

MINDO-Forces Calculations of 1-Substituted Cyclopropyl Cations and Anions

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MINDO-Forces calculations are reported, after complete optimization of geometry, for 1-X-substituted cyclopropyl cations and anions, where X is H, O[−], OH, NH₂, CH₃, NO₂, CN, F, CHO. All the substituents are stabilizing. It was found that the π -donating groups interact strongly with the cyclopropyl cations, whereas the π -withdrawing groups interact strongly with cyclopropyl anion depending on the electron demand.

Introduction

Recently [1], we have studied the effect of substituents on the 2-position of allyl cation and anion. In this paper, we extend our work on 1-X-cyclopropyl cation [2, 3] and anion, where X is H, O[−], OH, NH₂, CH₃, NO₂, CN, F and CHO.

This paper reports the geometry, heat of formation and electron density of 1-substituted cyclopropyl from calculations by the semiempirical MINDO-Forces MO method [4]. The molecular energy of the 1-substituted cyclopropyl system obtained by the semiempirical MINDO/3 method [5] was completely optimized according to Murtagh-Sargent minimization technique [6]. The derivative of the energy was calculated according to Pulay's force method [7]. A full description of the program and its application is given in [4a].

Results and Discussion

The calculated heats of formation and electron densities are given in Tables 1, 2 and 3. The geometrical parameters of the system are given in Tables 4 and 5. The calculated heat of formation (cf. Table 1) of the parent cyclopropyl cation (237.868 kcal/mole) is in very good agreement with the experimental value (238 kcal/mole) [8]. Also the calculated heat of formation of the parent cyclopropyl anion (55.883 kcal/mole) is in good agreement with MINDO calculations (56.93 kcal/mole) [9].

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1. Effect of Substituents on the 1-Cyclopropyl Cation

Structural Details

Introduction of O[−] into the 1-position of cyclopropyl cation causes an increase in the carbon-carbon bond lengths C1–C2 and C1–C3, and a decrease in \angle CCC, while OH, NH₂, CH₃, NO₂ and CN as substituents affect only little the carbon-carbon bond lengths and produce a small decrease in \angle CCC (Table 4). F produces an increase in \angle CCC and has little effect on the carbon-carbon bond lengths, similar to our recent calculations on the 2-substituted allyl cation [1].

Stabilization by Substituents

The stabilizing effect of substituents is often assessed by using isodesmic reactions (conserve bond type) [1]. A positive heat of formation (Table 6) indicates stabilization of the reactant by the substituent. The results show that the substituents O[−], OH, NH₂,

Table 1. Calculated heats of formation (ΔH_f in kcal/mole) for parent cyclopropyl and 1-substituted cyclopropyl cations and anions.

No.	Substituent	ΔH_f	
		Cation	Anion
1	–	237.868	55.883
2	O [−]	177.087	−8.662
3	OH	146.651	5.876
4	NH ₂	169.232	33.409
5	CH ₃	205.796	26.422
6	NO ₂	235.127	−32.437
7	CN	239.866	43.380
8	F	173.232	6.899
9	CHO	203.338	−30.695

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Table 2. Calculated electron densities of 1-substituted cyclopropyl cations.

Atom	Cations								
	1	2	3	4	5	6	7	8	9
C1	3.556	3.354	3.428	3.812	3.607	3.781	3.590	3.257	3.690
C2	4.046	3.989	4.094	3.974	4.042	4.000	4.031	4.076	4.036
C3	4.037	3.973	4.009	3.967	4.031	3.991	4.025	4.066	4.009
C4					4.046		3.990		3.473
H1	0.884	0.882	0.889	0.922	0.894	0.870	0.891	0.866	0.882
H2	0.868	0.882	0.889	0.917	0.893	0.870	0.891	0.866	0.882
H3	0.868	0.885	0.891	0.916	0.895	0.872	0.891	0.866	0.880
H4	0.870	0.885	0.891	0.921	0.895	0.872	0.891	0.866	0.880
H5	0.870		0.674	0.858	0.886				1.001
H6				0.856	0.885				
H7					0.927				
O		6.149	6.236			6.412			6.266
O						6.412			
N				4.857		3.920	4.801		
F								7.137	

See Table 4 for numbering.

