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Influence of Substituents Having Lone Pairs on the Structure of Cyclopropanes

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Abstract: The influence of substituents, which have lone pairs, on the structure of the cyclopropane ring was investigated by using ab initio SCF MO methods. For the substituents X = F, OH, OH_2^+, NH_2 and NH_3^+ a lengthening of the opposite and a shortening of the adjacent ring bonds were found. The analysis of the results has revealed that neither π donation of the lone pair (hyperconjugation) nor the σ-acceptor property (electronegativity) of X can be responsible for the trends in the ring bond lengths. It rather seems to be the increased ring strain caused by local effects such as changes in hybridization which leads to the bond differentiation in the substituted cyclopropanes. The calculated angle deformation energies for the CH_3–X model system have supported this conclusion. In the case of X = O^- and CH_2^- a lengthening of all ring bonds is obtained as expected from π donation to the ring. The decrease in protonation energies and the shortening of the C–X bonds in the anions as compared to those of the corresponding CH_3–X compounds are considered as further evidence for the importance of π donation in the anion systems.

1. Introduction

The influence of substituents on the bond lengths in cyclopropane has received considerable attention in the past decade.[1] For π-acceptor substituents a coherant picture has emerged.[2–7] The shortening of the opposite and the lengthening of the adjacent bonds have been rationalized by Hoffmann[6] in terms of interactions of the fragment orbitals. On the other hand, for substituents having lone pairs the pattern of the structural changes in the three-membered ring seems to be less regular[8–12] and there are several theoretical studies[12–16] which try to explain the different effects by using different orbital interaction schemes. The influence of changes in the hybridization of carbon atoms in flouro-substituted hydrocarbons was discussed by Bernett,[17] and its effect on the observed bond lengths in fluoro-substituted cyclopropanes was recently emphasized by Jason and Ibers.[18]

Figure 1 gives a schematic representation of the Walsh[38] type MO's of cyclopropane as they have been obtained from a minimal basis SCF calculation, subsequent Boys' localization, and proper symmetry adaptation of the resulting C–C (occupied and virtual) bond MO's. Table I gives a qualitative survey of the geometry changes which are expected from interactions of the Walsh MO's with different substituent MO's of the proper symmetry.[6,12–16]

SCF MO energies depend much on the total charge of a molecule, and they are also influenced by local charges. If a single MO in a molecule changes by the influence of a substituent in such a way that some charge is redistributed in the molecule, the SCF MO energies of other orbitals may also change, even if the orbitals themselves remain essentially unchanged. Thus, the analysis of SCF MO energies of such large systems like cyclopropyl derivatives is a very complex task and might in fact be futile. We have chosen a different and a more chemical approach to the problem. We compared computed ring structures of cyclopropanes having a wide range of substituents in order to vary the substituent properties (σ acception, π donation) independently as far as possible.

Table I. Survey of the Different Types of Interactions of Substituent Orbitals with Walsh Orbitals of Cyclopropane

type of substituent	Walsh MO of cyclopropane involved[a]	effects on ring bonds lengths[b] adj bonds	opp bonds
π^c acceptor	←2[d]	+	−
π' acceptor	←3	−	+
σ acceptor	←3	−	+
	←1	+	+
π donor	→4	+	+
	→5	(−)	+
π' donor	→6	+	−
σ donor	→6	+	−

[a] The arrows indicate the direction of electron flow: ←, means electrons are substracted from that orbital and, →, means the orbital accepts charge from substituent. [b] The plus sign means lengthening and the minus sign shortening of a bond. [c] π means antisymmetric with respect to the C_s plane of monosubstituted cyclopropane; π' means symmetric with respect to that plane but essentially antisymmetric with respect to the C–X bond. [d] Numbering of the MO's from Figure 1.

