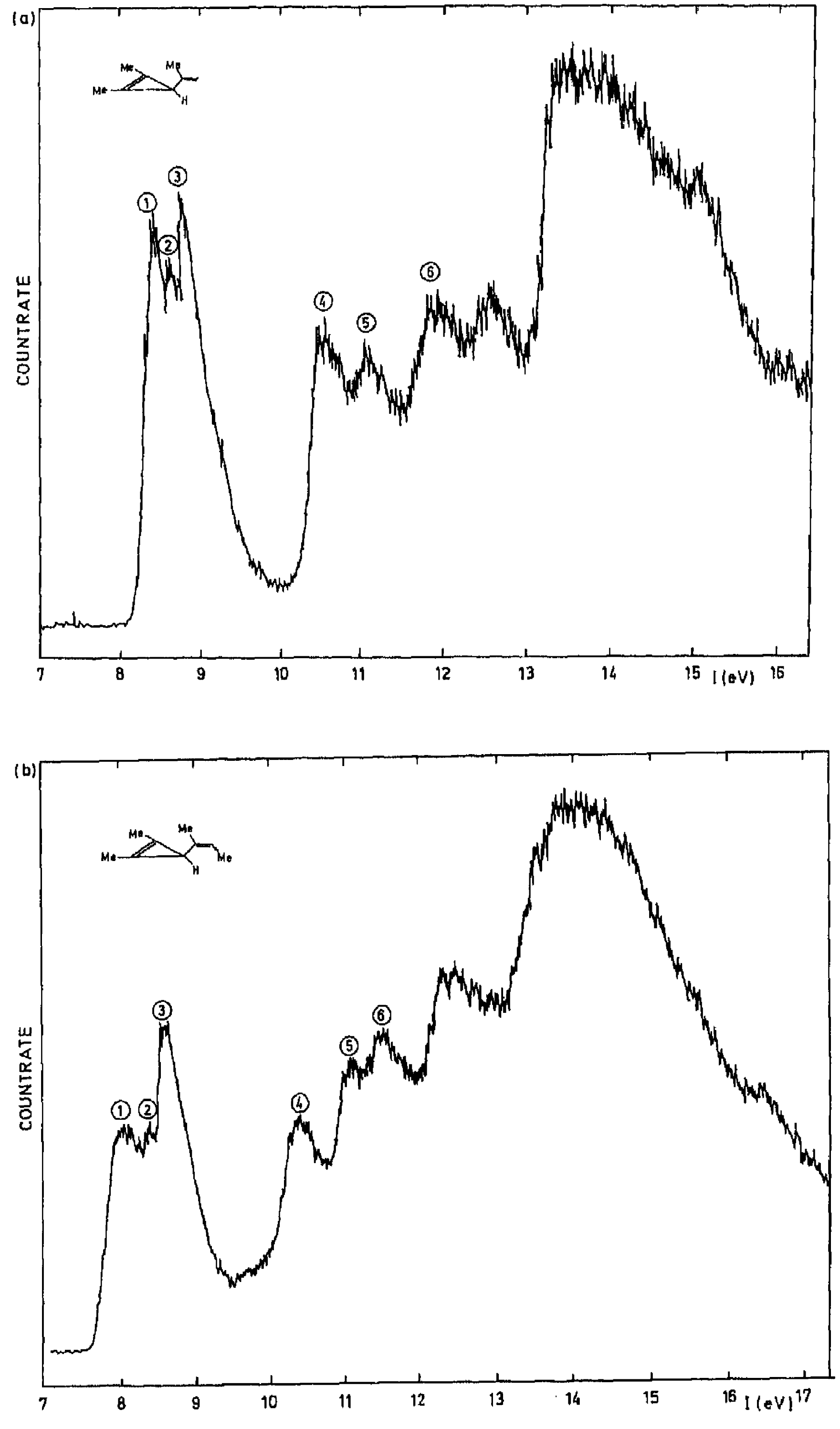


Figure 15. PE spectra of 1,2-dimethyl-3-isopropenylcyclopropene (**48**) and 1,2-dimethyl-3-(1-methyl-propenyl)-cyclopropene (**49**). Reprinted with permission from ref 110. Copyright 1996 The Croatian Chemical Society.

formation dependent. A few examples will be outlined briefly.

3.3.2 3-Alkenylcyclopropenes

3-Vinylcyclopropene (**46**), the simplest representative of the compounds considered here, has an antiperiplanar (ap) conformation.[104] Similar to vinylcyclopropane (**13**, see above), also for this compound a second conformer (sp or sc) is possible that will gain increasing importance with the size of substituents R, in particular on C^3 and C^{α}. For 3-methyl-3-vinylcyclopropene (**47**), a 3:1-mixture of ap and sc conformers has been determined by gas-phase electron diffraction.[105] This result is supported by Raman spectroscopic measurements and ab initio calculations.[106] A PE spectrum of the parent compound **46** is not available, but spectra of a number of derivatives most of which with a geminal second substituent have been studied.[91,107–110] The ionization potentials of these compounds and their assign-

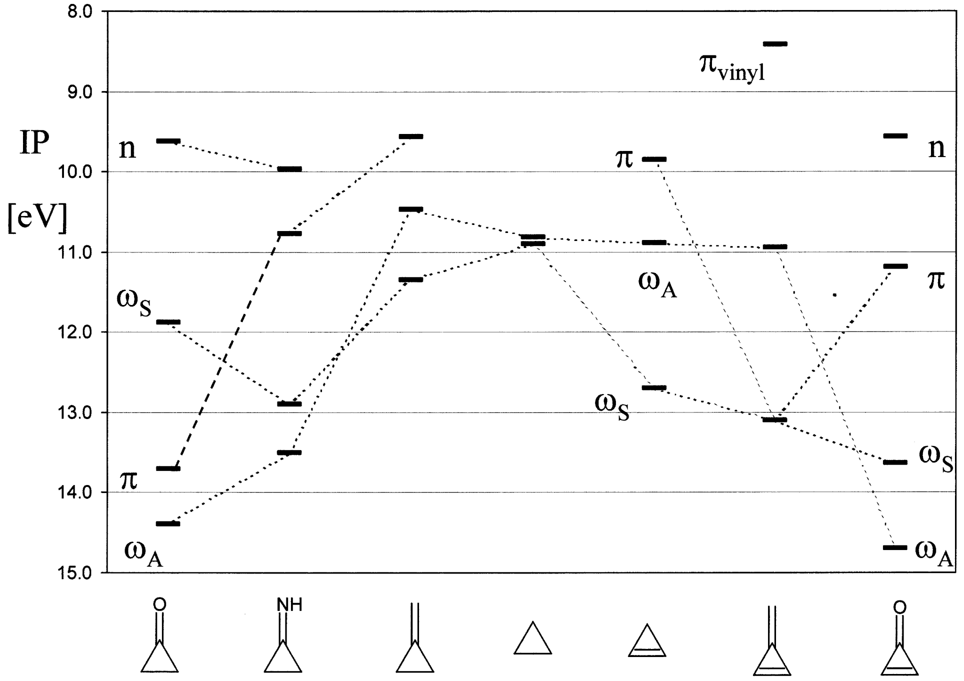
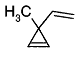
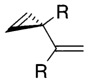


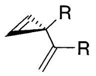
Figure 16. IP correlation diagram for the compounds cyclopropanone (**53**) to cyclopropenone (**58**).

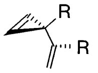
ments are included in Table 2 (entries 11−13).


46

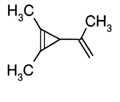

47

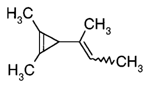

antiperiplanar (ap)

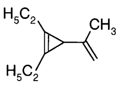

synperiplanar (sp)

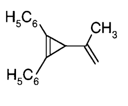

synclinal (sc)

Eckert-Maksic et al.[110] have investigated the electronic and molecular structures of a series of 1,2-dialkyl-3-isopropenylcyclopropenes (**48**−**50**) and of 1,2-diphenyl-3-isopropenylcyclopropene (**51**) by means of PE spectroscopy and ab initio MO calculations (Table 2, entries 25−28). The spectra of compounds **48** and **49** are depicted in Figure 15. The authors have interpreted the changes in the first ionization potential in terms of a conformation-dependent conjugative interaction between the alkenyl group and the cyclopropenyl ring.


48


49


50


51

In the PE spectra of **48**−**50**, there are clear indications for a mixture of two conformers in one of which the alkenyl substituent deviates significantly from the plane bisecting the cyclopropene ring indicating the sc form. The second band in the spectra is tentatively assigned to this second conformer.

3.3.3 Conclusion

The characteristic orbitals of the cyclopropene ring ($\pi_{C=C}$, ω_A, ω_S) are strongly modified by substituents. In derivatives with "simple" substituents that exert mainly inductive effects, these orbitals remain the three highest occupied MOs as in the parent compound. Stronger changes of electronic structure are induced by conjugative interactions with unsaturated groups that vary with conformation.

3.4 Cyclopropanes and Cyclopropenes with Exocyclic Double Bonds

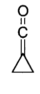
Methylenecyclopropane (**52**) and its isoelectronic congeners cyclopropanone (**53**) and cyclopropylidenamine (**54**), as well as ethenylidenecyclopropane (**55**) and cyclopropylidene-methanone (**56**), together with corresponding derivatives of cyclopropene (**57**, **58**), constitute an interesting series of important compounds, first of all because of their unusual electronic and geometric structures but also because of their exceptional chemical properties which deviate substantially from those of larger homologues.[111] The IP values of these and some related compounds and their assignments are summarized in Table 1 (entries 88−103) and Table 2 (entries 32−39).


52


53


54


55


56

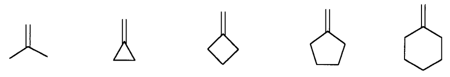

57


58

In Figure 16 a correlation diagram of the characteristic IPs is shown for these compounds together with the parent compounds cyclopropane (**1**) and cyclopropene (**2**). The close similarity of most IPs of **53** and **58** is evident. Because of the importance of these compounds with unique structural features their spectra as well as those of related compounds are discussed in some detail in the following sections.

3.4.1 Methylenecyclopropane

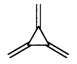
The PE spectrum of methylenecyclopropane (**52**) was investigated by Turner et al.[4] and by Wiberg et al.[56] IP_1 is assigned to ionization from the MO $2b_1$ which shows largely $\pi_{C=C}$ character. The following data of related molecules indicate an unexpectedly high value of this IP for **52**.