Table 3. Calculated electron densities of 1-substituted cyclopropyl anions.

Atom	Anions								
	1	2	3	4	5	6	7	8	9
C1	4.588	3.700	4.247	4.319	4.507	4.482	4.475	3.742	4.460
C2	3.804	4.033	3.857	3.940	3.835	3.865	3.850	4.169	3.878
C3	3.793	4.028	3.815	3.932	3.832	3.857	3.842	4.157	3.862
C4					3.653		3.758		3.353
H1	0.990	1.141	1.210	1.141	1.166	1.096	1.149	1.077	1.122
H2	1.205	1.141	1.210	1.134	1.166	1.096	1.149	1.077	1.122
H3	1.205	1.143	1.210	1.136	1.166	1.098	1.151	1.080	1.120
H4	1.208	1.143	1.210	1.142	1.166	1.098	1.151	1.080	1.120
H5	1.208		0.818	1.100	1.187				1.257
H6				1.096	1.187				
H7					1.136				
O1		6.637	6.422			6.733			6.707
O2						6.774			
N				5.060		3.861	5.475		
F								7.618	

See Table 5 for numbering.

CH₃, CN and F are stabilizing while NO₂ and CHO are only slightly stabilizing. It can be seen from Table 6 that NH₂ stabilizes the cyclopropyl cation more than OH because it is the strongest π -donor, in agreement with ab initio calculation [3]. Also, it was found that 1-hydroxycyclopropyl cation is more stable than 2-hydroxyallyl cation [1], in agreement with the ab initio calculation [3]. Experimentally, the 1-methoxycyclopropyl cation appears to be a more stable intermediate in substitution reactions in solu-

tions [10], and there is convincing evidence for the independent existence of both 1-methoxycyclopropyl and 2-methoxyallyl cations in the gas phase [11].

Electron Densities

It can be seen from Table 2 that O⁻, OH, F decrease the electron density on the carbon atom C1. That is, they act as electron releasing. In case of NH₂, CH₃, NO₂, CN and CHO, the electron density increases on





Table 4. Calculated geometrical parameters of 1-substituted cyclopropyl cations.

Cations	Bond lengths in Å, and bond angles in degrees
1	 C1–C2, 1.438; C1–C3, 1.443; C2–C3, 1.514; C1–H1, 1.092; C2–H2, 1.106; C2C1C3, 63.4; C3C2C1, 58.4; H2C2H3, 108.1; C1C2H2, 119.8.
2	 C1–C2, 1.523; C1–C3, 1.561; C2–C3, 1.460; C1–O, 1.151; C2–H1, 1.107; C2C1C3, 56.5; C3C2C1, 63.0; H1C2H2, 110.8; C1C2H1, 116.1.
3	 C1–C2, 1.452; C1–C3, 1.463; C2–C3, 1.522; C1–O, 1.236; O–H5, 0.962; C2–H1, 1.105; C2C1C3, 62.9; C3C2C1, 58.8; H1C2H2, 108.4; C1C2H1, 120.5.
4	 C1–C2, 1.475; C1–C3, 1.481; C2–C3, 1.503; C1–N, 1.262; N–H6, 1.020; C1C2C3, 61.1; C3C2C1, 59.6; H1C2H2, 108.9; C1C2H1, 118.6; C1NH6, 124.9; H6NH5, 110.6.
5	 C1–C2, 1.471; C1–C3, 1.473; C2–C3, 1.496; C1–C4, 1.432; C4–H5, 1.111; C4–H7, 1.107; C2–H1, 1.105; C2C1C3, 61.0; C3C2C1, 59.5; H1C2H2, 108.7; C1C2H1, 119.2; C1C4H5, 110.1; H6C4H7, 107.6.
6	 C1–C2, 1.458; C1–C3, 1.463; C2–C3, 1.503; C2–H1, 1.107; C1–N, 1.473; N–O1, 1.208; C2C1C3, 61.9; C1C2C3, 59.1; H1C2H2, 107.7; C1C2H1, 119.7; C1NO1, 110.6; O1NO2, 139.1.
7	 C1–C2, 1.467; C1–C3, 1.471; C2–C3, 1.496; C2–H1, 1.105; C1–H4, 1.401; C4–N, 1.165; C2C1C3, 61.2; C3C2C1, 59.5; H1C2H2, 108.6; C1C2H1, 119.4.
8	 C1–C2, 1.434; C1–C3, 1.438; C2–C3, 1.543; C2–H1, 1.105; C1–F, 1.284; C2C1C3, 65.0; C3C2C1, 57.6; H1C2H2, 108.6; C1C2H1, 120.5.
9	 C1–C2, 1.462; C1–C3, 1.466; C2–C3, 1.497; C2–H1, 1.106; C1–C4, 1.493; C4–C5, 1.120; C4–O, 1.184; C2C1C3, 61.5; C1C2C3, 59.3; H1C2H2, 108.2; C1C4H5, 112.9; C1C4O, 120.9; C2C1C4, 147.8.

