Photoelectron Spectra and Electronic Structures of Some Cyanocyclopropanes[‡]

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Dedicated to the memory of Gerd Schrumpf

Keywords: Density functional calculations / Electronic structure / Ionization potentials / Molecular structure / Photoelectron spectroscopy / Small ring systems

The molecular structures of four cyanocyclopropanes **1**–**4** have been investigated by DFT B3LYP calculations. PE spectra of *trans*- and *cis*-1,2-dicyanocyclopropane (**3** and **4**) have been measured and analysed by semiempirical PM3 and B3LYP calculations. For compounds **1**–**4** a linear relationship, $\Delta IP_\omega = 0.218\ \Delta r$, between ΔIP_ω (in eV), the difference in the *IP*s associated with the Walsh orbitals ω_S and ω_A of the three-membered ring, and Δr (in pm), the difference of vicinal and distal C–C bond lengths, is established.

Introduction

In preceding communications in this series of investigations into the relationships between electronic and geometrical structures of cyclopropane derivatives we have shown that for most compounds a linear relationship, expressed by the equation $\Delta IP_\omega = 0.2544\ \Delta r$, applies for the difference ΔIP_ω [eV] of the ionization potentials associated with the Walsh orbitals ω_S and ω_A, and Δr [pm], the difference between the vicinal and distal C−C bond lengths.[1−3] In order to investigate such a relationship, monosubstituted cyclopropanes were first studied,[1,3] but some derivatives with two or three substituents were also found to follow the correlation.[1,2] However, the problem of the inclusion of polysubstituted cyclopropanes still needs further elucidation. In the first paper in this series,[1] cyanocyclopropane (**1**) and 1,1-dicyanocyclopropane (**2**) were included. We have now investigated two further cyclopropane nitriles, *trans*- and *cis*-1,2-dicyanocyclopropane (**3**, **4**), by the same technique and analysed the data for all four compounds for the correlation between bond lengths and ionization energies.

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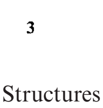

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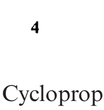

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Results and Discussion

Molecular Structures of Compounds 1−4

The molecular structures of compounds **1**−**4** were investigated by the density functional theory (DFT) B3LYP method.[4] The obtained bond lengths are summarized in Table 1. Experimental structure data are available only for two compounds: the nitrile **1**[5] and the dinitrile **2**[6] have been investigated by microwave spectroscopy, although for compound **2** only an estimated value of 148.5 ± 10 pm was given for the distal bond length. The calculated bond lengths are in good agreement with the experimentally determined values; in almost all cases the deviations fall within the uncertainties of the latter.

In the monosubstituted compound **1**, the average C−C bond length is increased by 0.5 pm relative to unsubstituted cyclopropane (151.1 pm, the experimental value is 150.3 pm[7]), and comparison with the data for the disubstituted compounds **2**−**4** indicates that the effect of the nitrile groups is approximately additive. The *trans* and *cis* isomers **3** and **4** show identical bond lengths except for the $C^1{-}C^2$ bond, which − obviously for steric reasons − is slightly expanded in the latter compound.

In the 1,2-disubstituted compounds **3** and **4**, no distinction of vicinal and distal C−C bonds is possible in the proper meaning. However, with respect to the symmetry of the Walsh orbitals ω_A and ω_S (Figure 1), two types of C−C bonds can be distinguished, and we will call these bonds *pseudo-vicinal* and *pseudo-distal*. For both molecules there are two equivalent C−C bonds which are pseudo-vicinal, while the third is pseudo-distal; vicinal and distal are thus

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Table 1. Calculated bond lengths [pm] in compounds **1**−**4** [B3LYP/6-31+G(d) results]

