Photoelectron Spectra and Electronic Structures of Some Acceptor-Substituted Cyclopropanes: Linear Correlation of Substituent Effects on MO Energies with Molecular Structures

Paul Rademacher,*[a] Timur Coskun,[a] Klaus Kowski,[a] Oleg Larionov,[b] and Armin de Meijere[b]

Abstract: The relationship between electronic and geometrical structures in acceptor-substituted cyclopropanes has been investigated by B3LYP DFT calculations and photoelectron (PE) spectroscopy. The spectra of cyclopropanecarbaldehyde (**2**), cyclopropanecarboxylic acid (**3**), cyclopropanecarboxylic acid methyl ester (**4**), nitrocyclopropane (**5**), isothiocyanatocyclopropane (**6**), cyanocyclopropane (**7**), and 1,1-dicyanocyclopropane (**8**) have been analyzed. The first ionization potential (IP_1) of compounds **2**–**5** was found to be 0.1–0.4 eV higher than that of the analogous isopropyl derivatives indicating—contrary to expectation—that in these compounds the cyclopropyl group acts as a weaker electron donor than an isopropyl group. In the other compounds, IP_1 values are 0.4–1.1 eV lower than in the open-chain congeners. The Walsh orbitals ω_S and ω_A of the three-membered ring are substantially stabilized to different extents by interactions with substituent orbitals, and this is reflected in shortened distal and elongated vicinal C–C bonds. Although the nitro group in compound **5** causes large stabilizations of both ω_S and ω_A, their energy difference $\Delta\omega$ remains rather small; this is in agreement with a relatively small difference Δr of the C–C bond lengths. For the investigated monosubstituted cyclopropanes **2**–**7**, the largest effects with respect to $\Delta\omega$ and Δr are caused by the formyl group in carboxaldehyde **2**. Comparison of the results for nitriles **7** and **8** indicates that the effects of the cyano groups are additive. A linear relationship between $\Delta\omega$ and Δr was established by B3LYP DFT calculations on geometrically distorted cyclopropane (**1**) and from the PE data of **2**–**8**.

Keywords: conformational analysis · cyclopropanes · density functional calculations · electronic structure · ionization potentials · photoelectron spectroscopy

Introduction

The cyclopropyl group is considerably smaller than an isopropyl group, but it is a better electron donor for electron-deficient centers than all other alkyl groups.[1, 2] Accordingly, cyclopropyl-substituted compounds generally have a lower first ionization potential (IP_1) than the corresponding isopropyl derivatives.[3] However, there are exceptions, in particular when interactions between the ring and the substituent depend on the conformation. Examples are cyclopropyl methyl ketone ($IP_1 = 9.50$ eV)[4] and isopropyl methyl ketone ($IP_1 = 9.30$ eV).[5] The acetyl group, present in both compounds, is a *Z* type (electron acceptor) substituent[6] and the question arises whether other *Z*-substituted cyclopropanes behave in a similar manner. Considering the vast number of known photoelectron (PE) spectra of rather complex cyclopropane derivatives,[3, 7] it is surprising that many "simple" compounds—some are even commercially available—have apparently been overlooked. In particular, compounds with electron-acceptor substituents, such as cyclopropanecarbaldehyde (**2**), cyclopropanecarboxylic acid (**3**), cyclopropanecarboxylic acid methyl ester (**4**), nitrocyclopropane (**5**), isothiocyanatocyclopropane (**6**), cyanocyclopropane (**7**), and 1,1-dicyanocyclopropane (**8**) are of great interest with respect to their unusual structural and spectroscopic as well as chemical properties.[1] We have now analyzed the PE spectra

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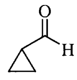

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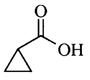

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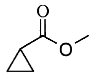

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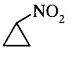

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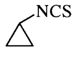

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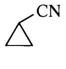

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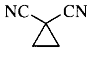

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of these compounds and investigated their geometric and electronic structures by quantum chemical methods. A possible correlation between the molecular and electronic structures was considered as the main purpose of this study.

Results and Discussion

Walsh orbitals and bonds lengths of distorted cyclopropane rings: Two models are common for the cyclopropane ring: the bent bond model of Förster,[8] Coulson, and Moffitt[9] and the Walsh model.[10] For the interpretation of PE spectra, the Walsh model and the related canonical SCF molecular orbitals (MOs) are widely used. In particular, the two degenerate σ_{C-C} orbitals ($2e'$) are important. They can be used to describe electronic interactions of the cyclopropane ring with orbitals of substituents or other neighboring groups (see below). These orbitals are 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 **1**, the orbitals ω_A and ω_S are no longer degenerate. It has been pointed out by Gleiter et al.[7, 11] and by Heilbronner et al.[12] 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, the MOs termed "ω_S" or "ω_A" are actually linear combinations of the Walsh orbitals, and usually show also contributions of $\pi(CH_2)$ and $\sigma(CH_2)$ orbitals. For short, such MOs are termed ω_S and ω_A that have high contributions of the Walsh-model orbitals.

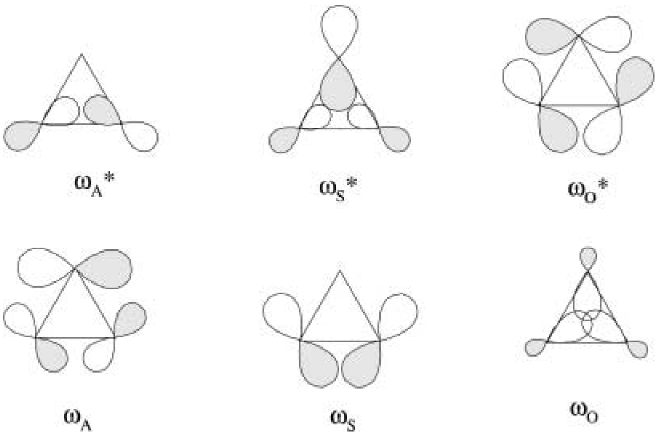


Figure 1. Walsh orbitals of cyclopropane.