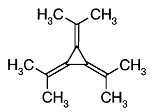
9.45 eV[53] 9.57 eV[56] 9.35eV[56] 9.14 eV[56] 9.13 eV[112]

3.4.2 Trimethylenecyclopropane

Trimethylenecyclopropane (**59**) is the simplest radialene. It is isomeric with benzene and extremely unstable, but has three essential single and double bonds, the latter are completely cross-conjugated. This intriguing feature is also present in its more stable hexamethyl derivative (**60**). The PE spectra of **59**[113] and **60**[114] have been investigated by Bally and Haselbach (Table 1, entries 91 and 92). Because of the D_{3h} symmetry of the molecules, several ionizations bands show Jahn–Teller splitting. A Green's function ab initio study of the outer valence IPs which confirmed original assignments was published by Galasso.[115,116]



59



60

3.4.3 Alkylidenecyclopropanes

In alkylidenecyclopropanes such as ethenylidenecyclopropane (**55**) and a number of its substitution products (Table 1, entries 93–98) only a small interaction between the π system and the three-membered ring is observed.[117]

3.4.4 Cyclopropanone, Cyclopropylidenamine, and Cyclopropylidene-Methanone

Cyclopropanone (**53**; Table 1, entry 101) was investigated by Martino et al.[118] The PE spectrum (Figure 17) shows an isolated band centered at 9.63 eV and a series of strongly overlapping bands above 11.5 eV. The authors have analyzed the spectrum making use of ab initio and MINDO/3 calculations, which resulted in the same interpretation of the first two IPs (IP_1: $3b_2$, n_O; IP_2: $5a_1$, ω_S) but opposite assignments of IP_3 and IP_4 to either $2b_1$ ($\pi_{C=O}$) or $1a_2$ (π_{CH2}). PM3 calculations support the MINDO/3 results, and we have used this assignment in Figure 16, although we cannot decide this question here. The first band does not show the appearance for the ionization of a nonbonding MO. This indicates that the n_O orbital is highly delocalized, which is the result of an interaction between the in-plane p orbital on oxygen and an antibonding Walsh orbital of the ring.

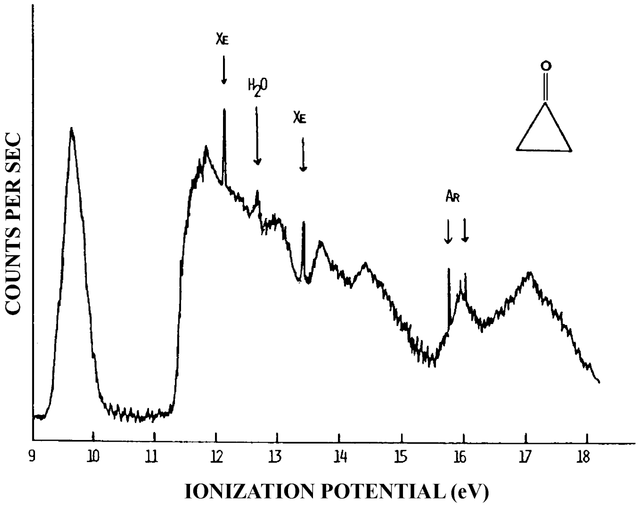
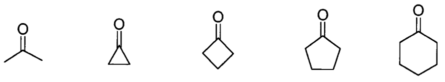


Figure 17. PE spectrum of cyclopropanone (**53**). Reprinted with permission from ref 118. Copyright 1977 American Chemical Society.

The influence of ring size on the first IP is demonstrated by the following data:



9.70 eV[53] 9.63 eV[118] 9.61 eV[119] 9.25 eV[119] 9.29 eV[112]

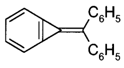
The series resembles that of the methylenecycloalkanes (see above), although the value of the cyclopropane compound is not so exceptional. Alkyl groups as substituents on C^2 and C^3 lower the first IP considerably (Table 1, entries 102–103).

The unstable cyclopropylidenamine (**54**) has been prepared by Bock and Dammel[120] in a gas-phase reaction and the PE spectrum has been recorded in situ (Table 1, entry 100). From Figure 16, it is evident that in **53** and **54** the Walsh orbital ω_A is considerably stabilized in comparison with the isoelectronic methylene compound **52**. This is caused by interaction with the lone-pairs orbitals (n_N and $n_\pi(O)$, respectively) in **53** and **54**. That ω_S is 1 eV lower in the imine (**54**) than in the ketone (**53**) is a result of the interaction of this orbital in the latter compound with the second oxygen lone-pair orbital ($n_\sigma(O)$).

The ketene cyclopropylidene-methanone (**56**; Table 1, entry 99) was generated by pyrolysis of a precursor and its PE spectrum was recorded together with that of a side product.[121]

3.4.5 Methylenecyclopropene

The PE spectrum of methylenecyclopropene (**57**; Table 2, entry 32), the smallest nonalternant hydrocarbon and fulvene, has been investigated by Staley and Norden.[122] The spectrum is depicted in Figure 18. It shows six major bands, the first exhibits vibrational progression (1590–1370 cm^{-1}) with positive anharmonicity.



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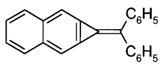

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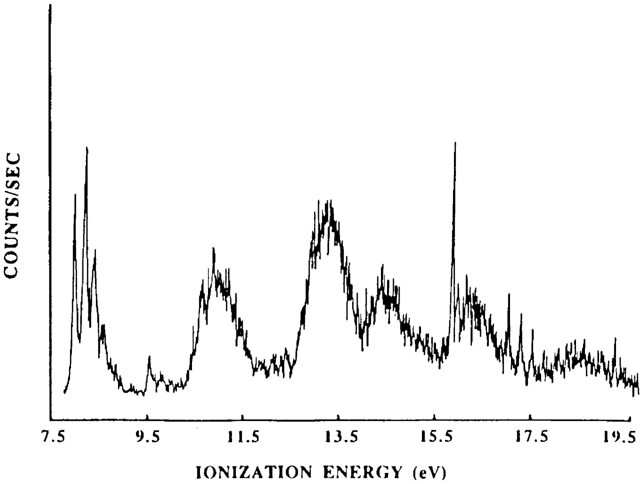


Figure 18. PE spectrum of methylenecyclopropene (**57**). Reprinted with permission from ref 122. Copyright 1989 American Chemical Society.

Koenig et al.[123] have measured the PE spectra of benzo and naphtho derivatives of 1,1-diphenylmethylenecyclopropene (**61**, **62**). The spectra have been analyzed with the aid of HAM/3 and HAM/3/CI calculations. It is suggested that the effects of the fused cyclopropene groups are to be found in small reductions (by about ca. 0.2 eV) of the second or higher ionization energies. A correlation of gas-phase ionization potentials (IP_1 values) and electrochemical oxidation potentials ($E_{1/2}^{\bullet+}$ values) of a series of aromatic hydrocarbons is discussed.

3.4.6 Cyclopropenone

He–I and He–II PE spectra of cyclopropenone (**58**) were measured by Harshbarger et al.[124] and in some detail by Schweig et al.[125] The spectra are depicted in Figure 19; the IPs and their assignments are summarized in Table 2 together with those of some derivatives (entries 33–36). The He–I spectrum of **58** exhibits six bands, three of which display vibrational fine structure. Since eight MOs with binding energies less than 25 eV are obtained by MO calculations, two bands are each assigned to two ionization events.

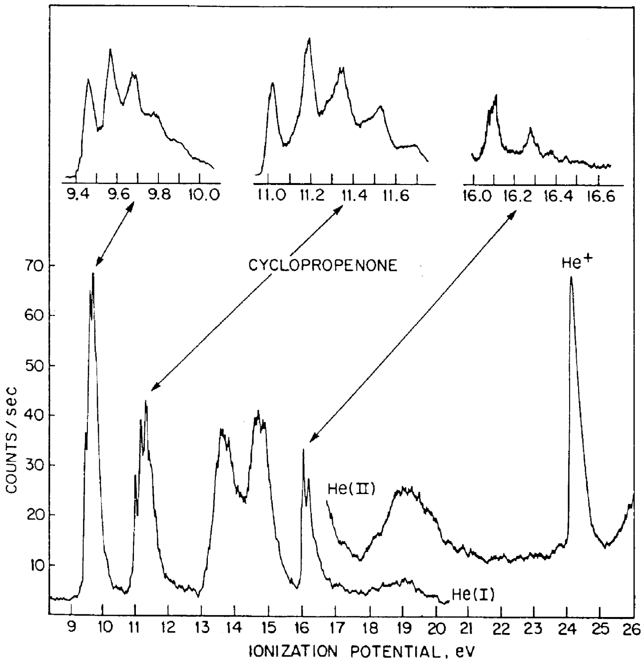


Figure 19. He–I and He–II PE spectra of cyclopropenone (**58**). Reprinted with permission from ref 124. Copyright 1974 The American Institute of Physics.

The first IP relates to the oxygen lone-pair orbital n_O. However, the ionization causes a significant change in the structure of the radical cation relative to the molecular ground state, which is indicated by the fact that the band shows a vibrational progression of 820 cm^{-1} with the second and the third members of the progression being nearly equal in intensity. Such a nonvertical transition indicates that the "lone-pair" orbital in fact is intimately involved in the bonding scheme of the molecule. The vibrational progression most probably corresponds to the totally symmetric C–C single bond stretching mode, for which a frequency of 1043 cm^{-1} was observed for solid **58**. IP_2 is assigned to ionization from the $2b_1$ MO that has mainly $\pi_{C=C}$ character, and its vibrational progression of 1380 cm^{-1} corresponds to the C=C double bond stretching vibration ($\nu_{C=C}$) which has a frequency of 1467 cm^{-1} in the molecular ground state. The only other band in the PE spectrum with a resolved vibrational fine structure is found at 16.11 eV and is assigned to ionization from the $4a_1$ MO. The spacing between the two prominent peaks is 1370 cm^{-1} and also this vibration is assigned to $\nu_{C=C}$.

In Figure 20 the five highest occupied MOs of cyclopropenone (**58**) are depicted. Delocalization of the orbitals, in particular of n_O that is mixing with ω_A in $3b_2$ and $2b_2$, and of the π MOs, is obvious. The cross-conjugated system is characterized by four π MOs. $1b_1 = \pi_1$ is the totally bonding combination of the four 2p AOs. $2b_1 = \pi_2$ is C=C bonding and nonbonding for the O atom. The remaining two unoccupied π orbitals, not shown in Figure 20, are C=C ($1a_2 = \pi_3$) or C=O ($3b_1 = \pi_4$) antibonding, respectively.