2. Computational Methods

The calculations were performed with an SCF program, the integral part of which originates from Ahlrichs.[20] For C, N, O, and F the 7s,3p Gaussian basis sets of Huzinaga[21] were used in the double-ζ contraction [4,1,1,1·2,1]. For the H atoms the three s lobes were contracted to one basis function with the contraction coefficients taken from an SCF calculation of H_2. In the case of the anions, the basis sets were augmented by diffuse p functions (one set for O with an exponent of 0.12; two sets for C with the exponents 0.04 and 0.01). Since we did not include polarization

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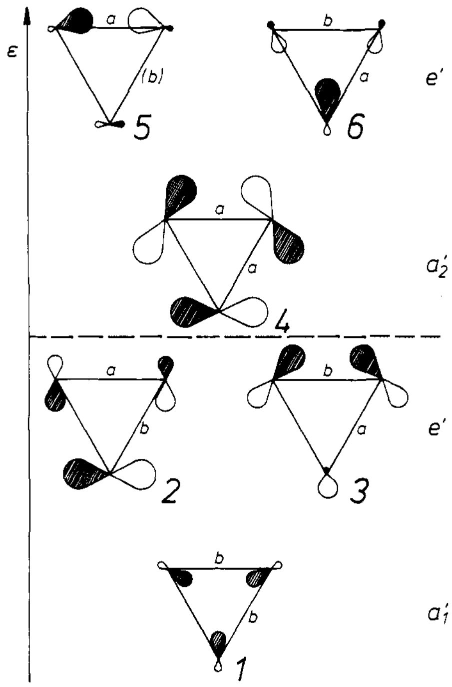

Figure 1. The Walsh MO's of cyclopropane. a and b indicate, if occupation of the MO would add to the corresponding bond, antibonding or bonding contributions, respectively.

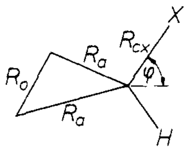

Figure 2. Geometrical parameters in substituted cyclopropanes which were optimized.

functions in our basis sets, our calculations cannot be very reliable for predicting the relative energies with respect to isomeric open-chain compounds. The structural changes induced by substituents, which we are concerned with, can be reproduced satisfactorily within a double-ζ basis.[13,16]

The four structural parameters depicted in Figure 2 were optimized: (a) the opposite (R_o) and (b) the adjacent (R_a) CC bonds of the ring; (c) the C–X bond distance and (d) the ring–C–X out-of-plane angle. C_s symmetry was assumed and experimental values[22] were taken for the CH bond lengths (1.08 Å) and for the angle between the CH bonds and the ring plane (122.5°).

3. Results

1. Conformations. Since hyperconjugative interactions between the three-membered ring and lone pairs of substituents may result in large rotational barriers around the C–X bond (cf. the substituent CH_2^+),[7] the question of the preferred conformation and of the barriers separating them is of some relevance. The dependence of the total energy on the rotational angle around the C–X bond was computed under the assumption of a rigid molecular frame (all structural parameters were kept fixed at standard values).

For cyclopropanol, the lowest energy is found for a gauche conformation (HCOH dihedral angle = 60°). Of the two conformations with C_s symmetry the trans conformation (Figure 3a) comes out to be 2.2 kcal/mol and the cis conformation 3.0 kcal/mol above the gauche conformation. From a recent microwave study[23] it was concluded that cyclopropanol has a gauche conformation with a dihedral angle of 106°. The latter result, however, was based on several assumptions made for the remaining structural parameters of the system.

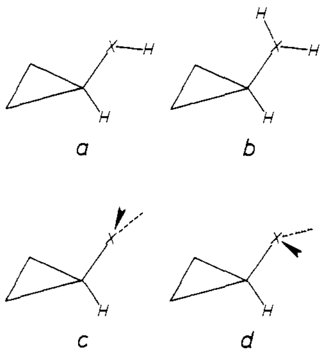

Figure 3. Conformations of XH and XH_2 substituents: (a) trans conformation, (b) bisected conformation, (c) perpendicular conformation (b and c with planar arrangement of the C-XH_2 group), and (d) perpendicular conformation with pyramidal C–XH_2 arrangement.

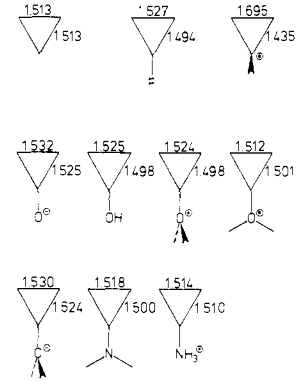

Figure 4. Ring bond lengths computed for substituted cyclopropanes.

The conformation of cyclopropylamine with the C–N–lone pair plane being perpendicular to the ring plane (Figure 3d) has the lowest energy. Rotation around the C–N bond by 90° requires 4.0 kcal/mol; further rotation to 180° lowers the energy slightly to 3.1 kcal/mol above the energy of the conformation of Figure 3d. These results are in good agreement with a previous ab initio result[36] (4.4 kcal/mol for 90° rotation) and also with recent IR and Raman values[37] of 3.6 and 2.9 kcal/mol for 90 and 180° rotations, respectively.