A comprehensive analysis of X-ray structural data of cyclopropane derivatives has been carried out by Allen et al.[13] It shows systematic geometrical changes that are evidence for conjugation with π acceptor groups. In particular, a shortening of the C2–C3 distal bond by an amount δ (relative to the mean ring C–C bond length for that compound) occurs that is characteristic for each substituent, and a concomitant lengthening of the C1–C2 and C1–C3 vicinal bonds by approximately δ/2. Molecular orbital theory suggests that conjugation involves transfer of electron density from the cyclopropane Walsh orbitals to the π* orbitals of the substituent.[14–17] The degree of conjugation depends on the extent of orbital overlap, which is maximized for ω_A in the bisected (*synperiplanar* and *antiperiplanar*) conformation and for ω_S in the perpendicular (*synclinal*) conformation.[18, 19] This is illustrated in Figure 2 by a qualitative MO diagram that shows typical interactions of ω_A and ω_S with π and π* of a substituent in the *ap* or *sc* conformation, respectively. To our knowledge, no systematic investigation with regard to a quantitative correlation between the energy of the Walsh orbitals and the length of the C–C bonds has been published.

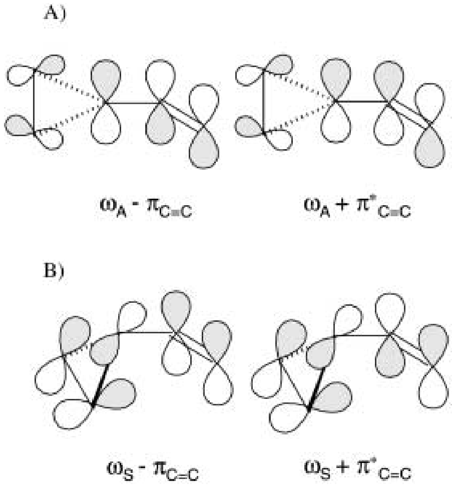


Figure 2. Interactions of the Walsh orbitals ω_A and ω_S with π and π* orbitals of a substituent. A) Bisected (*ap*), B) perpendicular (*sc*) conformation.

We have calculated the energy of the Walsh orbitals ω_A and ω_S for geometrically distorted cyclopropane (**1**) by means of the density functional theory (DFT) B3LYP method.[20] One C–C bond length (C2–C3) was fixed at certain values while the other parameters were optimized with C_{2v} symmetry of the molecule. The "frozen" bond length was varied between 148.0 and 154.0 pm, in steps of 0.5 pm. The results are summarized in Table 1. In Figure 3, the energies of ω_A and ω_S are plotted against the difference of the bond lengths Δ*r*. Both

Table 1. Energy of Walsh orbitals ω_A and ω_S [eV] for different structures of cyclopropane (bond lengths [pm], B3LYP/6-31+G(d)/results).

C2–C3[a]	C1–C2 = C1–C3[b]	Δ*r*[c]	ω_A	ω_S	Δω[d]
148.000	151.108	3.108	–8.2152	–7.9219	0.2933
148.500	151.105	2.605	–8.1859	–7.9404	0.2455
149.000	151.102	2.102	–8.1565	–7.9587	0.1978
149.500	151.099	1.599	–8.1274	–7.9769	0.1505
150.000	151.093	1.093	–8.0980	–7.9954	0.1026
150.500	151.091	0.591	–8.0691	–8.0136	0.0555
151.000	151.114	0.114	–8.0411	–8.0299	0.0112
151.500	151.089	–0.411	–8.0114	–8.0501	–0.0387
152.000	151.034	–0.966	–7.9807	–8.0724	–0.0917
152.500	151.028	–1.472	–7.9519	–8.0909	–0.1390
153.000	151.022	–1.978	–7.9236	–8.1091	–0.1855
153.500	151.017	–2.483	–7.8953	–8.1276	–0.2323
154.000	151.012	–2.988	–7.8670	–8.1459	–0.2789

[a] Independent (frozen) variable. [b] Dependent (optimized) variable. [c] Δ*r* = C1–C2 – C2–C3. [d] $\Delta\omega = \omega_S - \omega_A$.

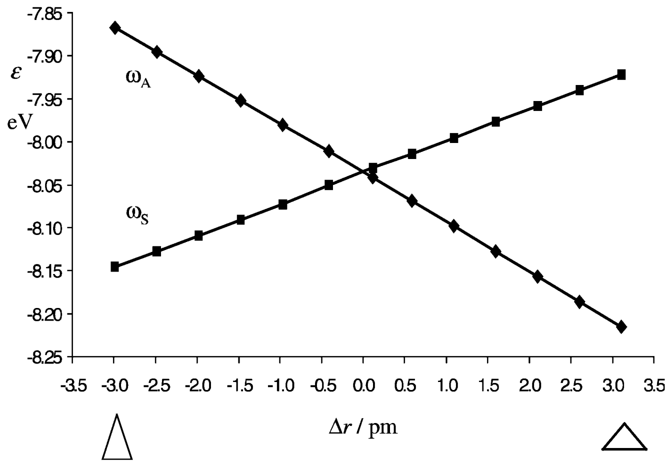


Figure 3. Energy of Walsh orbitals ω_A and ω_S for distorted cyclopropane (**1**).

parameters follow a straight line, crossing, as expected, at $\Delta r = 0.0$ pm where these orbitals are degenerate. At negative Δr values, ω_A is the highest (HOMO) and ω_S the second highest (HOMO – 1) occupied MO, and at positive Δr values the sequence is inverted. In the investigated range of Δr, the energy of ω_A changes by 0.34 eV and that of ω_S by 0.22 eV. This is in agreement with the differing shapes of the two Walsh orbitals.

As a consequence of the linear variation of both orbitals with Δr, their energy difference $\Delta\omega = \omega_S - \omega_A$ is also a linear function of Δr. Accordingly, it is obvious that there is a linear correlation between $\Delta\omega$ and Δr, as expressed by Equation (1), with $\Delta\omega$ in eV, Δr in pm, and a correlation coefficient $R = 1.000$.

$$\Delta\omega^{\mathrm{B3LYP}} = 0.094\,\Delta r \tag{1}$$

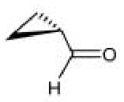
This simple linear relationship certainly results from the overlap of two orbitals on neighboring atoms changing linearly for small distance variations. Since Kohn–Sham orbitals obtained by DFT methods[21] are actually not SCF MOs, we have repeated the calculations with the HF method. Similar results were obtained as those from the B3LYP method, leading to a slightly different slope in the linear relationship [Eq. (2)] between $\Delta\omega$ and Δr, with all the points exactly on a straight line ($R = 1.000$).

$$\Delta\omega^{\mathrm{HF}} = 0.125\,\Delta r \tag{2}$$

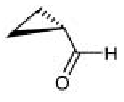
It can thus be concluded that the linear proportionality between the geometrical distortion of the cyclopropane ring and the energy difference of the two Walsh orbitals ω_S and ω_A is well established. Within the context of the present investigation, it appears to be most interesting to find out whether this or a similar relationship also holds for substituted cyclopropanes and whether it can be investigated by PE spectroscopy.