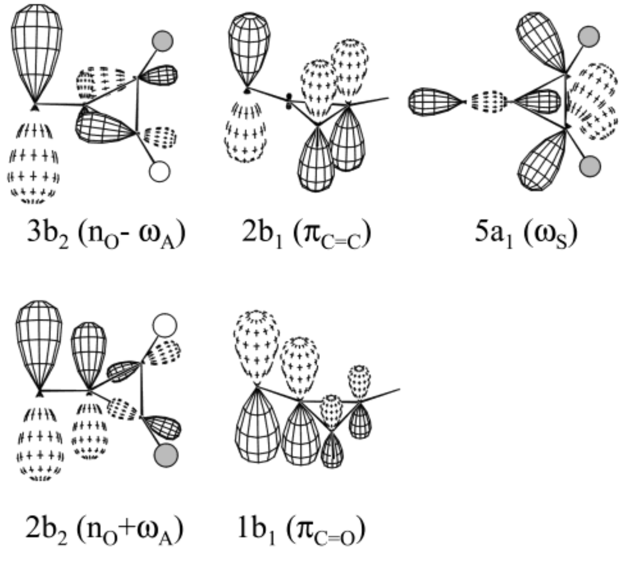
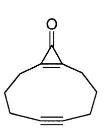


Figure 20. The five highest occupied MOs of cyclopropenone (**58**).

3.4.7 Bicyclic Cyclopropenones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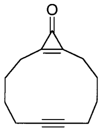
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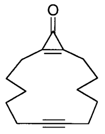
65

Gleiter et al.[126] have studied a series of bicyclic compounds (**63**−**65**) in which a cyclopropenone unit is opposed to a triple bond in a 10-, 12-, or 14-membered ring. The PE investigations revealed a considerable transannular through-space interaction between the triple bond and the cyclopropenone moiety in **63**, but only a small or no interaction in **64** and **65**.

The PE spectra of **63**−**65** are depicted in Figure 21; the relevant PE spectroscopic data are included in Table 2 (entries 37−39. The first band at about 8.5 eV is assigned for all three compounds to ionization from the n_O orbital. Three π ionizations, one from the C=C double bond of the cyclopropenone unit and two from the C≡C triple bond, are found between 9.3 and 10.1 eV. However, while in **64** and **65** the range of π bands is only about 0.3 eV resulting in a strong composite band, in **63** three individual peaks are discernible that spread over more than 0.8 eV. The ionization pattern of **64** and **65** is more characteristic for isolated π systems while in **63** the ten-membered ring adopts a conformation that favors overlap of the π orbital of the cyclopropenone ring with the in-plane π orbital of the triple bond. This interpretation is substantiated by X-ray structure analysis on single crystals of **63**, which revealed a boat conformation with C_s symmetry for the ten-membered ring. In Figure 22 a ball-and-stick-view of this conformer is shown. The transannular distance between the C=C double and the C≡C triple bond is 310 pm. IP_2 (9.33 eV) and IP_4 (10.14 eV) are thus assigned to ionizations from the antisymmetrical and the symmetrical combination, respectively, of $\pi_{C=C}$ and the in-plane π orbital of the triple bond, $\pi_{(C\equiv C)i}$, while IP_3 (9.64 eV) is assigned to $\pi_{(C\equiv C)o}$, the unperturbed out-of-plane π orbital of the triple bond. PE spectroscopy is well suited to investigate such transannular interactions of functional groups in medium-sized rings.[127]

3.4.8 Conclusion

Exocyclic double bonds on an unsaturated three-membered ring lead to an essentially new electronic system that can be largely modified by heteroatoms in this bond.

3.5 Polycyclic Cyclopropane and Cyclopropene Compounds

The three-membered ring is the smallest cyclic structural unit and cyclopropane rings are frequently found as a structural constituent in numerous compounds including natural products such as terpenes. Also in several other classes of interesting compounds such as bicyclics and polycyclics, asteranes and propellanes those members with a cyclopropane ring hold the pole position. Oligo- or polycyclic compounds offer the possibility to combine certain structural units in a definite and rigid orientation so that their mutual interactions can be studied more easily than in open-chain systems. The PE spectra of a large number of such compounds have been investigated and Gleiter's review[1] covers many of them. Among these are vinylcyclopropanes with a fixed conformation; bicyclopropyl derivatives; tricyclopropyl derivatives; rotanes; tricyclo[3.1.0.0^{2,4}]hexane derivatives; homoderivatives of triquinacene, barrelene, and bullvalene; compounds containing a bicyclobutane moiety.

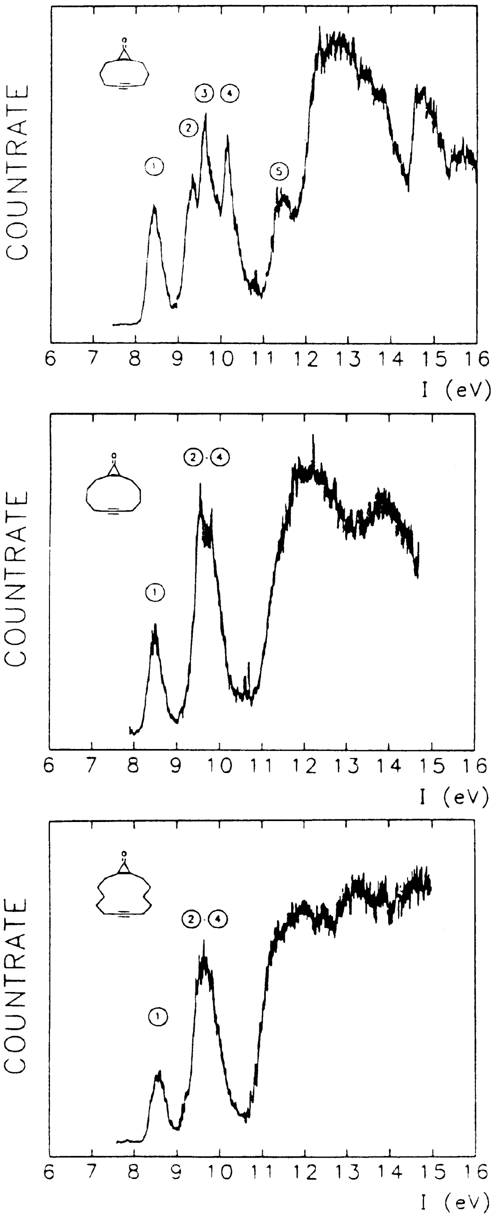

Figure 21. PE spectra of bicyclo[8.1.0]undec-1(10)-en-5-yn-11-one (**63**), bicyclo[8.1.0]tridec-1(12)-en-6-yn-13-one (**64**), and bicyclo[8.1.0]pentadec-1(14)-en-7-yn-15-one (**65**). Reprinted with permission from ref 126. Copyright 1995 American Chemical Society.

The PE spectra of such interesting compounds are often disappointing because of strong overlap of the ionization bands, which prevents a detailed inter-

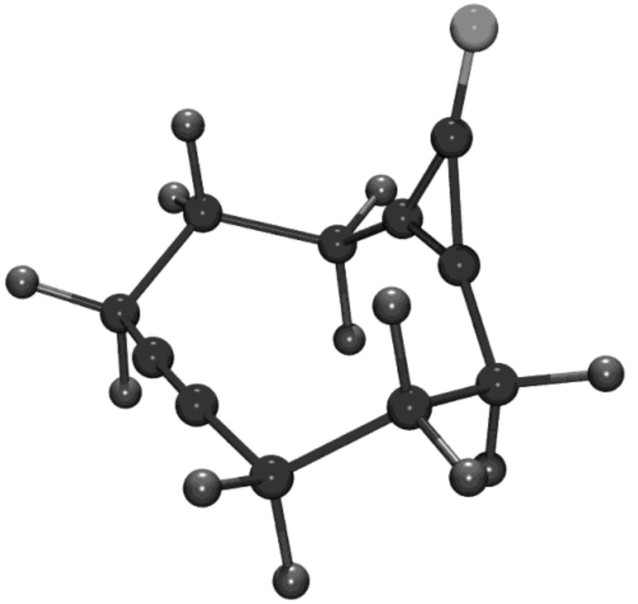

Figure 22. Conformation of bicyclo[8.1.0]undec-1(10)-en-5-yn-11-one (**63**).

pretation and analysis of the electronic structure of the molecules. We will refrain from repeating the work of Gleiter.[1] However, important examples of compounds with unique structural features will be mentioned here. But otherwise we will concentrate on more recent investigations. The IP values of the compounds discussed in this section are collected in Table 3.

3.5.1 Compounds with Two Three-Membered Rings and Small Polycyclics

In this section, we will discuss PE spectra of compounds that can be constructed from two cyclopropane or cyclopropene rings. Such compounds are spiropentane (**66**), bicyclo[1.1.0]butane (**67**), tetrahedrane (**68**), bicyclopropyl (**69**), 3,3′-bicyclopropenyl (**70**), bicyclopropylidene (**71**), and [1.1.1]propellane (**72**). Tetrahedrane (**68**) is actually a tetracyclic compound with four three-membered rings, and [1.1.1]propellane (**72**) has three three-membered rings, but because of their close structural relationship to bicyclobutane (**67**) they are included here. If a certain compound has been investigated together with some of its derivatives or congeners, these will also be mentioned here.

Spiropentane. Spiropentane (**66**) is the simplest saturated spiro hydrocarbon. Its PE spectrum had been recorded in 1970 by Bodor et al.[128] but was reinvestigated in 1986 by Gleiter et al.[129] together with the spectra of tricyclo[4.1.0.0^{1,3}]heptane (**73**) and 4,5-benzotricyclo[4.1.0.0^{1,3}]hept-4-ene (**74**). These compounds offer the possibility to study the conjugative interactions of two directly linked orthogonal cyclopropane rings. The molecular symmetry of **66** is D_{2d}, and that of **73** and **74** is C_2. From a simple MO scheme for **66**, the authors deduced that ionizations from three of the four highest occupied valence orbitals are to be expected at low energies followed by the fourths IP at some distance. The corresponding bands could be identified, although at different energies, in the PE spectra of **66**, **73**, and **74**. This led to the conclusion that the C_2H_4 bracket in **73** acts purely inductively, and that in **74** there is essentially no interaction between the valence MOs of the spiropentane moiety and the benzene part.