In the OH_2^+-substituted cyclopropane, the bisected conformer (Figure 3b) has a higher energy (3.8 kcal/mol) than the sterically less hindered perpendicular conformation (Figure 3c). The C-OH_2^+ group was assumed to be planar; OH_2^+ has a small inversion barrier[24] which cannot be reproduced with a DZ basis.

In the cyclopropylmethyl anion, the bisected conformation (Figure 3b) is favored by 1.1 kcal/mol over the perpendicular conformation (Figure 3c). A tetrahedral arrangement around the carbanionic C atom is 1.3 kcal/mol higher in energy than the planar carbanion. In CH_3–CH_2^- we have found with the same basis set the co-planar C–CH_2^- structure about 2.6 kcal/mol less stable than the staggered pyramidal conformation. The experimental inversion barrier of CH_3^- is 1.4 kcal/mol.[25]

2. Ring Structures. Figure 4 shows the computed CC bond lengths in the three-membered rings of various substituted cyclopropanes. For cyclopropane itself our computed value of 1.513 Å for the C–C bond agrees with the experimental value 1.512 (3).[22] Our values obtained for the substituents NH_2 and F agree well with those computed by other authors[13,14,16] and also with the experimental structure[12] (cyclopropylamine, R_o = 1.513 (3) and R_a = 1.486 (8) Å). Experimental data are also available for 1,1-difluorocyclopropane[8] for which the R_a (1.464 (2) Å) and R_o

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Table II. C–X Bond Lengths and Out-of-Plane Angles (in Deg) in Substituted Cyclopropanes and C–X Bond Lengths (in Å) in Substituted Methanes

	$c\text{-}C_3H_5\text{-}X$			
X	out-of-plane angle[a]	R_{CX}	$CH_3\text{-}X$ R_{CX}	ΔR[b]
F	56.3	1.380	1.404	−0.024
OH	58.7	1.429	1.453	−0.024
$\pi\text{-}OH_2^+$ [c]	54.9	1.495		
perp OH_2^+ [d]	57.8	1.482	1.511	−0.029
O^-	55.5	1.379	1.466	−0.087
NH_2	60.6	1.452	1.482	−0.030
NH_3^+	55.9	1.502	1.544	−0.042
CH_2^-	52.5	1.491	1.587	−0.096

[a] Out-of-plane angle φ of Figure 2. [b] Differences between R_{CX} values of cyclopropyl and of methyl derivatives. [c] Bisected conformation (Figure 2b).

Table III. Protonation Energies of Cyclopropyl and of Corresponding Methyl Derivatives (Values in kcal/mol)

X	$C_3H_5\text{-}X$	$CH_3\text{-}X$	difference
O^-	370	381	−11
CH_2^-	428	438	−10
OH	183	183	0
NH_2	212	215	−3

(1.553 (1) Å) differ from each other even more than in our computed structure of fluorocyclopropane.

Except for the anions, we have found for all cases studied a lengthening of the opposite and a shortening of the adjacent bonds. For the anions, the opposite bonds are also longer than the adjacent bonds; however, all ring CC bonds are longer than those of cyclopropane.

3. The C–X Bond Lengths and Out-of-Plane Angles. The C–X bonds in the substituted cyclopropanes according to our calculations are generally shorter than the corresponding bonds in methyl derivatives CH_3X (Table II). This trend has to be expected because of the differences in hybridization. The very large bond length differences for the anions obviously need a different explanation.

The optimum values for the out-of-plane angles φ (Figure 2) are also given in Table II. They do not seem to follow any easily explainable pattern.

4. Protonation Energies. Due to the limited flexibility of our basis set, one can not expect to obtain reliable absolute values of protonation energies. The calculated values of 183 and 212 kcal/mol for CH_3OH and CH_3NH_2 are nevertheless in perfect agreement with the experimental values[26] of 182 and 211 kcal/mol, respectively. For $C_2H_5^-$ our value differs only by 3 kcal/mol from the one obtained with a much better basis.[27]

Table III gives a comparison of the protonation energies of cyclopropyl compounds with those of corresponding methyl derivatives. For OH and NH_2 the cyclopropyl substitution exerts only minor influence on the protonation energies, while the anions seem to be stabilized approximately by 10 kcal/mol by cyclopropyl substitution.