Molecular structures of compounds 2–8: We have investigated the molecular structure of **2**–**8** by B3LYP calculations and the 6-31 + G(d) basis set. We refrain from presenting all structural data, but restrict the material to the most important bond lengths of the cyclopropane ring. These are summarized in Table 2 together with the average bond lengths and Δr values.

The molecular structure and the conformational properties of cyclopropanecarbaldehyde (**2**) have been investigated recently by the B3LYP method.[22] The *antiperiplanar* conformer (*ap*-**2**) was found to be slightly more stable than the *synperiplanar* conformer (*sp*-**2**). This is in agreement with experimental findings.[23, 24]



ap-**2**



sp-**2**

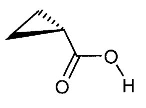
Marstokk et al.[25] have determined the structure of gaseous cyclopropanecarboxylic acid (**3**) by means of microwave spectroscopy, electron diffraction, and ab initio calculations at the 4-21G level of theory. An X-ray analysis has been performed by de Boer and Stam.[26] The results were confirmed recently by Hou and Huang[22] in a B3LYP study. The molecule was found to prefer a conformation that has the carbonyl group *synperiplanar* (*sp*) to the cyclopropane ring. A second conformer with the carbonyl group *antiperiplanar* (*ap*) to the ring is also present with an energy 3–5 kJ mol^{-1} less stable. In both rotamers the OH group was found to be *synperiplanar* to the carbonyl group. These two conformers are termed *ss*-**3** (*syn*–*syn*) and *as*-**3** (*anti*–*syn*).

No structural data could be found in the literature for methyl cyclopropanecarboxylate (**4**). It appears, however, to be reasonable to assume a similar conformational behavior as

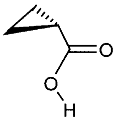
Table 2. Calculated bond lengths [pm] of compounds **2**–**8** (B3LYP results).

	ap-**2**	*sp*-**2**	*ss*-**3**[a]	*as*-**3**	*ss*-**4**	*as*-**4**	*b*-**5**	*ap*-**6**[b]	*sp*-**6**	**7**	**8**[c]
C1–C2 = C1–C3	152.8	153.0	152.4 (152.4)	152.5	152.3	152.4	151.2	151.3 (152.0)	151.5	152.4	154.1
C2–C3	149.1	148.7	149.2 (149.3)	149.4	149.4	149.5	149.8	150.8 (151.5)	151.0	149.9	148.8 (148.5)
mean[d]	151.6	151.6	151.3 (151.4)	151.5	151.3	151.4	150.7	151.1 (151.8)	151.3	151.6	152.3
Δr[e]	3.7	4.3	3.2 (3.1)	3.1	2.9	2.9	1.4	0.5 (0.5)	0.5	2.5	5.3

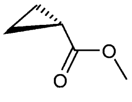
[a] Experimental (ED, MW) values[25] in parentheses. [b] Experimental (ED, MW) values[28] in parentheses. [c] Experimental (MW) value[29] in parentheses. [d] (C1–C2 + C1–C3 + C2–C3)/3. [e] (C1–C2 + C1–C3)/2 – C2–C3.



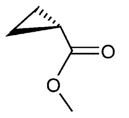
ss-**3**



as-**3**

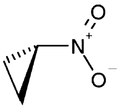


ss-**4**

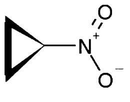


as-**4**

for compounds **2** and **3**. Therefore, we have investigated two conformers (*ss*-**4**, *as*-**4**). The conformational properties of nitrocyclopropane (**5**) have been investigated by microwave spectroscopy.[27] However, molecular structure parameters were not determined. Only the bisected conformer (*b*-**5**) was found, but the existence of small amounts of other, less stable conformers could not be ruled out. In analogy to compounds **2** and **3**, for which such conformations were found to be transition states,[22] it seems to be quite unlikely that the perpendicular form (*p*-**5**) is a second stable conformer.

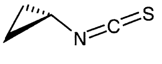


b-**5**

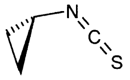


p-**5**

For isothiocyanatocyclopropane (**6**), two distinct conformers, *ap*-**6** and *sp*-**6**, were identified by Durig et al.[28] in an electron diffraction study, with the proportion of the former being 72 ± 5% at 35 °C. Since the cyano group is linear, no conformational preferences have to be considered for cyanocyclopropane (**7**) and 1,1-dicyanocyclopropane (**8**). The dinitrile **8** has been investigated by microwave spectroscopy.[29] However, only an estimated value of 148.5 ± 10 pm was given for the distal bond lengths.



ap-**6**



sp-**6**

To avoid confusion, it is worth mentioning that the structures *ap*-**2**, *sp*-**2**, *ss*-**3**, *as*-**3**, *ss*-**4**, and *as*-**4** are bisected conformers. The molecular symmetry of all conformers of compounds **2**–**7** is C_s, that of compound **8** is C_{2v}.

The known or expected conformational and structural properties of **2**–**8** are confirmed by our B3LYP calculations (Table 2). The average bond length is approximately 0.4–2.0 pm greater than the C–C bond length in cyclopropane (**1**, 150.3 pm).[30] In agreement with expectations,[13] the distal bond of the three-membered ring is shortened by 0.4–1.6 pm relative to the value in the parent molecule while the vicinal bonds are lengthened by 0.9–3.8 pm. The corresponding Δr values range from 0.5 (*sp*-**6**) to 5.3 pm (**8**). The largest effect on the bond lengths is thus found in the dinitrile **8**: however, of the singly substituted compounds, aldehyde *sp*-**2** shows the maximum modifications, whereas the isothiocyanate *sp*-**6** suffers the smallest modifications. The latter compound is exceptional in so far as its distal bond length is also increased relative to that of cyclopropane (**1**) itself. This is an indication that the isothiocyanato group acts as a weak electron donor with respect to the cyclopropyl ring. Compounds **2**–**4**, for which different conformers have been studied, exhibit slight differences (0.1–0.4 pm) for *syn*- and *antiperiplanar* orientations of the carbonyl group. To compare the effect of the nitrile group with those of the other substituents, the mononitrile **7** has also been investigated. The Δr value for the dinitrile **8** is approximately twice as large as that for the mononitrile, indicating additivity of the effects of the two substituents in **8**.