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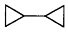
72



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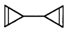

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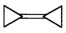

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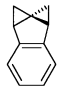

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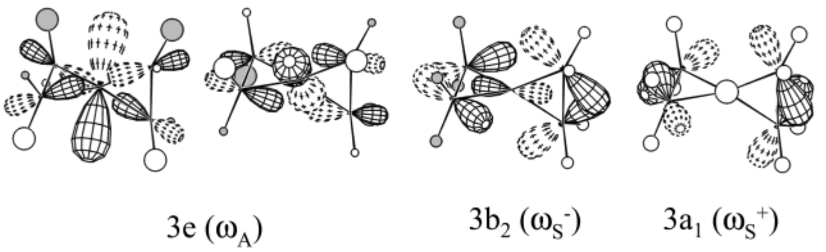
In Figure 23 some MOs of **66** are depicted that illustrate the interaction of the Walsh orbitals. The 3e orbitals resemble ω_A, and the orbitals $3a_1$ and $3b_2$ can be described as symmetrical and antisymmetrical combinations of ω_S, respectively. The assignments given by the authors for the first four IPs are summarized in Table 3 (entries 1−3).

Bicyclo[1.1.0]butane. For the PE spectra, electronic structures and bonding properties of bicyclo[1.1.0]butane (**67**), the smallest bicyclic hydrocarbon, and numerous compounds containing this moiety, including benzvalene (**77**) and tricyclics such as tricyclo[3.1.0.0^{2,6}]hexane (**75**) and tricyclo[4.1.0.0^{2,7}]heptane (**76**), reference is made to Gleiter's review.[1] Compound **77** has been reinvestigated together with the phenylene and naphthylene bicyclobutanes **78**−**80**.[130] The experimental data (Table 3; entries 4, 7, and 9−12) were analyzed in terms of empirical correlation diagrams and semiempirical MINDO/3 and CNDO/S calculations. The investigations reveal a strong impact of the bicyclobutylene group on the spectroscopic properties of the aromatic π systems in **78**−**80** that is due to hyperconjugative interactions involving bicyclobutane Walsh orbitals.



$3e\ (\omega_A)$ $3b_2\ (\omega_S^-)$ $3a_1\ (\omega_S^+)$

Figure 23. MOs of spiropentane (**66**).

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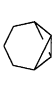

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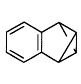

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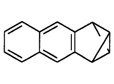

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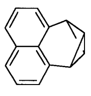

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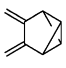

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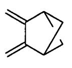

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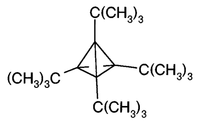
Gleiter et al.[131] have also investigated the PE spectra of 3,4-bis(methylene)tricyclo[3.1.0.0^{2,6}]hexane (**81**; Table 3, entry 8) and some related compounds such as 2,3-bis(methylene)bicyclo[2.1.1]hexane (**82**) and 2-bicyclo[2.1.1]hexene (**83**) with special emphasis on the interaction of the bicyclobutane moiety and the π electron system. The assignments were based on a ZDO model and semiempirical calculations. Together with the PE data of benzvalene (**77**), the data allow a comparison between compounds **81**/**82** and **77**/**83**. The resonance integral of the interactions between a bicyclobutane or a cyclobutane moiety and a double bond system within a ZDO model amounts to −2,3 and −1.9 eV, respectively. The increase of interaction is reflected in the lower ionization energy of bicyclobutane derivatives (**81**, **77**) as compared with the cyclobutane derivatives (**82**, **83**).

Tetrahedrane. Tetrahedrane (**68**) can hardly be considered as a derivative of cyclopropane in the direct sense. It is rather a compound of its own, and the first member of compounds called Platonic hydrocarbons.[132] However, it is mentioned here because of its close resemblance to bicyclobutane: two hydrogen atoms are replaced by a C−C bond.

Owing to its high molecular symmetry (T_d), many of the MOs of tetrahedrane (**68**) are degenerate. This applies for the two highest occupied MOs (1e), which are followed by three triple degenerate MOs ($2t_2$). From the remaining five occupied valence MOs there are only two nondegenerate ($1a_1$ and $2a_1$), while the other are again triple degenerate ($1t_2$). The PE spectrum should thus be determined by several Jahn−Teller splittings. Since the parent hydrocarbon **68** is unknown, the PE spectrum of its simplest stable derivative, tetra-*tert*-butyltetrahedrane (**84**; Table 3, entry 55), has been recorded and interpreted by Heilbronner et al.[133] The spectrum displays two bands in the low-energy region that are separated from a broad, structureless strong band commencing at about 10 eV that originates from the *tert*-butyl groups. It is shown by the authors that the double-humped band with centroid IP ca. 7.9 eV corresponds to the removal of an electron from the HOMO, of e symmetry, which is indicative of the expected Jahn−Teller distortion of the radical cation. The separation of 0.7 eV between the two maxima indicates a pronounced distortion of the radical cation. This result certainly does not give as much insight into the interesting electronic structure as might be expected from a technique like PES. However, it has to be taken into consideration that the molecule's C_4 cage contributes only 12 of the 116 valence electrons of **84**. The tetrahedrane moiety is thus nearly lost inside the four *tert*-butyl groups. For the first ionization energy of the parent hydrocarbon **68** the authors estimate a value of 9.3−9.6 eV.



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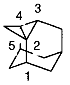
Propellanes. A PE spectroscopic study of [1.1.1]-propellane (or tricyclo[1.1.1.0^{1,3}]pentane, **72**) was carried out by Honegger et al.[134] The most remarkable feature of its spectrum is the appearance of an extremely narrow ionization band ($IP_1 = 9.74$ eV) corresponding to a HOMO that should thus be nonbonding or even slightly antibonding, in agreement with the inverted geometry at the bridgehead carbon atoms.[132,135]

Because **72** is a small molecule of high symmetry (D_{3h}), the orbital sequence is almost entirely symmetry conditioned and there is hardly any doubt that the assignment presented in Table 3 (entry 56) is the correct one. In particular the typical Jahn−Teller envelopes of the second, third, and fifth band point to correspondingly degenerate, and thus unstable, states of the radical cation, whereas the sharpness of the first band clearly indicates that the electronic ground state of **72**$^+$ is definitely not degenerate.

The most remarkable feature of the PE spectrum of **72** are that the 0,0 vibrational component of the first band is the most intense one, which means that the adiabatic energy is very close to the vertical one ($IP_a \approx IP_v$), and that the width at half-height of this band is extremely narrow, namely, only 0.25 eV. This is a clear indication that ionization of **72** to yield ground-state **72**$^+$, i.e., electron ejection from the HOMO ($3a_1'$), leads to only minute changes in geometry of the molecular frame. It could be argued that this is evidence for a nonbonding or slightly antibonding character of this orbital. However, the rather tight cage structure of **72**, that leaves little leeway for geometric distortions, could also be the determining factor. Indeed, high-level calculations reinforce the conclusion that the bridgehead atoms in **72** are bonded in the ground state.[135]

Eckert-Maksic et al.[136] have studied 2,4-methano-2,4-didehydroadamantane (**85**), a [3.1.1]propellane. The first IP (7.9 eV; Table 3, entry 57) is assigned to the ionization from the MO localized in the region between the inverted carbons atoms (C^2 and C^4). Its rather Gaussian shape with a bandwidth at half-height of ca. 0.45 eV, being significantly larger than that of the first band of **72**, suggests that the HOMO of **85** has a bonding character.



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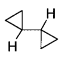
Bicyclopropyls. Molecules containing bicyclopropyl moieties are systems in which the conformation-dependent interactions of two saturated three-membered rings, in particular via their Walsh orbitals, can be studied. The parent compound bicyclopropyl (**69**) and more than 20 polycyclics with this structural unit are covered in Gleiter's review.[1] Gleiter et al.[137]

have reinvestigated the PE spectrum of **69** together with those of its 1,1′-dimethyl derivative **86**, some dispiro compounds **87**−**92** and some tricyclic systems **93**−**97** (Table 3, entries 24−36).



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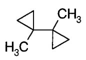

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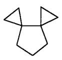

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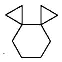

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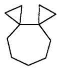

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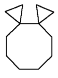

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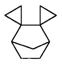

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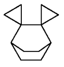

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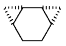

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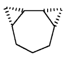

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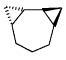

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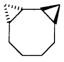

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In addition, the electronic and molecular structures of these compounds have been analyzed by model calculations and empirical correlation procedures. Low-energy PE bands of **69**, **86**−**97** were assigned to ejection of electrons from the bicyclopropyl Walsh orbital system and were discussed in terms of a simplified linear combination of Walsh orbitals (LCWO) model, allowing tentative prediction of conformational features from the PE data. However, in addition to the occupied Walsh orbitals also their antibonding counterparts (Figure 1) had to be included to yield acceptable qualitative rationalizations of the PE spectra. In the case of the mobile species **69** and **86**, the PE spectra are best understood under the assumption that the observed maxima in the low-energy region correspond to the synclinal (sc) conformer, implying that contributions from the antiperiplanar (ap) conformer are either weak or broad and featureless. This assumption is at variance with previous interpretations but is supported by a consideration of torsional amplitudes and the results of LCWO and all-valence-electrons calculations.

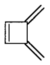
The PE spectrum of the parent compound **69** has been the subject of several earlier investigations.[1,59] The low-energy region is characterized by four almost equally spaced bands. Apart from a shift toward lower energies and a somewhat narrower spacing of the peaks, the spectrum of **86** is quite similar to that of **69**. **69** exists as a mixture of sc and ap conformers with almost equal parts at room temperature.[138−142] The PE spectrum should thus represent a superposition of the spectra of both conformers, and a total of eight ionizations should be expected in the low-energy region. However, since only four bands are observed, the assignment of these to eight expected transitions is problematic. The same holds for the dimethyl derivative **86**.