Compound Symmetry	**1**[a] C_s	**2**[b] C_{2v}	3 C_2	**4** C_s
C^1-C^2	152.4 [152.9(5)]	154.1	153.7	153.8
C^2-C^3	149.9 [150.0(3)]	148.8 [148.5(1.0)]	151.3	151.3
C^1-CN	144.1 [142.0(6)]	144.7	144.2	144.2
C^2-CN	−	−	144.2	144.2
$C{\equiv}N$	116.3 [116.1(4)]	116.2	116.2	116.2
C^1-H	108.7	−	108.7	108.7
C^2-H	108.6[c] 108.6[d]	108.6	108.7	108.7
C^3-H	108.6[c] 108.6[d]	108.6	108.5	108.6[c] 108.5[d]
Mean ring C−C[e]	151.6	152.3	152.1	152.1
Δr[f]	2.5	5.3	−2.4	−2.5

[a] Experimentally determined (MW) values[5] with uncertainties in parentheses. [b] Experimentally determined (MW) value[6] with error limit in parentheses. [c] *trans.* [d] *cis.* [e] $(C^1-C^2 + C^1-C^3 + C^2-C^3)/3$. [f] Difference between vicinal (or pseudo-vicinal) and distal (or pseudo-distal) C−C bond length.

defined with respect to symmetry and not, as they would normally be, to the position of a substituent. From the structure data in Table 1 we can easily determine the difference Δr between vicinal (or pseudo-vicinal) and distal (or pseudo-distal) C−C bond lengths for all compounds **1**−**4**. For **3** and **4**, Δr has the same magnitude as for **1**, but the sign is opposite. For the 1,1-dinitrile **1** Δr is a little more than twice as large as for the mononitrile **1**.

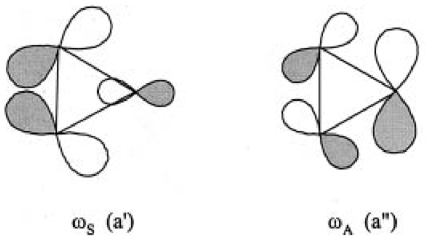

Figure 1. Walsh orbitals ω_S and ω_A of cyclopropanes

Photoelectron Spectra of Compounds 3 and 4

The PE spectra of compounds **1**[1,8,9] and **2**[1] have been investigated previously. The measured spectra of compounds **3** and **4** are depicted in Figure 2. The spectroscopic data for these two compounds are summarized in Tables 2 and 3, together with the relevant results of quantum chemical computations. The ionic states are indicated by the spectroscopic symbols of the molecular orbitals (MOs) from which electrons were ejected. For the labelling, the core orbitals (i.e., 1s orbital for carbon and nitrogen) were neglected and only valence orbitals were taken into account.

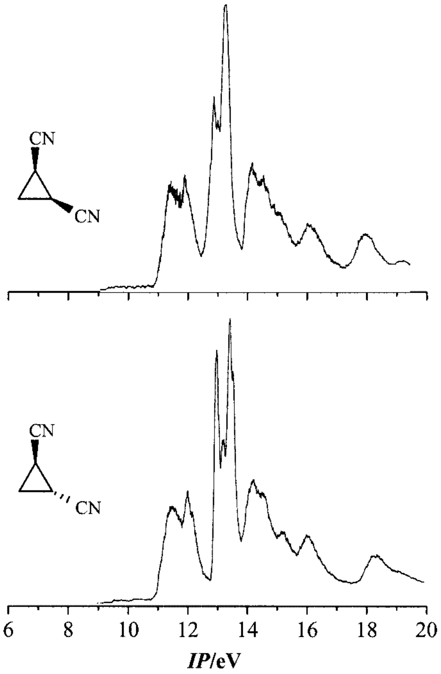

Figure 2. PE spectra of compounds **3** and **4**

ble 2. Vertical ionization potentials IP_v [eV], orbital energies ε [eV], enthalpy of formation ΔH_f [kJ·mol^{-1}], and total energy E_0 [au] of *trans*-1,2-dicyanocyclopropane (**3**)