The bisected conformation of molecules **2**–**8** maximizes the donor–acceptor interaction between the HOMO of the cyclopropyl group and the LUMO of the substituent's π system (cf. Figure 2). 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. The perpendicular conformation would enhance the interactions of the cyclopropyl LUMO and the HOMO of the π system to result in the donation of electron density from the π system to the cyclopropyl group, which, incidentally, is a weak π acceptor.[31]

Electronic structures: For the interpretation of PE spectra, the Walsh model and the related canonical orbitals are generally used.[3, 7] As mentioned above, the two degenerate σ_{C-C} orbitals (2e′, ω_A and ω_S) are important which can be employed to describe electronic interactions of the cyclopropane ring with orbitals of substituents. In derivatives of cyclopropane with lower symmetry than that of the parent molecule (point group D_{3h}), ω_A and ω_S are no longer degenerate and are often, but by no means always, the highest (HOMO) and second highest (HOMO − 1) occupied MOs.

All monosubstituted derivatives of cyclopropane 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 C1 lying in this plane. Accordingly, in such cyclopropane derivatives, ω_S can have a contribution on C1 that is directed towards the centre 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.

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 (Figure 2).

The PE spectrum of cyanocyclopropane (cyclopropanecarbonitrile, **7**) has been investigated.[32, 33] The PE spectra of **2**–**6**, and **8** are depicted in Figures 4 and 5. The relevant ionization potentials are summarized in Tables 3–9 together with some results of quantum chemical calculations.

Assignment of the IPs can be achieved by means of Koopmans theorem,[34] $IP_i = -\varepsilon_i$, which relates vertical ionization energies to SCF MO energies. Although Kohn–Sham orbitals obtained by DFT methods[21] are not SCF MOs 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.[35, 36] Much better agreement between experimental and theoretical values can be expected for the first vertical IP (IP_{1v}) when the energies of the molecule M and the radical cation $M^{\cdot+}$ are calculated by the B3LYP method. For IP_{1v} a single point calculation is performed for $M^{\cdot+}$ with the molecular geometry. The corresponding energy values are included in Tables 3–9. We can now correct the other ε^{B3LYP} values by the difference between $-\varepsilon$(HOMO) and the calculated IP_{1v} to obtain higher IP_v values.[36] Whereas typical energy differences between IP_i and $-\varepsilon_i^{B3LYP}$ values are about 2 eV, experimental and calculated IP_i values differ only by 0.1–0.4 eV. Furthermore, both $-\varepsilon_i^{B3LYP}$ and calculated IP_i (calcd) values are linearly correlated with the experimental IP_i(exp) values with correlation coefficients (0.990, 0.986) close to 1.000. The orbital energies ε_i obtained by the semiempirical method PM3 (Tables 3–9) also correlate acceptably well with the experimental IP_i values ($R = 0.939$). In several cases, in particular for compounds **4**, **5**, **7**, and **8**, the PM3 orbital sequence differs from that obtained by the B3LYP method. The semiempirical method can thus only be used with reservation for the analysis of the PE spectra of these compounds.

The first IP (9.84 eV) of compound **2** arises from the removal of a lonepair electron from the oxygen atom (Figure 4, Table 3). The corresponding value of the closely related isobutyraldehyde is 9.71 eV.[5] The energy of the n(O) orbital of **2** is thus increased by ≈0.1 eV relative to the acyclic congener. The next two IPs of **2** (10.95, 11.79 eV) are assigned to the Walsh orbitals ω_A (4a″) and ω_S (9a′), and the fourth IP (13.30 eV) is ascribed to an MO that has mainly $\pi(CH_2)$ character. These three IPs (IP_2–IP_4) are thus related to characteristic MOs of the parent hydrocarbon cyclopropane (**1**), in which they have the values 10.86 (ω_A, ω_S) and 12.96 eV ($\pi(CH_2)$)[37, 38] The MO 4a″ exhibits a significant out-of-phase contribution from the π(C=O) orbital. The corresponding in-phase combination leads to MO 2a″, which has mainly π(C=O) character; and the strong ionization band at 13.95 eV is assigned to this orbital. The calculated MO energies and IP^{B3LYP} values differ generally by less than 0.2 eV for the two conformers (*ap*-**2**, *sp*-**2**) so that it would be very difficult to assign individual peaks to the different rotamers, particularly because *sp*-**2** should be present only in minor amounts. The energy difference between *ap*-**2** and *sp*-**2** is calculated to be 0.62 kJ mol^{-1}.

The PE spectrum of the carboxylic acid (**3**) exhibits three strong bands between 10 and 14 eV that arise from several ionization events (Figure 4, Table 4). This means that some bands overlap strongly. This renders the determination of exact IP values difficult in these cases. The first IP (10.80 eV) is 0.3 eV larger than that of isobutyric acid (10.50 eV[39]). This ionization is related to the oxygen lonepair MO of the carbonyl oxygen atom. The second IP (≈11.2 eV) originates from the removal of an electron from the orbital 5a″ that can be described as an out-of-phase combination of ω_A and the π_2 orbital of the carboxyl group. Two ionization events contribute to the third IP (11.85 eV), namely that of ω_S (11a′) and of the in-phase combination of ω_A and the π_2 orbital of the carboxyl group. Alternatively, as an approximation, the latter

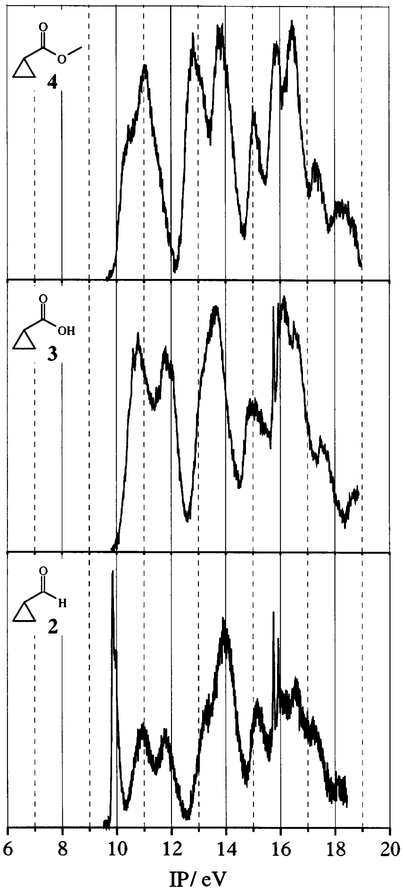


Figure 4. PE spectra of compounds **2**–**4**.