Different attempts[1,143] to solve this problem had remained unsatisfying. With regard to the different flexibility of the ap and the sc conformer, Gleiter et al.[137] reached the following conclusion: The sc conformer exhibits a well-defined equilibrium torsional angle, corresponding to a fairly rigid molecular structure. In contrast, the angle of the ap conformer is distributed in a large region with a governing potential approximating a square well, so that this conformer is by no means a rigid species. Accordingly, the PE spectrum of this conformer exhibits broad bands, approaching a structureless continuum that is superimposed to the well-structured spectrum of the sc conformer. The four maxima close to 9.5, 10.1, 11.0, and 11.7 eV indicate ionizations of the rigid sc conformer while no definite IP values can be assigned to the ap conformer.

The PE spectrum of **86** is consistent only with the presence of the sc conformer of this compound and shows no indication of significant contributions of the ap form.

The dispiro compounds **87**−**92** can be divided in two groups: compounds **87**, **91**, and **92** where the bicyclopropyl moieties have equilibrium torsional angles close to zero, and compounds **88**−**90** where the torsional angle is expected to deviate significantly from zero. The PE spectra of the first group of compounds each exhibit a well-resolved band with maximum close to 9.0 eV, separated by about 1 eV from the other. For **88**, a torsional angle $\theta \approx 60°$ of the bicyclopropyl unit can be expected. Four bands close to 9.2, 9.7, 10.2, and 10.8 eV are observed, that correlate nicely with the data for **69** and **86**. The spectrum of **89** is very poorly resolved, indicating a flexible structure. Two peaks at 9.1 and 9.6 eV are recognized in the case of **90**, corresponding to a preferred conformation with a torsional angle different from zero.

The tricyclic compounds **93**−**97** are expected to be rigid, strained species. This is consistent with the fact that their spectra are generally better resolved, allowing more explicit conclusions. With some limitations, in particular for **93** and **94**, the observed spectral data are either consistent with known torsional angles or predictions are possible: **93** ($\theta = 18°$), **94** ($\theta = 56°$), **95** ($\theta = 0°$), **96** ($\theta = 120°$), **97** ($\theta = 90°$).



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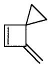
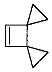


99



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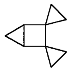


101

Blickle et al.[144] have studied the PE spectra of the cyclopropanation products of 3,4-dimethylene-1-cyclobutene together with that of the parent compound (**98**−**101**; Table 3, entries 16−18). The spectra were analyzed with the aid of ab initio calculations on the STO-3G level of theory. We will restrict the discussion here to the dispiro derivative of bicyclo[2.1.0]-pentane (**101**) that consists of three cyclopropane rings linked by a cyclobutane ring. The most relevant MOs of **101** are shown in Figure 24 together with a numbering of the cyclopropane rings. The authors find a satisfying agreement between observed IPs and calculated MO energies and show diagrams of the eight highest occupied STO-3G orbitals. In most cases, the mutual interactions of the orbitals of the four rings prevent a simple description of the resulting MOs. However, it can be stated that 14a′ is essentially the ω_S of the three-membered ring 1 in the bicyclopentane moiety, and 7a″ can be considered as the corresponding ω_A. Likewise, 12a′ and 10a″ are mainly the symmetrical and antisymmetrical, respectively, combination of the ω_A orbitals of the two spiro rings 2 and 3. And finally, 9a″ can be described as symmetrical combination of ω_S of the spiro rings. On the basis of their STO-3G results, the authors have assigned IPs to the MOs. The corresponding data are summarized in Table 3 (entry 18).

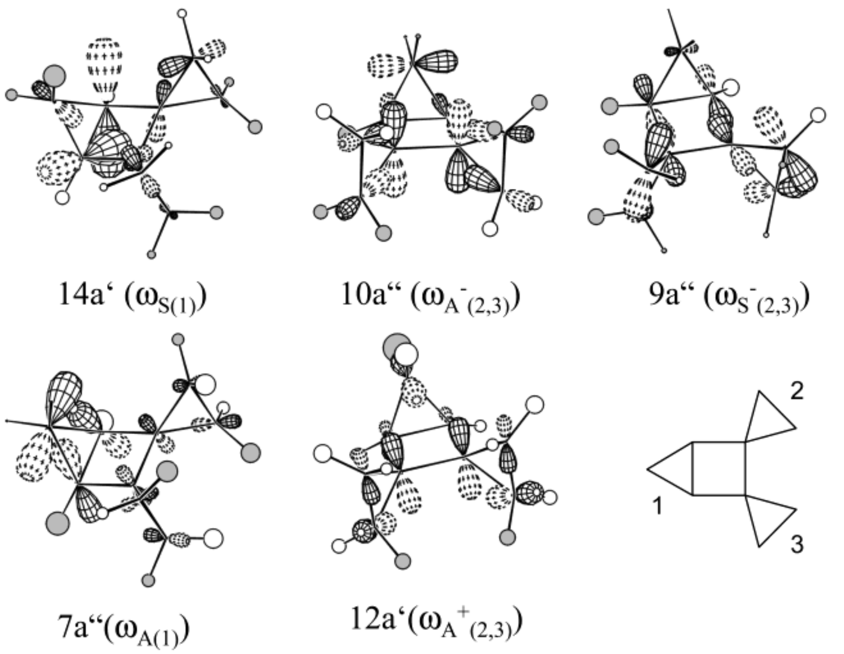
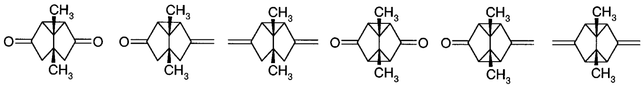


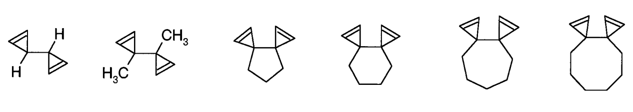
Figure 24. MOs of dispirobicylo[2.1.0]pentane derivative **101** and numbering of the three-membered rings.

Tricyclo[3.3.0.0^{2,8}]octanes and Tetracyclo[3.3.0.0.^{2,8}0^{4,6}]octanes. Gleiter et al.[145−147] have investigated a series of 1,5-dimethyltricyclo[3.3.0.0^{2,8}]octane (**102**−**104**) and 1,5-dimethyltetracyclo[3.3.0.0.^{2,8}0^{4,6}]octane derivatives (**105**−**107**) together with related compounds. They found considerable interactions between n(O) orbitals and the σ frame in the carbonyl compounds as well as of the C=C double bonds and the σ frame in the dienes. The lower IP values of the latter compounds (**104**, **107**) are included in Table 3 (entries 37 and 38).



102 **103** **104** **105** **106** **107**

3,3-Bicyclopropenyls. 3,3-Bicyclopropenyl (**70**) is probably the least stable of the known four valence isomers of benzene.[132] It was prepared by Billups and Haley in 1989, and its structure in the crystalline state was determined by X-ray analysis.[148] In the same paper, its electronic structure was investigated by PE spectroscopy and quantum chemical computations. A few years earlier, the spectra of the 3,3′-dimethyl derivative **108** and the spiro compounds **109**−**112** had been analyzed by Spanget-Larsen et al.[149] Greenberg and Liebman[150] studied the electronic structures and the conformational properties of **70** and **108** by ab initio calculations. The bicyclopropenyls have been the object of considerable interest with regard to interactions between the isolated double bonds.[151] Such interactions may be caused by overlap through-space (homoconjugation) or through the σ-framework of the molecule (through-bond interaction).[152] As mentioned above for bicyclopropyl compounds, such systems are candidates for the investigation of conformation-dependent interactions, in this case of two unsaturated three-membered rings. The relevant IP data are summarized in Table 3 (entries 45−50).



70 **108** **109** **110** **111** **112**

In the solid state, the conformation of **70** was found to be antiperiplanar (ap); however, this conformer is only slightly more stable than the synclinal (sc) forms, and the PE spectrum of **70** has been interpreted in terms of about a 2:1 mixture of ap and sc conformers in the gas phase. On the other hand, from its PE spectrum preference of the sc form was predicted for the dimethyl derivative **108**. The spectrum of **70** is depicted in Figure 25.

The spectrum exhibits three peaks of different intensities, which are well separated from a smaller fourth one. MO calculations have shown that for the

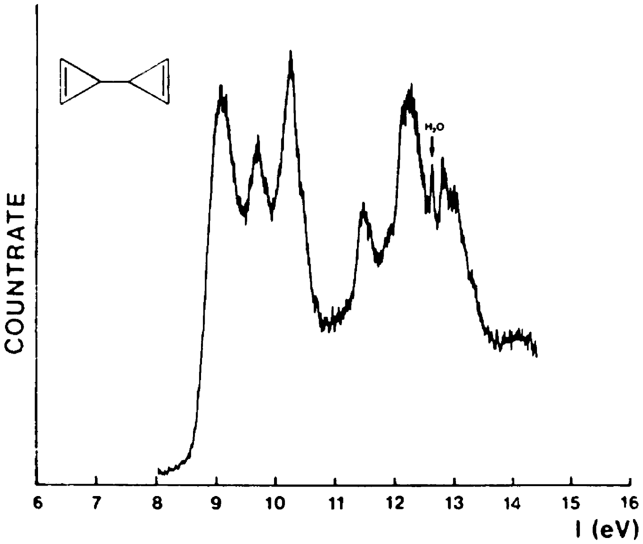


Figure 25. PE spectrum of 3,3‘-bicyclopropenyl (**70**). Reprinted with permission from ref 148. Copyright 1993 American Chemical Society.

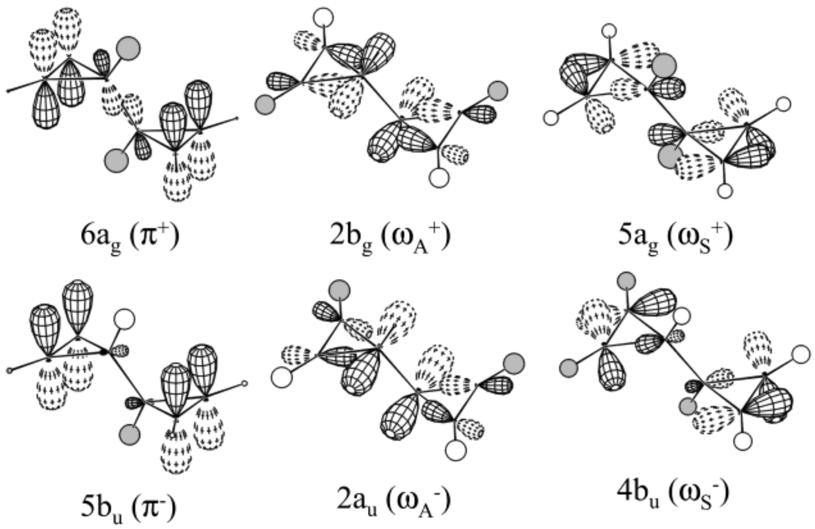


Figure 26. MOs of 3,3′-bicyclopropenyl (**70**).