IP_v	$-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	IP^{B3LYP} [a]	
11.34	11.94	8.82	10.96	9a, ω_S-π(CN)
11.95	12.30	9.21	11.39	8b, ω_A-π(CN)
12.92	13.09	9.97	12.15	8a, π(CN)
	13.32	10.03	12.21	7b, π(CN)
13.38	12.75	10.57	12.75	7a, *n*(N)
	12.76	10.62	12.80	6b, *n*(N)
14.16	14.71	11.41	13.59	5b, π(CN)+ω_A
14.5	14.81	11.63	13.81	6a, π(CN)+ω_S
15.2	14.03	12.35	14.53	4b, π(CH_2)
16.0	15.72	13.40	15.58	5a, σ
18.3	19.00	15.71	17.89	4a, σ
ΔH_f	376.49			
E_0(M)		−302.385975		
$E_0(M^{\cdot +})$		−301.983343		

[a] Calculation of first vertical *IP*: energy difference of molecule M and radical cation $M^{\cdot +}$ with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 2.18$ eV.

Assignment of the *IP*s can be achieved by application of Koopmans' theorem,[10] $IP_i = -\varepsilon_i$, by which vertical ionization energies and SCF MO energies are related. Although Kohn−Sham orbitals obtained by DFT methods[11] 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 (see, for example, refs.[12,13]). Much better agreement between experimentally determined and theoretical values can be expected for the first vertical *IP* (IP_{1v}) when the energies of the molecule M

Table 3. Vertical ionization potentials IP_v [eV], orbital energies ε [eV], enthalpy of formation ΔH_f [kJ·mol^{-1}], and total energy E_0 [au] of *cis*-1,2-dicyanocyclopropane (**4**)

IP_v	$-\varepsilon^{PM3}$	$-\varepsilon^{B3LYP}$	IP^{B3LYP} [a]	
11.40	11.88	8.78	10.95	10a′, ω_S-π(CN)
11.85	12.17	9.05	11.22	7a′′, ω_A-π(CN)
12.83	13.25	9.78	11.95	6a′′, π(CN)
	13.06	9.88	12.05	9a′, π(CN)
13.23	12.63	10.39	12.56	5a′′, *n*(N)
	12.66	10.46	12.63	8a′, *n*(N)
14.15	14.58	11.40	13.57	4a′′, π(CN)+ω_A
14.6	14.84	11.63	13.80	7a′, π(CN)+ω_S
15.1	14.01	12.20	14.38	6a′, π(CH_2)
16.1	15.74	13.51	15.68	3a′′, σ
18.3	18.55	15.27	17.44	5a′, σ
ΔH_f	381.58			
E_0(M)		−302.383218		
E_0($M^{\cdot+}$)		−301.980649		

[a] Calculation of first vertical *IP*: energy difference of molecule M and radical cation $M^{\cdot+}$ with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 2.17$ eV.

and the radical cation $M^{\cdot+}$ are calculated by the B3LYP method. Since a vertical *IP* corresponds to the transition with the highest Franck-Condon factor without any structural change, a single-point calculation is performed for $M^{\cdot+}$ with the molecule's geometry in order to obtain IP_{1v}. The corresponding energy values, which do not include any zero-point corrections, are given in Tables 2 and 3. We can now correct the other ε^{B3LYP} values from the difference between −ε(HOMO) and the calculated IP_{1v} in order to obtain higher IP_v values.[13] Whereas typical energy differences between IP_i and $-\varepsilon_i^{B3LYP}$ values for the compounds studied here are about 3 eV, experimentally determined and calculated IP_i values differ only by 0.1−0.8 eV. Furthermore, both $-\varepsilon_i^{B3LYP}$ and calculated IP_i(calcd.) values are linearly correlated with the experimentally obtained IP_i(exp.) values with correlation coefficients (both $R = 0.992$) close to 1.000. The orbital energies ε_i obtained by the semiempirical method PM3 (Tables 2 and 3) also correlate acceptably well with the experimental IP_i values ($R = 0.940$). In some cases, however, the PM3 orbital sequence differs from that obtained by the B3LYP method. In particular, the n(N) orbitals are placed above the π(CN) orbitals for both compounds by this method.