Table 3. Ionization potentials IP [eV] and orbital energies ε [eV] of cyclopropanecarbaldehyde (**2**).

IP	*ap*-**2** – ε^{PM3}	– ε^{B3LYP}	$IP^{B3LYP[a]}$	*sp*-**2** – ε^{PM3}	– ε^{B3LYP}	$IP^{B3LYP[b]}$		
9.84	10.67	7.16	9.71	10.64	7.19	9.76	10a′	n(O), ω_s
10.95	11.94	8.49	11.04	11.87	8.33	10.90	4a″	$\omega_A - \pi(C{=}O)$
11.79	12.25	9.12	11.67	12.19	8.94	11.51	9a′	ω_S
13.30	12.75	10.67	13.22	12.53	10.33	12.90	3a″	$\pi(CH_2)$
	13.95	11.09	13.64	13.73	11.04	13.61	8a′	$\pi(CH_2)$
13.95	14.50	11.27	13.82	14.45	11.10	13.67	2a″	$\pi(C{=}O) + \omega_A$

[a] Calculation of first vertical IP: energy difference of molecule M (–231.229611 au) and radical cation $M^{\cdot+}$ (–230.872788 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.55$ eV. [b] Calculation of first vertical IP: energy difference of molecule M (–231.229375 au) and radical cation $M^{\cdot+}$ (–230.870691 au) with identical geometry. Higher IPs: $IP_i = -\Delta\omega_i + 2.57$ eV.

Table 4. Vertical ionization potentials IP [eV] and orbital energies ε [eV] of cyclopropanecarboxylic acid (**3**).

IP	*ss*-**3** $-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[a]}$	*as*-**3**-ε^{PM3}	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[b]}$		
10.80	11.36	7.91	10.48	11.32	7.70	10.13	12a′	$n(C{=}O)$
11.2 sh	11.91	8.41	10.98	11.87	8.44	10.87	5a″	$\omega_A - \pi_2(CO_2)$
11.85	12.35	8.83	11.40	12.39	9.13	11.56	11a′	ω_S
	12.43	9.09	11.66	12.48	9.14	11.57	4a″	$\pi_2(CO_2) + \omega_A$
13.2 sh	12.71	10.46	13.03	12.76	10.51	12.94	3a″	$\pi(CH_2)$

[a] Calculation of first vertical IP: energy difference of molecule M (−306.485058 au) and radical cation $M^{\cdot+}$ (−306.099899 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.57$ eV. [b] Calculation of first vertical IP: energy difference of molecule M (−306.483465 au) and radical cation $M^{\cdot+}$ (−306.111321 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.43$ eV.

MO (4a″) may be considered as a lonepair orbital of the hydroxy group ($n_\pi(OH)$). A value of 13.2 eV, which is found as a shoulder on the strong band centered at 13.65 eV, is assigned to a $\pi(CH_2)$ orbital. For this compound, the calculated IP^{B3LYP} values of the two conformers differ by up to ≈0.4 eV, which might be large enough to distinguish them. The energy difference between *ss*-**3** and *as*-**3** is calculated as 4.18 kJ mol^{-1}.

In the PE spectrum of methyl cyclopropanecarboxylate (**4**), a broad composite band is observed between 10 and 12 eV, which displays maxima at 10.50 and 11.04 eV (Figure 4, Table 5). In addition, two shoulders on the high-energy side can be found at approximately 11.5 and 11.8 eV. This band system is followed by two overlapping bands with maxima at 13.00 and 13.82 eV and a shoulder at ≈12.6 eV. The calculated orbital energies and IP values differ only slightly for the two conformers *ss*-**4** and *as*-**4**; however, the former is calculated to be more stable by 5.16 kJ mol^{-1} than the latter. Comparison of the first IP of **4** with that of isobutyric acid methyl ester (10.18 eV)[40] indicates that the cyclopropyl group in **4** is obviously a weaker electron donor than the isopropyl group. Assignments of the IPs of **4** are similar to those of compound **3**, and the values of the methyl ester **4** for $n(C{=}O)$ and $\omega_A - \pi(CO_2)$ (6a″) are 0.2–0.3 eV lower than for the carboxylic acid **3**. On the other hand, the IP value for ω_S of **4** (13a′) is quite similar to that of **3** (11a′) indicating that this MO does not interact significantly with orbitals of the substituent.

For compound **5**, the first three ionization events are related to MOs which are essentially localized on the nitro group (Figure 5, Table 6). As in acyclic aliphatic nitroalkanes. such as nitromethane, nitroethane and nitropropane,[41] these ionizations involve the removal of electrons from the orbitals $n(NO_2)^+$, $n(NO_2)^-$, and $\pi_2(NO_2)$, respectively. In 2-nitropropane, the corresponding IP values are 10.48 and 11.26 eV, the latter is related to two ionizations.[37] The characteristic IPs of the nitro group are thus lowered by the isopropyl group to a higher degree than by the cyclopropyl group. The next two IPs of **5** are assigned to the removal of electrons from the Walsh orbitals ω_A (4a″) and ω_S (10a′), respectively. Both orbitals interact with orbitals of the nitro group with the correct symmetry: ω_A is destabilized by interaction with $\pi_1(NO_2)$ and ω_S suffers stabilization by interaction with $n(NO_2)^+$. The destabilizing (antisymmetric) interaction corresponding to the latter MO is present in 12a′. Finally, an ionization at 13.87 eV is assigned to a $\pi(CH_2)$ orbital.

Table 6. Ionization potentials IP [eV] and orbital energies ε [eV] of nitrocyclopropane (bisected conformer *b*-**5**).

IP	$-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[a]}$		
10.87	12.30	8.27	10.76	12a′	$n(NO_2)^-$
11.38	12.10	8.71	11.20	11a′	$n(NO_2)^+ - \omega_S$
11.6 sh	12.06	8.84	11.33	5a″	$\pi_2(NO_2)$
12.0 sh	13.00	9.31	11.80	4a″	$\omega_A - \pi_1(NO_2)$
12.57	13.15	9.82	12.31	10a′	$\omega_S + n(NO_2)^+$
13.87	13.24	11.06	13.55	3a″	$\pi(CH_2)$

[a] Calculation of first vertical IP: energy difference of molecule M (−322.414459 au) and radical cation $M^{\cdot+}$ (−322.018864 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.49$ eV.