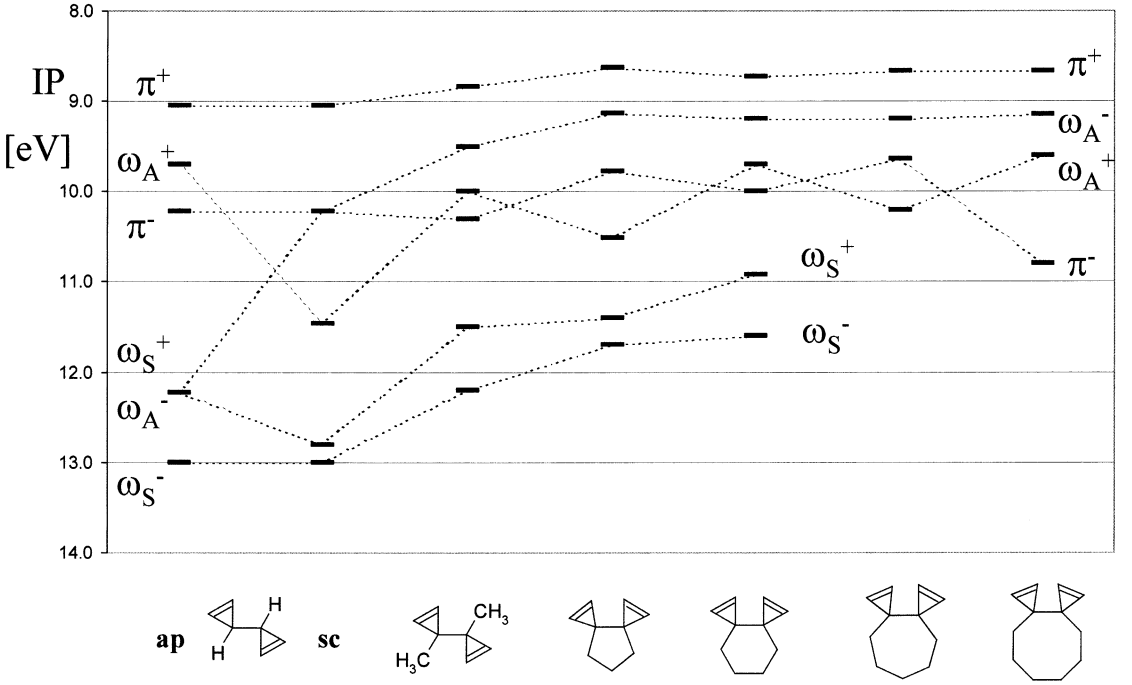


Figure 27. IP correlation diagram for 3,3′-bicyclopropenyls.

ap conformer three nearly equally spaced bands [6a$_g$ (π^+), 2b$_g$ (ω_A^+), and 5b$_u$ (π^-)] well separated by about 2 eV from two close bands [5a$_g$ (ω_S^+) and 2a$_u$ (ω_A^-)] are expected, while 4b$_u$ (ω_S^-) is predicted at much higher energy. These orbitals are depicted in Figure 26. "+" and "−" signs in the orbital notations indicate symmetrical and antisymmetrical combinations, respectively, of the respective orbitals with regard to the center of symmetry. The relay-function of the central C−C bond in the interaction of the π orbitals is quite evident from the shape of 6a$_g$. As we shall see, this interaction is essentially conformation-independent, whereas the interaction of the ω_A orbitals (2b$_g$, 2a$_u$) shows strong variation with conformation.

For the sc conformer the bands originating from 7a (ω_A^-) and 7b (π^-) are expected to be very close together, and the band from 6b (ω_A^+) is anticipated to be well separated by about 1.6 eV from those bands arising from 7a, 7b, 6a (ω_S^+), and 5b (ω_S^-). A reasonable agreement between calculation and experiment could only be found if it was assumed that both conformers were present in the above-mentioned ratio.

In Figure 27 an IP correlation diagram is shown for the relevant IPs of **70**, **108**−**112**. The splitting of the two π ionizations (1.0−1.5 eV), caused by through-bond interaction, varies only little in these compounds, indicating that this type of interaction is essentially independent of conformational changes. On the other hand, the splitting of the Walsh bands varies considerably and can be used for conformational analysis. For the energy difference of the ω_A orbitals a simple qualitative relation with the torsional angle θ was found:

$$\epsilon(\omega_A^-) - \epsilon(\omega_A^+) \approx A \cos\theta \text{ with } A = 1.6-1.8 \quad (4)$$

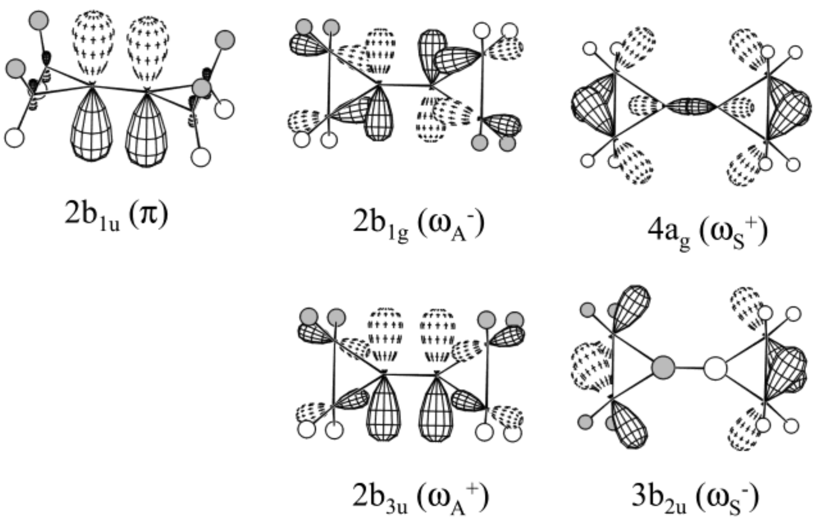
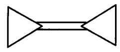


Figure 28. MOs of bicyclopropylidene (**71**).

The torsional angles of the preferred conformation in the gas phase, obtained with this relation from the PE spectra, are **108** ($\theta = 75°$), **109** ($\theta = 30°$), **110** ($\theta = 60°$), **111** ($\theta \approx 30°$), **112** ($\theta = 90°$).

Bicyclopropylidene. The PE spectrum of bicyclopropylidene (**71**) has been investigated together with those of related compounds such as rotanes by Gleiter et al.[153] Since the results have been summarized in Gleiter's review,[1] we will refrain from discussing them here in detail but will only report the most important results for **71** (Table 3, entry 51). The spectrum displays six peaks with only partial overlap, and six of them have been assigned making use of MINDO/3 and STO-3G calculations.



71

The most relevant orbitals are depicted in Figure 28. The antisymmetrical and the symmetrical combinations of ω_A are found in MOs $2b_{1g}$ and $2b_{3u}$, respectively. The corresponding combinations of ω_S are represented by $4a_g$ and $3b_{2u}$. The first IP is assigned to the π ionization ($2b_{1u}$) and the next four to combinations of the Walsh orbitals. The split of 2.85 eV between ω_A^+ (IP_5) and ω_A^- (IP_2) corresponds to a value of $\beta = -2.14$ eV for the resonance integral between the linked 2p AOs of the two adjacent cyclopropane rings. It is of particular interest that this interaction parameter is considerably larger than that found for bicyclopropyl compounds ($\beta = -1.73$ eV),[1] which is in accord with the short C=C double bond (131 pm).[154-156]

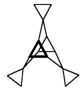
Conclusion. Two three-membered rings in close proximity strongly interact depending on the actual geometric properties. In bicyclopropyls and 3,3-bicyclopropenyls, such interactions can be used for conformational analysis.

3.5.2 Compounds with More than Two Cyclopropane Rings

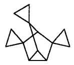
Polycyclic Cyclopropane Spiro Compounds Derived from Triasterane, Nortricyclane, and Norbornane. De Meijere et al.[157] have synthesized trimethylenetriasterane (**120**), 3,7,9-tris(spirocyclopropyl)triasterane (**115**), tris(spirocyclopropyl)nortricyclane (**116**), and the tris(spirocyclopropyl)norbornanes **117**−**119**. **120** contains six vinylcyclopropane units rigidly held in an antiperiplanar (ap) conformation in a D_{3h} symmetric framework. **115** and **116** are the first model compounds with bicyclopropyl units rigidly fixed in an s-trans (ap) conformation (torsional angle $\theta = 180°$). The PE data of these compounds are collected in Table 3 (entries 52 and 53).

113

114



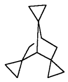
115



116

117

118



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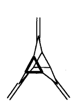
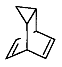


120

PE spectra of the cage hydrocarbons triasterane (**113**) and nortricyclane (**114**) had already been fully interpreted;[1,158] the spectra of the other compounds were recorded. The spectra of **117**−**119** show a broad structureless band between 9 and 11 eV such that a detailed analysis and assignments to individual ionizations is not possible. Also the spectra of the remaining compounds exhibit strongly overlapping composite bands. The shape of the first band in all three compounds indicates a Jahn−Teller effect in the radical cations with a splitting of 0.4 eV in **116** and **120**, but a smaller split (0.3 eV) in **115**. This observation agrees with the finding that the splitting decreases with increasing delocalization of the Walsh e orbital.