The PE spectra of the dicyano compounds **3** and **4** are fairly similar in their appearance, and the *IP*s of both compounds also differ only by about 0.1 eV. It would therefore be difficult to identify the isomers from their spectra or to determine their relative amounts in a mixture.

The spectra are dominated by two strong and relatively sharp bands between 12.5 and 13.8 eV. As the calculations indicate (Tables 2 and 3), each band has to be assigned to a pair of closely adjacent ionizations, which renders analysis of fine structure difficult. In **3**, both bands (12.92 and 13.38 eV) seem to display vibrational fine structure ($\Delta\tilde{\nu} \approx$ 1900 and 900 cm^{-1}, respectively). The former frequency is assigned to a C≡N stretching vibration of the radical cation and the latter to a C−CN bending vibration. In **4**, vibrational fine structure is discernible only for the band at 12.83 eV ($\Delta\tilde{\nu} \approx 1100$), which relates to a C−CN bending vibration. The vibrational fine structure of the bands supports the assignments based on the B3LYP results to π(CN) and *n*(N) ionizations of the two nitrile groups, but because of the difficulties in the analysis of composite bands this cannot be regarded as a proof that the different result of the PM3 method is false. For compound **2**, strong bands corresponding to π(CN) and n(N) ionizations of the nitrile groups have been found in a similar range (12.8−13.6 eV)[1] as for **3** and **4**. For direct comparison with the latter compounds, the *IP*s of succinonitrile as an open-chain molecule with two vicinal nitrile groups are most informative. The corresponding *IP*s of this compound have recently been found at 12.49 (sh), 12.63, 12.7, 13.11, 13.41, and 13.58 eV.[14]

All ionizations up to 15 eV are related to MOs largely localized on the nitrile groups. The first two *IP*s correspond to orbitals that can be characterized as out-of-phase combinations of ω_S and ω_A, respectively, with π(C≡N) and π′(C≡N) combinations of the two nitrile groups with the same symmetry. Ionizations at about 14.2 and 14.5 eV correspond to the respective in-phase combinations. It is worth mentioning that the splitting of the first two *IP*s, which is essential for the following section, is close to 0.5 eV for both compounds. The corresponding value is predicted quite well for **3** at the B3LYP level (0.43 eV) but not in the case of compound **4** (0.27 eV). Investigations on other cyclopropane derivatives[1−3] have shown that the corresponding ΔIP values are usually equal within ±0.1 eV, but may occasionally differ by up to ±0.3 eV.

According to the total energies E_0(M), obtained by the B3LYP method (Tables 2 and 3), the *trans* isomer **3** is 7.24 kJ·mol^{-1} more stable than the *cis* isomer. If zero-point corrections are included, this values is slightly modified to 7.28 kJ·mol^{-1}. The corresponding difference in the ΔH_f values, calculated by the PM3 method, amounts to 5.09 kJ·mol^{-1}.

Quantitative Correlation between Ionization Energies and Bond Lengths of Compounds 1−4

It is well known that the geometry of the three-membered ring is connected with its electronic structure. For a recent discussion, see ref.[15] As we have been able to show for a large number of substituted cyclopropanes,[1−3] there is a quantitative relationship between the energy difference ΔIP_ω between the Walsh orbitals ω_S and ω_A (see above) and the difference Δr in the lengths of vicinal and distal C−C bonds. Figure 3 shows a diagram for compounds **1−4** in which the ΔIP_ω values are plotted versus the Δr values, and it is obvious that a linear relationship between these parameters also exists for these compounds. The ΔIP_ω values for compounds **1** (0.63 eV) and **2** (1.14 eV) have been published previously.[1] Analysis of the corresponding data gives Equation (1). If the correlation line is forced to pass through the origin of the coordinate system, a slightly different Equation (2) with nearly the same correlation coef-