For the assignment and interpretation of the PE spectrum of isothiocyanatocyclopropane (**6**) comparison to the spectra of methyl isothiocyanate[42–45] and isopropyl isothiocyanate[45] is quite useful. Two ionization events, which can be described as out-of-phase combinations of π_2 of the isothiocyanato group and ω_A or ω_S, respectively, contribute to the first broad band (Figure 5, Table 7). These interactions lower the IP values by ≈0.3 eV relative to those of the methyl compound. The double band, with maxima at 11.23 and 11.73 eV, is assigned to ionizations from the Walsh orbitals ω_A or ω_S, respectively, with destabilizing contributions of π_1 of the isothiocyanato group. The IPs of the corresponding symmetrical combina-

Table 5. Ionization potentials IP [eV] and orbital energies ε [eV] of cyclopropanecarboxylic acid methyl ester (**4**).

IP	*ss*-**4** $-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[a]}$	*as*-**4** $-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[b]}$		
10.50	11.19	7.71	10.17	11.15	7.51	9.84	14a′	$n(C{=}O)$
11.04	11.46	8.27	10.73	11.46	8.30	10.63	6a″	$\omega_A - \pi(CO_2)$
11.5 sh	12.01	8.45	10.91	12.02	8.47	10.70	5a″	$n_\pi(OMe) - \omega_A$
11.8 sh	12.26	8.66	11.12	12.27	8.97	11.30	13a′	ω_s
12.6 sh	13.10	9.92	12.38	13.24	10.01	12.34	12a′	$n_o(OMe) - \pi(CH_3)$
13.00	12.63	10.27	12.73	12.68	10.39	12.72	4a″	$\pi(CH_2)$
13.82	13.75	10.95	13.41	13.72	10.81	13.14	11a′	$\pi(CH_3)$
	13.98	11.09	13.55	14.01	11.07	13.40	3a″	$\pi(C{=}O) + \omega_A$

[a] Calculation of first vertical IP: energy difference of molecule M (−345.790739 au) and radical cation $M^{\cdot+}$ (−345.417024 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.46$ eV. [b] Calculation of first vertical IP: energy difference of molecule M (−345.788772 au) and radical cation $M^{\cdot+}$ (−345.427131 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.33$ eV.

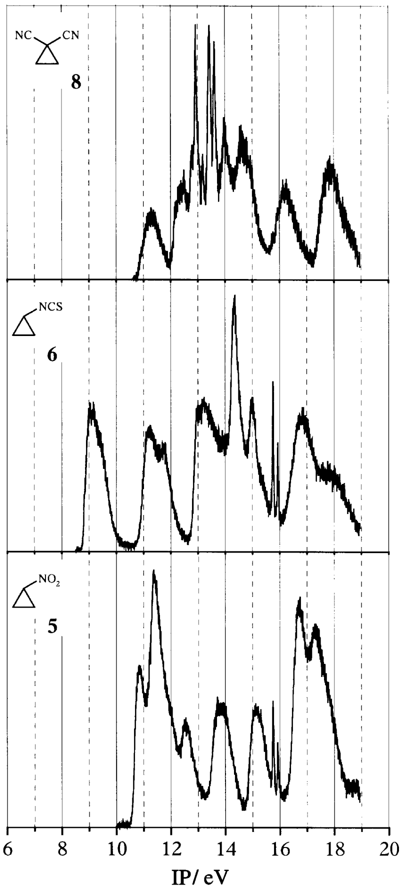


Figure 5. PE spectra of compounds **5**, **6**, and **8**.

tions of π_1 and the Walsh orbitals are found at 13.5 and 14.33 eV. The latter band also contains an ionization contribution from the n(S) orbital that has a value of 14.60 in Me-NCS. In compound **6** we observe that the first IP is ≈0.4 eV lower than in the corresponding isopropyl derivative (9.47 eV[45]). For this compound, the calculated IP^{B3LYP} values of the two conformers generally differ by less than 0.1 eV, so that individual peaks cannot be assigned to the different rotamers. The energy difference between *ap*-**6** and *sp*-**6** is calculated to be 1.47 kJ mol^{-1}. For both conformers, the quantum chemical calculations predict a very close energy of the third and the fourth highest occupied MO, to which ω_A and ω_S, respectively, mainly contribute. The PE spectrum reveals, however, two overlapping ionization bands with well-separated maxima at 11.23 and 11.73 eV, leading to $\Delta IP_\omega = 0.50$ eV.

Our analysis of the PE spectrum of cyanocyclopropane (**7**) confirms the interpretation given by Gochel–Dupuis[33] (Table 8). The PE spectrum of the dicarbonitrile **8** exhibits two isolated bands at 11.31 and 12.45 eV that are assigned as $3b_1$ and $7a_1$, respectively (Figure 5, Table 9). The corresponding orbitals can be characterized preliminarily as out-of-phase combinations of ω_S and ω_A, respectively, with $\pi(C{\equiv}N)$ and $\pi'(C{\equiv}N)$ combinations of the same symmetry. Ionizations at 13.99 ($5a_1$) and 14.8 eV ($2b_1$) correspond to the respective in-phase combinations. At 12.94 ($2a_2$), 13.42 ($4b_2$) and 13.62 eV ($6a_1$) there are three intense and sharp ionizations as well as a broader band at 12.80 eV ($5b_2$). As indicated, these four IPs

Table 8. Ionization potentials IP [eV] and orbital energies ε [eV] of cyclopropanecarbonitrile (**7**).

IP[a]	$-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[b]}$		
10.91	11.67	8.24	10.65	4a″	$\omega_A - \Delta\omega$CN)
11.54	12.06	8.78	11.19	9a′	$\omega_S - \Delta\omega$CN)
12.54	12.41	9.80	12.21	8a′	σ
13.00	13.36	10.10	12.51	7a′	n(N)
13.37	12.91	10.45	12.86	3a″	$\Delta\omega$CN)
13.94	14.05	10.98	13.39	2a″	$\Delta\omega CH_2$)

[a] Ref. [33]. [b] Calculation of first vertical IP: energy difference of molecule M (−210.146759 au) and radical cation $M^{\cdot+}$ (−209.755403 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.41$ eV.