The investigations on **115**, **116**, and **120** included semiempirical MNDO calculations or an empirical ZDO approach. The results support a strong interaction between the three-membered rings in **115** and **116**, and between the cyclopropyl rings in **120** and the double bonds. These findings are in accord with other PE spectroscopic investigations on polycyclopropyl compounds.[1]

Homobarrelenes. Gleiter et al.[159] have analyzed the PE spectra of a series of homobarrelenes (**121**–**124**; Table 3, entries 59–62) including exo/endo isomers (**122**, **123**). The first bands were assigned on the basis of MINDO/2 and INDO calculations. The authors have used the localized orbitals derived from the INDO calculations to discuss the magnitude of through-space and through-bond interactions in particular between the two π orbitals in compound **121**.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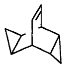
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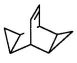
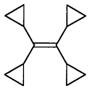

123


124

Spirocyclopropanated Bicyclobutylidenes. De Meijere et al.[160] have synthesized and investigated a series of spirocyclopropanated bicyclobutylidenes (**126**–**129**; Table 3, entries 64–67). The PE spectra have been analyzed together with that of tetracyclopropylethene (**125**; Table 1, entry 27) with special emphasis on electronic interactions in these compounds. The conjugation between the double bond and α-spirocyclopropane groups in the bicyclobutylidenes **126**, **128**, and **129** is evident in their UV spectra. Each α-spirocyclopropane group causes a bathochromic shift of the $\pi-\pi^*$ band compared to that of the parent bicyclobutylidene by about 9 nm. This indicates a significant decrease in the HOMO–LUMO energy gap. Due to the short 1,3-transannular distance in a four-membered ring (e.g., 214.7 pm in **128**), there is also significant electronic interaction between the double bond and the β-spirocyclopropane groups in **127**–**129**, as evidenced by the bathochromic shifts of 3–6 nm for each added β-spirocyclopropane group. The four α- and two β-spirocyclopropanes in the perspirocyclopropanated bicyclobutylidene **128** in total cause a bathochromic shift of the $\pi-\pi^*$ band by 40 nm.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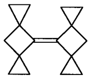
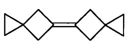

126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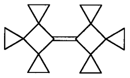
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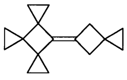

129

The effect of added spirocyclopropane groups on the HOMO energies of bicyclobutylidenes has been estimated rather accurately from their PE spectra. Thus, comparing the IP_1 values, corresponding to π-ionization energies, a value of 0.05 eV per any additional β-spirocyclopropane group and 0.22–0.28 eV per additional α-spirocyclopropane groups is derived. This indicates an increasing nucleophilicity of the double bonds in the order **125** < **127** < **126** < **128**.

Conclusion. In a polycyclic compound, a cyclopropane ring is found either as a spirocyclic or an annellated ring. Such compounds often show unusual structures with unusual properties. By the incorporation of three-membered rings, a given molecular structure can thus be modified in a characteristic way. Electronic interactions can be studied using the concept of through-space and through-bond interactions.

3.6 Miscellaneous Cyclopropane and Cyclopropene Compounds

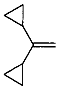
3.6.1 Cyclopropenylidene

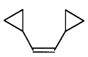
An adiabatic ionization potential of 9.15 ± 0.03 eV has been measured by PES for the carbene cyclopropenylidene (**130**) produced by supersonic jet flash pyrolysis of 3-chlorocyclopropene.[161,162] Insertion of this IP into a thermodynamic cycle yields a heat of formation of $\Delta H_f = 477 \pm 17$ kJ/mol.

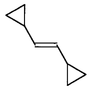

130

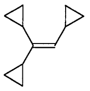
3.6.2 Cyclopropyl-Substituted Ethenes and 1,3-Butadienes

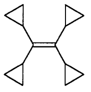

13
9.15 eV[63,86,87]


131
8.87 eV[92,160]

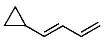

132
8.50 eV[160]


133
8.40 eV[160]


134
8.0 eV[160]


125
7.90 eV[160]

PE spectra have been measured of the complete series of cyclopropyl-substituted ethenes (**13**, **125**, **131**–**134**; Table 1, entries 17, and 23–27).[160] However, except for the first two members of the series that were investigated in detail, only the first IP is reported. This value relates to the $\pi_{C=C}$ orbital, and the data nicely illustrate the electron donor character of the cyclopropyl groups.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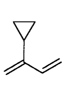
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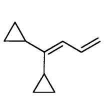
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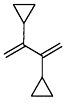
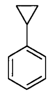

138

A more thorough analysis has been performed on cyclopropyl-substituted 1,3-butadienes (**135**–**138**).[163] The relevant data are summarized in Table 1 (entries 50–53). In particular, the effect of the cyclopropyl groups in different positions on the energies of the π orbitals is obvious.

3.6.3 Cyclopropyl-Substituted Benzenes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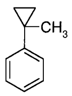
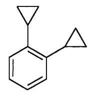


18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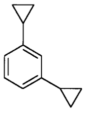
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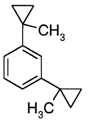

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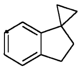
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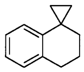
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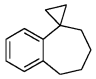
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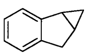
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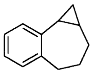
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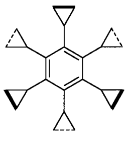
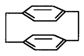

147

Heilbronner and co-workers[164] have recorded and discussed the PE spectra of a series of cyclopropyl-substituted benzenes (**17**, **141**–**147**). The spectra are reproduced and briefly discussed in Ballard's review.[2] Compounds **17**[63,94,95] and **18**[80,95] had been investigated previously (see section 3.2.1). Several derivatives of **17** with substituents in the 4-position of the benzene ring and in the 1-position of the cyclopropyl group were studied by Prins et al.[95] (Table 1, entries 54–58). For most compounds, interpretation is made difficult by conformational problems, with a few possible exceptions such as hexacyclopropylbenzene (**147**) and 4,5-benzo-spiro[2.4]hept-4-ene (**142**). From an X-ray structure analysis,[165] one knows that in the former compound the six cyclopropyl groups assume an alternating up–down D_{3d} conformation. This means that all cyclopropyl groups are practically perpendicular with respect to the plane of the π system. Therefore, only the Walsh ω_S orbitals can interact with the e_{1g} and a_{2u} π orbitals of the benzene ring. From the basis energies of the e_{1g} orbitals of benzene (−9.25 eV), those of the ω_S orbitals of the cyclopropyl groups (−10.8 eV), and the first IP of **147** (7.75 eV) a value $B(\omega_S,2p) = -2.14$ eV is obtained for the interaction term in the Fock matrix between an orbital ω_S and an atomic 2p orbital of the benzene ring.

The PE spectrum of compound **142**, in which the bisected conformation of the cyclopropyl group is enforced, is compatible with a cross term $B(\omega_a,2p) \approx -2.5$ eV to −3.0 eV. From these results, it is clear that both orbitals ω_A and ω_S interact with the 2p atomic orbital to a similar extent; the ratio of the coupling elements is $B(\omega_A,2p)/B(\omega_S,2p) \approx 1.4$. It is thus confirmed that the Walsh orbitals of the cyclopropyl group interact appreciably with the aromatic π system to which they are attached in both the bisected and perpendicular conformation (cf. section 3.2.1).

3.6.4 Paracyclophanes

In [2.2]paracyclophane (**148**), the b_{3u} (π) orbital interacts strongly with the corresponding b_{3u} (σ) combination of the C_2H_4 bridges. The degree of interaction can be modified by variation of the energies of the participating orbitals. Gleiter et al.[166] have investigated [1:2;9:10]bismethano[2.2]paracyclophane (**149**; Table 3, entry 58). The PE spectra of **148** and **149** exhibit a strong composite band centered at about 8 eV. Deconvolution of these bands permitted the conclusion that the $^2B_{3u}$ state of the radical cation of **149** is shifted toward lower energy. σ/π interaction in the molecule with the two cyclopropyl rings (**149**) is thus even stronger than in the parent compound **148**.



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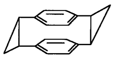
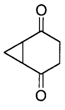


149

3.6.5 Cyclohexane-1,4-dione and Cyclohexene-1,4-dione Derivatives with Annellated Cyclopropane Rings



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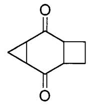

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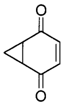

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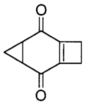
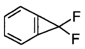


153

To investigate the amount of interaction between the n(O) orbitals and the σ frame, Gleiter et al.[167] have measured the PE spectra of cyclohexane-1,4-dione derivatives such as **150**–**153** and several related compounds. The experiments demonstrate that replacement of an unstrained C–C single bond by one of a strained system such as cyclopropane or cyclobutane enlarges the interaction between the 2p lone-pairs and the σ framework. This leads to an increase of the splitting of the first two IPs that are related to the oxygen lone-pair orbitals n^+ and n^-. Data of compounds **152** and **153** are summarized in Table 3 (entries 14 and 15).

3.6.6 Difluorocycloproparenes



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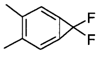

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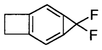

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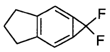

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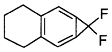

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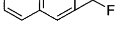

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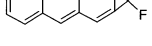

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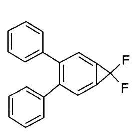

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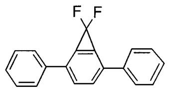
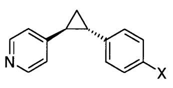


162

The PE spectra of a series of cycloproparenes and their 1,1-difluoro derivatives (**154**–**162**) have been recorded, analyzed, and assigned by correlation with the PE spectra of the parent molecules benzene, naphthalene, and anthracene.[98] It is shown that the PE spectroscopic data yield no information about the presence or absence of a Mills-Nixon effect (i.e., double bond fixation in the aromatic system) in the molecules investigated. The inductive effect of the bridging CH_2 group of the cyclopropeno ring is close to zero, whereas that of the CF_2 group leads to positive ionization energy shifts in good agreement with previous experience. The hyperconjugative interaction of the local pseudo-π orbital of the CH_2 group yields a significant destabilization of the π orbitals of B_1 symmetry.

3.6.7 1-Aryl-2-(4-pyridyl)-cyclopropanes

Distefano et al.[168] have investigated four pairs of cis/trans isomers of 1-aryl-2-(4-pyridyl)-cyclopropanes (**163**, **164**; X = H: Table 1, entries 60 and 61). They found that corresponding IP values of cis and trans derivatives are equal within the limits of experimental error. This finding indicates, at variance with solution results previously obtained, that in the gas phase there is no sizable through-space interaction between the MOs of the two cis aryl groups. A possible explanation of different conformations of the cis derivatives in the two phases is proposed.