4. Factors Affecting the Ring Structure

1. π Donation of the Substituent. O^- and CH_2^- are the strongest π donors of our substituents. There is strong evidence for the presence of substantial conjugation between the lone pairs and the three-membered ring: (a) The protonation energies indicate a stabilization of the anions approximately by 10 kcal/mol. For the sake of comparison, it should be noted that a vinyl substituent stabilizes the CH_2^- group by 45 kcal/mol (with the same basis the protonation energy of the allyl anion is computed to be 393 kcal/mol). (b) The MO energies of the highest occupied MO's of the anion-substituted cyclopropanes (−0.086 au for O^- and −0.004 au for CH_2^-) are lower than those of methyl compounds (−0.078 au for O^- and +0.010 au for CH_2^-). The value for the allyl anion is −0.015 au. It must be noted that the highest MO of the cyclopropyl oxide anion has π symmetry, while the lone pair in the plane perpendicular to the ring has a lower MO energy (−0.111 au). It is the interaction with the occupied e′ Walsh MO of π symmetry which pushes up the energy of the π lone pair. (c) In the cyclopropylmethyl anion the sterically (more hindered) bisected conformation and the planarity of the carbanionic center are preferred. (d) For anion substitution the R–X bonds are much shorter in the cyclopropyl than in the corresponding methyl compounds.

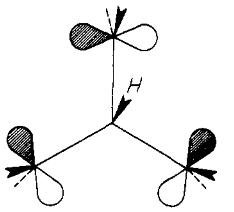

Figure 5. Möbius' system of trimethylene methyl.

The structural changes on the ring bond lengths agree with the predicted[6] lengthening of all bonds corresponding to the interaction of the π lone pair with the lowest virtual Walsh MO (Figure 1, Table I). In the case of the cyclopropylmethyl anion the interaction of the lone pair with the higher lying virtual e′ MO of π symmetry seems to be of less importance. This interaction should weaken the opposite bond, ultimately leading to ring opening and the formation of the four-electron aromatic Möbius-type system[28] depicted in Figure 5. This system was previously discussed by Stohrer and Hoffmann.[29] With our basis, the C_{3v} structure of this anion is found to be 49 kcal/mol less stable than its classical isomer. The absolute value of this energy difference should not be taken too seriously since both d functions and electron correlation are expected to contribute to this energy difference.

For all other substituents π conjugation seems to be of minor importance. This can be concluded from the absence of all those points discussed above for the anion systems. In addition, the structural effects computed for the three-membered ring are different from the effects calculated for the anions.

2. σ-Acceptor Capability of the Substituent. Even though the opposite has been claimed[16] our results show clearly that the electronegativity of the substituents does not seem to be an important factor in the determination of the ring structure. The increase in the electronegativity of substituents (OH and NH_2) by protonation has virtually no effect on the ring structure. That extreme electronegativity of a substituent can entirely change the ring structure is demonstrated by a model calculation on a system, obtained from cyclopropane by removing a hydrogen atom with its bonding electron pair. The geometry of this cyclopropyl cation was optimized within the same restrictions as the substituted cyclopropanes. Thus, it was prevented from opening up to the allyl cation. Nevertheless, it shows (Figure 3) a dramatic lengthening of the opposite and shortening of the adjacent bonds. In the case of the NH_3^+ and OH_2^+ substituents, the leaving groups (NH_3 and OH_2, respectively) are still bound to the ring by a covalent bond and no influence on the ring structure can be seen. In fact, the lengthening of the CX bond by protonation (Table II) is less pronounced than that in the corresponding methyl compounds.

3. Changes in Hybridization: Local Effects. Lengthening of the opposite and shortening of the adjacent bonds can also be due to an increase in ring strain caused by a change in hybridization of the carbon atom bonded to the substituent. Well-known examples are methylenecyclopropane and cyclopropanone where the differences between adjacent and opposite bonds amount to 0.085 and 0.10 Å, respectively.[22,30] However, substituents at a saturated

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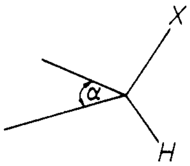

Figure 6. CH_3–X model system for the calculation of deformation energies of the angle α.