Table 9. Ionization potentials IP [eV] and orbital energies ε [eV] of cyclopropane-1,1-dicarbonitrile (**8**).

IP	$-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[a]}$	$-\varepsilon^{B3LYP[b]}$	$IP^{B3LYP[b,c]}$		
11.31	11.86	8.70	10.86	8.77	10.94	$3b_1$	$\omega_A - \pi(CN)^+$
12.45	12.69	9.69	11.85	9.77	11.94	$7a_1$	$\omega_S - \pi(CN)^+$
12.80	13.20	9.78	11.94	9.88	12.05	$5b_2$	$\pi(CN)^-$
12.94	12.75	10.01	12.17	10.10	12.27	$2a_2$	$\pi(CN)^-$
13.42	13.23	10.61	12.77	10.65	12.82	$4b_2$	$n(N)^-$
13.62	12.97	10.78	12.94	10.80	12.97	$6a_1$	$n(N)^+$
13.99	14.19	11.22	13.38	11.30	13.47	$5a_1$	$\omega_S + \pi(CN)$
14.68	13.67	11.77	13.93	11.79	13.96	$1a_2$	$\pi(CH_2)$
14.8 sh	15.12	11.90	14.06	11.98	14.15	$2b_1$	$\omega_A + \pi(CN)$

[a] Calculation of first vertical IP: energy difference of molecule M (−302.379730 au) and radical cation $M^{\cdot+}$ (−301.980455 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.16$ eV. [b] Basis set: 6-311+G(d,p). [c] Calculation of first vertical IP: energy difference of molecule M (−302.451284 au) and radical cation $M^{\cdot+}$ (−302.049367 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.17$ eV.

Table 7. Ionization potentials IP [eV] and orbital energies ε [eV] of isothiocyanatocyclopropane (**6**).

IP	*ap*-**6** $-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[a]}$	*sp*-**6** $-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	$IP^{B3LYP[b]}$		
9.09	9.09	6.59	8.74	9.12	6.58	8.76	5a″	$\pi_2(NCS) - \omega_A$
9.45 sh	9.65	7.05	9.20	9.64	6.94	9.12	11a′	$\pi_2(NCS) - \omega_S$
11.23	12.41	8.98	11.13	12.48	9.01	11.19	4a″	$\omega_A - \pi_2(NCS)$
11.73	12.44	9.00	11.15	12.59	9.14	11.32	10a′	$\omega_S - \pi_2(NCS)$
13.20	12.86	10.70	12.85	12.99	10.76	12.94	3a″	$\pi(CH_2)$
13.5 sh	14.18	11.01	13.16	13.98	11.08	13.26	9a′	$\pi_2(NCS) + \omega_S$
14.33	14.88	11.76	13.91	14.90	11.80	13.98	2a″	$\pi_2(NCS) + \omega_A$
	15.11	11.83	13.98	15.09	11.82	14.00	7a′	n(S)

[a] Calculation of first vertical IP: energy difference of molecule M (−608.3420886 au) and radical cation $M^{\cdot+}$ (−608.020708 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.15$ eV. [b] Calculation of first vertical IP: energy difference of molecule M (−608.341529 au) and radical cation $M^{\cdot+}$ (−608.019656 au) with identical geometry. Higher IPs: $IP_i = -\varepsilon_i + 2.18$ eV.

are assigned to the two nitrile groups. The corresponding IPs of malononitrile have been found to lie in a similar range (13.1 – 14.02 eV).[46] For comparison with the corresponding isopropyl compounds, the first IP of isobutyronitrile (11.74 eV)[37] and 2,2-dicyanopropane (2,2-dimethylmalononitrile, 12.39 eV)[46] are most useful. IP^{B3LYP} data for dinitrile **8**, calculated with the larger basis set 6-311 + G(d,p), are included in Table 9. They show a significantly improved agreement with the experimental IP values compared to those obtained with the smaller basis set.

As we have seen in the above sections, the first IP of compounds **2** – **5** is approximately 0.1 – 0.4 eV higher than that of the isopropyl derivative with the same functional group. On the other hand, in isothiocyanate **6** and in the two nitriles **7** and **8**, the IP_1 value of the corresponding open-chain compounds is considerably larger (0.4 – 1.1 eV) than that of the cyclopropane derivative. Our expectation with regard to the higher electron-donor capacity of the cyclopropyl group as compared to the isopropyl group is only confirmed in the latter three examples. An explanation for this observation is found in the different interactions of the HOMO with unoccupied MOs. While in the latter group of cyclopropane derivatives the HOMO and LUMO are of the same symmetry (e.g. **8**: HOMO = $3b_1$, LUMO = $4b_1$), in the former group they differ in symmetry (e.g. **2**: HOMO = 10a′, LUMO = 5a″). The HOMO of **2** – **5** will thus be more efficiently stabilized than that of **6** – **8**. Since the LUMO always contains larger contributions of at least one of the antibonding Walsh orbitals (Figure 1) a similar interaction in the open-chain congeners is absent or much weaker.

Quantitative correlation between ionization energies and bond lengths: When we compare the IP values assigned to the Walsh orbitals ω_A and ω_S of compounds **2** – **8** with that of cyclopropane (**1**, 10.86 eV[37, 38]), a marked variation with the substituent is observed. We find the greatest stabilization for the nitro derivative **5** ($\Delta IP(\omega_S) = 1.71$ eV, $\Delta IP(\omega_A) = 1.14$ eV) and the smallest for the isothiocyanate **6** ($\Delta IP(\omega_S) = 0.87$ eV, $\Delta IP(\omega_A) = 0.37$ eV). However, there is a distinct difference for both values, expressed by $\Delta IP_\omega = IP(\omega_S) - IP(\omega_A)$. While in compound **5** both ω_S and ω_A are stabilized to larger extents, leading to a relatively small $\Delta IP_\omega = 0.57$ eV, in the dinitrile **8** ω_S has a considerably larger shift than ω_A ($\Delta IP_\omega = 1.14$ eV). Of the monosubstituted derivatives, the aldehyde **2** exhibits the largest value ($\Delta IP_\omega = 0.84$ eV), followed by the ester **4** ($\Delta IP_\omega = 0.76$ eV).