Table 5. Calculated molecular geometrical parameters of 1-substituted cyclopropyl anions.

Cations	Bond lengths in Å, and bond angles in degrees
1	 C1–C2, 1.426; C1–C3, 1.421; C2–C3, 1.491; C2–H1, 1.082; C2–H2, 1.138; C2C1C3, 63.1; C3C2C1, 58.2; C1C2H2, 124.3; H2C2H3, 101.1.
2	 C1–C2, 1.454; C1–C3, 1.452; C2–C3, 1.492; C2–H1, 1.135; C1–O, 1.239; C2C1C3, 61.7; C3C2C1, 59.0; C1C2H1, 124.4; H1C2H2, 101.5.
3	 C1–C2, 1.414; C1–C3, 1.412; C2–C3, 1.505; C2–H1, 1.144; C1–O, 1.350; O–H5, 0.959; C2C1C3, 64.3; C3C2C1, 57.7; H1C2H2, 98.8; C1C2H2, 126.0; C1–O–H5, 105.9.
4	 C1–C2, 1.499; C1–C3, 1.499; C2–C3, 1.485; C2–H1, 1.126; C1–N, 1.377; N–H5, 1.066; C2C1C3, 59.4; C3C2C1, 60.0; C1C2H1, 131.9; H1C2H2, 102.5; C1NH5, 116.5; H5NH6, 101.1.
5	 C1–C2, 1.450; C1–C3, 1.449; C2–C3, 1.487; C2–H1, 1.130; C1–C4, 1.416; C4–H5, 1.138; C4–H7, 1.124; H1C2H2, 101.7; C1C2H1, 121.2; C1C4H7, 115.1; H6C4H7, 102.7.
6	 C1–C2, 1.472; C1–C3, 1.468; C2–C3, 1.492; C2–H1, 1.117; C1–N, 1.311; NO1, 1.262; C2C1C3, 60.9; C3C2C1, 59.3; H1C2H2, 105.1; C1C2H1, 122.2; C1NO1, 117; O1NO2, 126.1.
7	 C1–C2, 1.459; C1–C3, 1.455; C2–C3, 1.485; C2–H1, 1.126; C1–C4, 1.381; C4–N, 1.179; C2C1C3, 61.2; C3C2C1, 59.2; H1C2H2, 102.9; C1C2H1, 123.3.
8	 C1–C2, 1.546; C1–C3, 1.543; C2–C3, 1.485; C2–H1, 1.114; C1–F, 1.330; C2C1C3, 57.4; C3C2C1, 61.1; H1C2H2, 106.8; C1C2H1, 121.6.
9	 C1–C2, 1.471; C1–C3, 1.469; C2–C3, 1.486; C2–H1, 1.120; C1–C4, 1.374; C4–H5, 1.162; C4–O, 1.232; C2C1C3, 60.6; C3C2C1, 59.1; H1C2H2, 104.1; C1C2H1, 122.6; C1C4H5, 111.7; OC4H5, 116.5.