Table IV. Deformation Energies in the Model System CH_3X (Values in 10^{-4} au)

X	60°/109° [a]	63°/60° [b]
H	794	95
F	865	106
OH	860	107
π-OH_2^+ [c]	953	110
perp OH_2^+ [d]	857	99
O^-	800	105
NH_2	781	96
NH_3^+	834	100

[a] Difference in total SCF energy (DZ basis) for $\alpha = 109°$ and for $\alpha = 60°$ (Figure 6). [b] Energy difference for $\alpha = 63°$ and $\alpha = 60°$. [c] Conformation corresponding to Figure 3b. [d] Conformation corresponding to Figure 3c.

carbon atom also can cause a change in hybridization.[17,31,32] This has been recognized for fluoro-substituted hydrocarbons for some time[17] and the consequences for the ring structures of halogen substituted cyclopropanes were discussed recently.[18] In CH_2F_2 the HCH valence angle[22] is opened up from the value of 109.5° in methane to 113.7°. This value compares with the HCH valence angles[22] of 117.8° in ethylene and of 116.5° in formaldehyde. It is evident from these data that fluoro substitution in cyclopropane will increase the ring strain[17] and the system will evade the increased strain by simultaneously lengthening the opposite and shortening the adjacent bonds. It is not necessary to make the additional assumption[18] that fluorine substituents tend to shorten α-C–C bonds, a trend which is anyhow not well supported by experiment (experimental C–C bond lengths[22] of fluorine-substituted hydrocarbons are CH_2F–CH_3 = 1.505, CHF_2–CH_3 = 1.54, CF_3–CH_3 = 1.53, CHF_2–CF_3 = 1.52, and CF_3–CF_3 = 1.545 Å).

The local effects exerted by substituents can best be studied by using the model system CH_3X. In this system the virtual σ^* MO's of the CH bonds are much higher in energy than the virtual Walsh MO's of cyclopropane and the CH_3 group cannot even stabilize carbanions by hyperconjugation.[27] We computed the energy difference for CH_3X with ideal tetrahedral arrangement and with a distorted structure in which one of the HCH valence angles was reduced to 60° (Figure 6). More realistically for the purpose of our comparison we computed also the release of strain energy occurring in our model system when α is opened up from 60 to 63°. Both deformation energies are listed in Table IV. The results show that hybridization changes are important not only for the flourine but also at least for the OH substitution. The deformation energies for O^-, OH, and OH_2^+ show that electronegativity is not the only cause for changes in hybridization.[31]

Our model cannot be satisfactory from a quantitative point of view, since the CH bonds present in the model and the CC bonds of the cyclopropane system may respond somewhat differently to hybridization changes. In addition, charge is transferred in our model from the substituents to the hydrogen atoms. This charge increases the repulsion between the hydrogen atoms which unlike the β-carbon atoms of the cyclopropyl ring system are not connected by a bond. The interactions between substituent and CH_3 group fragment orbitals have been studied in more detail elsewhere.[33]

The influence of additional steric interactions is shown by the comparison of the two conformers of CH_3–OH_2^+. For tetrahedral valence angles in the CH_3 group the two conformers have almost the same energy (difference 0.2 kcal/mol, sixfold barrier). After the HCH valence angle has been deformed to 60°, the energy of the conformation which corresponds to the bisected conformation (Figure 3b) becomes less stable by 6.1 kcal/mol than the perpendicular conformation (Figure 3c). In the corresponding cyclopropyl compound we find the same order of stability, though the energy difference between the two conformations is smaller (3.8 kcal/mol). Naturally, our model is not well suited for the quantitative simulation of such steric interactions.

5. Conclusions

The cyclopropyl ring system is a poor π-electron acceptor. Hyperconjugation with neutral π-donating substituents seems to be of minor importance. The ring structure of cyclopropanes with electronegative substituents is also not determined by the σ-electron acceptor capability of the substituent. Of importance are local effects such as changes in hybridization and steric interactions.

It seems to be noteworthy that in the cyclopropyl compounds considered here, bond lengths and bond strengths do not always correlate with each other. In fluoro-substituted cyclopropanes the opposite bond is indeed the weakest bond in thermal rearrangement reactions.[34] Thermolysis of 1,2-dimethoxy-3-methylcyclopropanes, on the other hand, involves the cleavage of the bond connecting the methoxy-substituted carbon atoms.[35] The influence of substituents on the stability of the diradicals occurring in these reactions will be the subject of a future study.

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