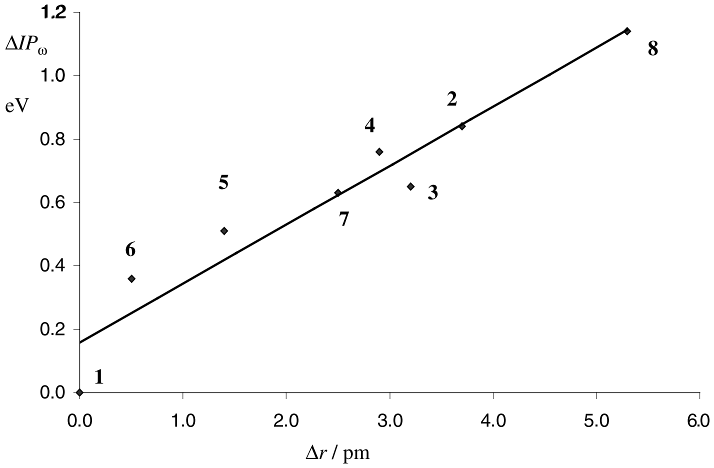


Figure 6. Correlation of ΔIP_ω and Δr for compounds **1** – **8**.

It has been outlined in the section dealing with the bond lengths of the cyclopropane ring in **2** – **8**, that the distortion of the ring—measured by the parameter Δr—is mainly caused by the interaction of the Walsh orbital ω_A with substituent orbitals. It would certainly be of great interest to find a quantitative relationship between the energy of ω_A (or the energy difference $\Delta\omega = \omega_S - \omega_A$) and Δr similar to that calculated for distorted unsubstituted cyclopropane [Eq. (1) and (2)]. In Figure 6, the energy difference $\Delta IP_\omega = IP(\omega_S) - IP(\omega_A)$ of ω_S and ω_A, as determined from the PE spectra, (Tables 3 – 9) is visualized for compounds **1** – **8** as a function of Δr (Table 2). The least-squares trend line follows Equation (3), with a correlation coefficient $R = 0.962$.

$$\Delta IP_\omega = 0.187\,\Delta r + 0.157 \tag{3}$$

Except for the constant term, Equation (3) is equivalent to Equations (1) and (2). This indicates that the quantitative correlation between the geometrical distortion of the cyclopropane ring and the energy split of the Walsh orbitals ω_A and ω_S is confirmed experimentally by PE spectroscopy for cyclopropane derivatives with electron-accepting substituents. If, instead of the experimental ΔIP_ω values, those calculated by the B3LYP method are used for this correlation, Equation (3) takes the form of Equation (4).

$$\Delta IP_\omega^{B3LYP} = 0.174\,\Delta r + 0.094 \; (R = 0.954) \tag{4}$$

That Equations (3) and (4), as opposed to Equations (1) and (2), include a constant term probably has to be interpreted as a consequence of different contributions of the substituents to Δr as well as to ΔIP_ω. This is certainly also reflected in the scattering of the points in Figure 6. Such contributions could most probably be distinguished as electronic (inductive and conjugative) and steric effects. It is evident that in a monosubstituted cyclopropane ring ω_A and ω_S would have different energies ($\Delta IP_\omega \neq 0$) even if all C–C bonds were equally long ($\Delta r = 0$). That this actually is the case is nicely demonstrated for the aldehyde **2**, for which a B3LYP calculation gives $\Delta\omega = 0.32$ eV for a structure with equal C–C bond lengths in the three-membered ring. As has been mentioned above, PE spectra of only very few *Z*-substituted cyclopropanes have been published.[3] The most important example is probably cyclopropyl methyl ketone, and the data of this compound ($\Delta r = 3.7$ pm, $\Delta IP_\omega = 0.8$ eV[4]) fit nicely into Figure 3.

Conclusion

The first IP of an acceptor-substituted cyclopropane derivative can be either lower or higher than that of the corresponding isopropyl congener, mainly depending on the amount of stabilization of the HOMO by interaction with unoccupied MOs which is most effective when HOMO and LUMO have the same symmetry.

A linear correlation between the difference Δr of the C–C bond lengths and the energy difference $\Delta\omega$ between the Walsh orbitals ω_S and ω_A was found for cyclopropane (**1**) by DFT B3LYP or HF calculations. A similar relationship holds for compounds **2**–**8**, and $\Delta\omega$ can be replaced by the difference ΔIP_ω of the corresponding ionization potentials.

Hoffmann's qualitative model[14–17] for the effect of substituents on bond lengths only considers interactions of the Walsh orbital ω_A with substituent orbitals. This model fails to explain the different behavior of—for example—nitro and carbonyl groups. At least for the investigated cyclopropane derivatives with electron-acceptor substituents, we can modify this model and substitute it by a quantitative expression: *The difference between the lengths of distal and vicinal bonds is proportional to the energy difference of the Walsh orbitals* ω_S *and* ω_A. More detailed investigations on cyclopropane derivatives—including donor-substituted ones—are desirable in order to further clarify these relationships.[47]

Experimental Section

General: PE spectra were recorded on a Leybold–Heraeus UPG200 spectrometer equipped with a He(I) radiation source (21.21 eV). Samples were directly evaporated into the target chamber at ambient temperature. Spectra were recorded repeatedly, and the reported IP values are the average of several runs. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements is approximately ±0.03 eV for ionization energies, while for broad and overlapping signals it is only ±0.1 eV.

Semiempirical PM3[48] calculations were performed with the MOPAC93[49] program package, ab initio Becke3LYP (B3LYP)[20] and Hartree–Fock (HF) calculations with the program GAUSSIAN 98.[50] For the latter methods, the basis set 6–31+G(d) was used, unless stated otherwise. Geometries were fully optimized at the respective levels of theory. Prior to quantum chemical calculations, molecular geometries were preoptimized by molecular mechanics calculations with the MMX[51] force field which were performed with the program PCMODEL.[52]

Materials: Cyclopropanecarbaldehyde (**2**) and cyclopropanecarboxylic acid (**3**) were purchased from Aldrich, methyl cyclopropanecarboxylate (**4**) from Acros, isothiocyanatocyclopropane (**6**) from Lancaster. Nitrocyclopropane (**5**) was synthesized by the procedure described by Lampman et al.[53] Cyclopropane-1,1-dicarbonitrile (**8**) was prepared according to Diez-Barra et al.[54]

Prior to measurement, the purity of all compounds was checked by GLC and GLC/MS.

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