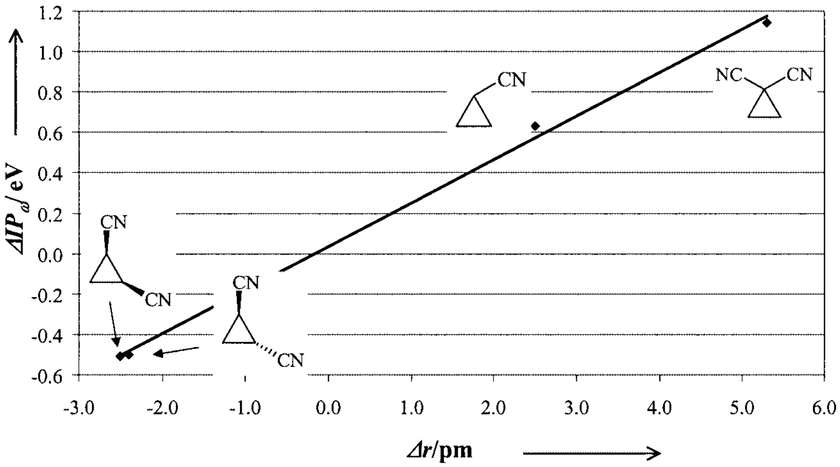

Figure 3. Correlation diagram of ΔIP_ω and Δr for compounds **1**−**4**

ficient R is obtained. The resulting correlation line corresponds to Equation (2). Equation (2) takes into account that ω_S and ω_A are supposed to be degenerate at $\Delta r = 0.00$, as in the unsubstituted parent compound. For a possible explanation of the constant term in Equation (1), see ref.[1] If instead of experimentally determined ΔIP_ω values the corresponding data calculated by the B3LYP method (**1**: 0.54 eV; **2**: 0.99 eV)[1] are used, a similar linear correlation as expressed by Equation (3) results.

$$\Delta IP_\omega = 0.2156\,\Delta r + 0.0337,\ R = 0.999 \qquad (1)$$

$$\Delta IP_\omega = 0.2177\,\Delta r,\ R = 0.998 \qquad (2)$$

$$\Delta IP_\omega = 0.1792\,\Delta r,\ R = 0.985 \qquad (3)$$

It can thus be stated that the relationship between geometrical and electronic structures discussed above also applies for mono- and disubstituted cyanocyclopropanes. Equations (1) and (2) may be compared with similar equations obtained for other cyclopropane derivatives.[1−3] If all the data for the parent cyclopropane and 20 derivatives are combined in a single linear correlation analysis, Equation (4) results.

$$\Delta IP_\omega = 0.250\,\Delta r + 0.052,\ R = 0.946 \qquad (4)$$

A brief discussion of the two orbital model used in this correlation of geometrical and electronic properties of cyclopropanes, its limits and possible improvement was made in the previous communication.[3]

Conclusions

In mono- and disubstituted cyanocyclopropanes, distal (or pseudo-distal) and vicinal (or pseudo-vicinal) C−C bonds can be distinguished, provided that the molecules possess at least twofold symmetry (C_s, C_2, C_{2v}).

The difference Δr in the lengths of these bonds is quantitatively correlated with the energy difference ΔIP_ω between the Walsh orbitals ω_S and ω_A, as determined from their ionization energies.

Experimental Section

General: PE spectra were recorded with a Leybold−Heraeus UPG200 spectrometer with a He(I) radiation source (21.21 eV). Samples were directly evaporated into the target chamber at ambient temperature. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 eV and of argon at 15.759 and 15.937 eV. The accuracy of the measurements is approximately ±0.03 eV for ionization energies, for broad and overlapping signals it is only ±0.1 eV. Semiempirical PM3[16] calculations were performed with the aid of the MOPAC93[17] program package, DFT Becke3LYP (B3LYP)[4] calculations with the program GAUSSIAN 98.[18] In the latter methods, the basis set 6-31+G(d) was used. Geometries were fully optimized at the respective levels of theory. Molecular orbitals were visualized for inspection by use of the programs PERGRA[19] and MOLEKEL.[20,21]

Materials: Compounds **3**[22] and **4** were synthesized and purified as described previously.[23] The chiral compound **3** was obtained and used as a racemate.

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