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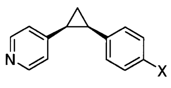
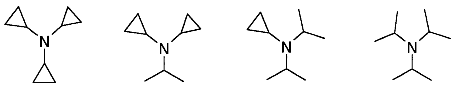


164

X = H, CH_3, OCH_3, NO_2

3.6.8 Cyclopropylamines

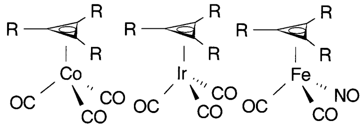
In connection with an investigation of the structure and properties of tricyclopropylamine and its radical cation, the PE spectra of tricyclopropylamine (**165**) and some related compounds, e.g., **166**−**168**, were analyzed by de Meijere et al.[169] The data are summarized in Table 1 (entries 72−78). Except for the first IP, which relates to the n_N orbital for all compounds, no analysis of the spectra has been attained. The IP_1 values for the tertiary amines with cyclopropyl or isopropyl groups show relatively large variation.



	165	166	167	168
IP_1:	8.44 eV	8.14 eV	7.79 eV	7.18 eV[170]
Σ<C-N-C	330.3°	338.9°	339.9°	348.6°

Replacement of an isopropyl by a cyclopropyl groups increases the first IP by 0.6−0.3 eV indicating delocalization of the n_N orbital into the cyclopropyl group (cf. section 3.2.1). This finding correlates with the variation of the degree of pyramidality of the nitrogen atom, as expressed by the sum of C−N−C bond angles. Planarization of the nitrogen atom leads to rehybridization from sp^3 to sp^2 so that the n_N orbital becomes a nearly plain p orbital.

3.6.9 Cyclopropenyl–Metal Complexes



R' = t-butyl

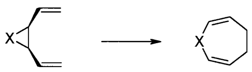
169 **170** **171**

Cyclopropenyl rings are known as π-ligands in transition metal complexes.[171,172] However, PE spectra of such compounds are rare. Lichtenberger et al.[173] have synthesized three η^3-cyclopropenylmetal complexes (**169**−**171**) and measured their He−I and He−II PE spectra. These compounds are of interest as possible intermediates in alkyne metathesis reactions. The PE spectra support a formal description of the complexes as d_{10} metals with ligands arranged in a tetrahedral array. The cobalt complex (**169**) reveals three peaks in the low ionization energy region that are primarily metal-based, consistent with the two states of e symmetry and one state of a_1 symmetry from the five d orbitals of the metal in C_{3v} symmetry. The spectrum of the iridium complex (**170**) has five peaks in this region due to large spin−orbit coupling that splits the e symmetry ionizations. The doubly degenerate peaks of the cobalt complex (**169**) are also expected to be split in the PE spectrum of the iron-nitrosyl complex (**171**) due to the lowering of the symmetry to C_s. Only four distinct peaks are seen for this complex, with two ionization bands at higher energy being merged in a broad envelope. The ionization cross sections indicate that the η^3-bound C_3R_3 ligand in these complexes is best described formally as a cation with a large amount of mixing and back-bonding from the metal d_π orbitals to the e_π* orbitals of the cyclopropenyl ring. The shifts and splittings in ionization energies with the metal and ligand perturbations in this series, the changes in ionization peak areas as a function of the excitation energy, and Fenske−Hall molecular orbital calculations[174,175] assist in the assignment and interpretation of the spectra.

4. Electronic Structure and Reactivity of Cyclopropane Compounds

4.1 Intramolecular Rearrangements Involving Cyclopropane Rings

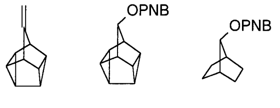
In substituted cyclopropanes, donor substituents weaken the remote C^2−C^3 bond by donation of electron density into the C^2−C^3 antibonding orbital ω_A, while acceptors strengthen this bond by withdrawing electron density from this high-lying orbital. These arguments have been used to explain the position of the equilibrium in substituted norcaradiene−cycloheptatriene interconversions, and to explain the rate of Cope rearrangements.[176−178] The rates of Cope rearrangements of 1,5-hexadienes are extraordinarily sensitive to groups substituting or bridging the 3 and 4 positions. While the activation enthalpy for the Cope rearrangement of 1,5-hexadiene through a boatlike transition state is about 172 kJ/mol,[179] that for the cyclopropyl compound is only 75 kJ/mol.[180] Mollere and Houk[181] have found a surprisingly good correlation between the rates of rearrangement of *cis*-1,2-divinylcyclopropane and related compounds (**172**) and the ionization energies (average of those related to the ω_A and ω_S orbitals) of the unsubstituted rings.



X = CH_2, SiH_2, NH, O, S, CH_2-CH_2 **172**

4.2 Anchimeric Assistance of Solvolytic Reactions of 7-Norbornyl Derivatives

Anchimeric assistance of solvoltytic reactions of 7-norbornyl derivatives by three-membered rings in endo−anti positions was analyzed by Martin et al.[182] The function of the three-membered rings is explained by formation of trishomocyclopropyl carbocations. The authors studied the PE spectrum of methylenehomocuneane (**173**; Table 3, entry 43; see also ref 1) and compared its first IP with those of related compounds. It was concluded that no vertical stabilization, but homoaromatic stabilization of a distorted, bridged transition state is responsible for the observed acceleration by a factor of 10^{12} of the rate of solvolysis of compound **174** as compared with the 7-norbornyl derivative **175**.



PNB = p-nitrobenzoyl

173 **174** **175**

4.3 Cycloaddition Reactions

Certain cyclopropanes afford five-membered carbocycles in [2σ + 2π] cycloaddition reactions with 2,3-

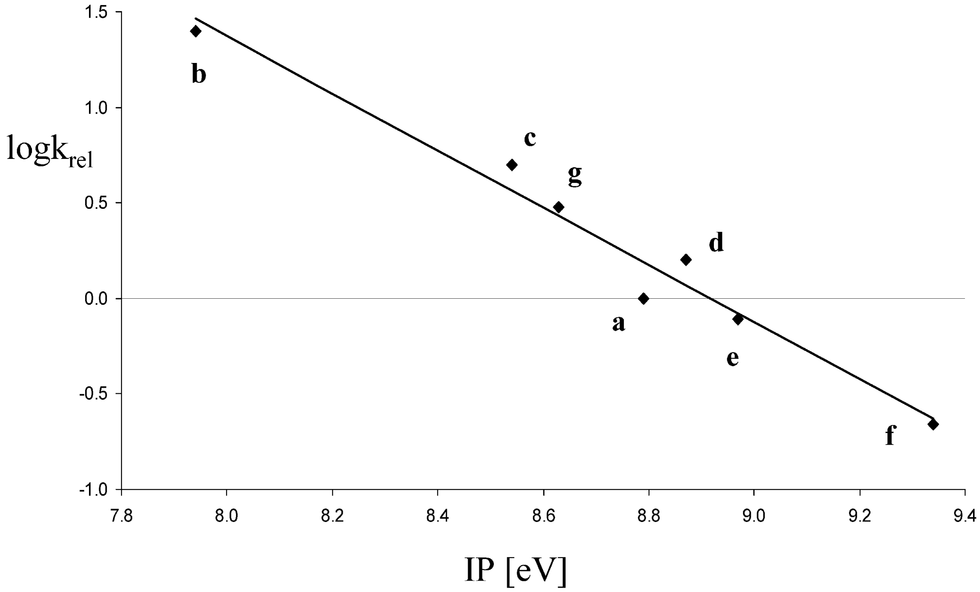
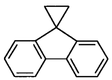


Figure 29. Correlation of relative rate constants log k_{rel} and IP_1 values of bicyclo[1.1.0]butanes (**177**).

dicyano-but-2-enedinitrile (TCNE). From the rather low first IP of dibenzo[d,f]spiro[2.4]heptane (**176**, $IP_1 = 7.84$ eV) as compared with 1,1-diphenylcyclopropane (**27**, $IP_1 = 8.50$ eV[80]) Nishida et al.[183] suggested that the reaction is initiated by an electron transfer between the reactants.



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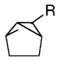
4.4 Radical Reactions of Bicyclo[1.1.0]butanes

Reactivity of bicyclo[1.1.0]butane (**67**) derivatives in addition reactions of phenylthiyl radicals to the central C^1-C^3 bond has been investigated by Szeimies and collaborators.[184] It was found that electron acceptor substituents in the 1-position of the bicyclus slowed the rate of the thiyl radical attack, whereas donor substituents enhanced this rate. In the series of 1-substituted tricyclo[4.1.0.0^{2,7}]heptanes (**177**) a linear correlation between IP_1 values and the log(k_{rel}) was found. This correlation is shown in Figure 29. The correlation coefficient is $r = 0.985$.

67



177

R	H	C_6H_5	CH_3	Cl	CO_2CH_3	CN	CH_3
	a	b	c	d	e	f	g

4.5 Conclusion

There are only few investigations combining PE spectroscopy and reactivity studies of cyclopropane compounds. However, the examples mentioned in the preceding section clearly indicate that valuable information can be obtained from such studies. Since PES allows measurement only of occupied MOs, first of all such reactions are suitable that are governed by HOMO energies.

5. Conclusions and Outlook

Because of its unusual properties, the three-membered carbocyclic ring is a unique structural unit in many important and interesting compounds, and its electronic interplay with other molecular fragments has been studied successfully in a great number of compounds by PE spectroscopy in the last thirty years (cf. ref 1, Tables 1–3). It is, however, surprising that several simple cyclopropane and cyclopropene derivatives—a few have been mentioned in this review—have not yet been investigated by this technique.

6. Acknowledgment

Assistance by Mr. Klaus Kowski with literature researches and acquisitions and by Mr. Wilhelm Sicking with orbital drawings is gratefully acknowledged.

7. Note Added after ASAP Posting

This paper has been amended since its original ASAP posting on 3/19/2003. A font error in ref 216 was corrected in the notations ΔIP_ω and Δr, and part (a), Cremer et al., was added to ref 37. The corrected version was posted 3/26/2003.

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(214) Whenever possible, Klyne-Prelog conformation nomenclature is used throughout this review: synperiplanar (sp), antiperiplanar (ap), and synclinal (sc) replace older terms such as s-cis, s-trans, and gauche, respectively. For cyclopropane and cyclopropene derivatives the reference angle (180° for ap, 0° for sp, 30−90° for sc) refers to the bisector of the ring. Likewise, this applies for substituents such as NH_2.

(215) Reinvestigation of the PE spectra of compounds **3** and **4** has shown that assignments have to be modified. Rademacher, P., to be published.

(216) Recent investigations of substituted cyclopropanes have revealed a linear correlation between ΔIP_{ω} and the difference Δr of the lengths of vicinal and distal C−C bonds. Rademacher, P.; Coskun, T.; Kowski, K.; Larionov, O.; de Meijere, A. *Chem. Eur. J.* **2003**, in print.

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