Table 6. Evaluation of substituent effects using MINDO-Forces calculations (energies are in kcal/mole).

	O ⁻	OH	NH ₂	CH ₃	NO ₂	CN	F	CHO
 + CH ₃ CH ₃ →  + CH ₃ CH ₂ X	83.378	49.917	76.636	28.372	4.423	23.964	20.036	7.130
 + CH ₃ CH ₃ →  + CH ₃ CH ₂ X	87.142	8.707	30.474	25.761	90.002	38.465	4.684	59.178

the carbon atom C1 and decreases on the carbon atoms C2 and C3. That is, these substituents act as electron withdrawing.

For the π -donating groups O⁻, OH and NH₂ the C–X bond length in 1-substituted cyclopropyl cation is shorter than that in 2-substituted allyl cation [1], while the π -withdrawing groups NO₂, CN and CHO show a very slight decrease in the C–X bond length. This is because in the cyclopropyl cation the positive charge is strongly localized at the carbon atom C1 (Table 2), whereas in the allyl cation most of the charge is located on the terminal carbon atoms. Thus in the cyclopropyl cation there is a relatively empty π -type orbital on the carbon atom C1 capable of a strong stabilizing interaction with π -donating substituents. This may explain why the stabilization of the cyclopropyl cation by O⁻, OH and NH₂ is so great compared to the corresponding 2-substituted allyl cation [1]. Previous ab initio orbital calculations [2, 3] have shown that the 1-hydroxy and 1-amino-cyclopropyl cations are more stable, and that the 1-dimethylamino- and 1-methyl-amino-cyclopropyl cations are sufficiently stable to allow for a characterization by NMR [12–14].

2. Effect of Substituents on the 1-Cyclopropyl Anion

Structural Details

Introduction of the substituents O⁻, NH₂, CH₃, NO₂, CN and CHO into the 1-position of the cyclopropyl anion has little effect on the carbon carbon bond lengths C1–C2 and C1–C3 and produces a small decrease in \angle CCC (Table 5), apart from OH. F increases the carbon-carbon bond lengths and decreases \angle CCC, opposite to the effect found in the case of the cyclopropyl cation.

Stabilization by Substituents

The stabilizing effect of substituents is also assessed by using isodesmic reactions in a similar manner to that of 1-substituted cyclopropyl cations. The results (Table 6) show that the substituents O⁻, NH₂, CH₃, NO₂, CN and CHO are stabilizing and OH and F are slightly stabilizing.

Electron Densities

All the substituents produce a decrease in the electron densities at the carbon atom C1 and an increase at C2 and C3 (Table 3).

For the π -withdrawing groups NO₂, CN and CHO, the C–X bond length in 1-substituted cyclopropyl anion (Table 5) is shorter than that in 2-substituted allyl anion [1], reflecting the considerable degree of double bond character, while the π -donating groups O⁻, OH and NH₂ produce a very slight decrease in C–X. This is because in the cyclopropyl anion the negative charge is localized at carbon atom C1 (Table 3), whereas in the allyl anion most of the charge is located on the terminal carbon atoms. This may explain why the stabilization of the cyclopropyl anion by the substituents NO₂, CN and CHO is so great in comparison with the corresponding 2-substituted allyl anion [1].

Thus it can be concluded that π -donating groups interact strongly with the cyclopropyl cation, whereas π -withdrawing groups interact strongly with the cyclopropyl anion, depending on the electron demand [1], [15–19].

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