A Theoretical Study of α-CF_nH_{3-n}-substituted Cyclopropyl Cations

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MINDO-forces calculations are performed, with complete optimization of geometries, on α-X-cyclopropyl cations, where X is CF_3, CF_2H, and CFH_2. It was found that the fluorine atom interacts with the localized empty P π-type orbital on α-carbon atom and forms a bridge with an angle 57.1 degree. Calculations also are performed on CF_3-cyclopropyl anion and CF_2H-cyclopropenyl cation. The fluorine atom in CF_3 and CF_2H shows no such interaction with the α-carbon atom because there is no localized empty P π-type orbital.

In the cyclopropyl cation, the positive charge is localized at the carbon atom C1 (α). Thus there is a relatively empty P π-type orbital on this carbon atom, capable of a strong stabilizing interaction with α-donating substituents [1, 2].

We study the effect on the α-cyclopropyl cation of CF_3, CF_2 and CFH_2 substituents, which is quite different from that of other substituents such as O, OH, NH_2, CH_3, NO_2, CN, F and CHO [2].

MINDO-forces calculations [3a] on the CF_3-cyclopropyl cation result in ridiculous geometrical structure. This is due to the failure of MINDO/3, which underestimates lone-pair lone-pair repulsions [4].

The fluorine atom F3 is replaced by hydrogen in order to overcome the failure of MINDFO/3, i.e. CF_2H is now substituted on α-cyclopropyl cation.

The results show that F2 approaches the carbon atom C1 (α) from a distance 2.209 Å to 1.489 Å during geometry optimization (Table 1). Thus the fluorine atom forms a single bridge [5] with an angle of 58.7°. As a result of this approach the angle C2C1C4 changes from 150.1° to 144.7° and the carbon atom C4 is by 29.6° below the plane of the cyclopropyl ring, as shown in Figure 1. Also it was noticed that the distance between F1 and F2 slightly decreases when F2 approaches the α-carbon atom, and sharply decreases after the formation of the single bridge. This is due to the underestimation of lone-pair lone-pair repulsion in MINDO/3 [4].

The electron density distributions on the fluorine atoms are almost the same, and the positive charge is mainly on the carbon atom C4. This indicats that the lone pairs are in the vicinity of F2 and F1 inspite of the formation of the donating bonds.

In order to overcome the lone-pair lone-pair repulsion of the fluorine atoms, F1 is replaced by hydrogen, and the calculation is performed on α-CFH_2-cyclopropyl cation.

The results show that F2 approaches the α-carbon atom (C1) from a distance 2.231 Å to 1.533 Å during geometry optimization (Table 2). Thus, the fluorine

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Table 1. Variation of ΔH_f (kcal/mole) with bond distances (in Å) during optimization of geometries of α-CF_2H cyclopropyl cation. See Fig. 1 for numbering.

ΔH_f	C1C2	C1C3	C2C3	C1C4	C4F2	C1F2	F1F2
114.372	1.416	1.484	1.473	1.436	1.355	2.209	2.219
113.242	1.464	1.479	1.484	1.439	1.357	2.192	2.211
112.104	1.467	1.478	1.489	1.439	1.359	2.151	2.214
110.812	1.471	1.476	1.492	1.439	1.360	2.115	2.195
109.502	1.475	1.476	1.495	1.439	1.363	2.073	2.178
108.788	1.478	1.475	1.496	1.439	1.364	2.049	2.170
107.66	1.481	1.475	1.497	1.438	1.342	2.010	2.158
106.157	1.485	1.475	1.498	1.437	1.369	1.960	2.146
105.873	1.486	1.475	1.498	1.436	1.369	1.951	2.144
103.324	1.492	1.475	1.499	1.434	1.375	1.874	2.127
100.708	1.498	1.476	1.500	1.433	1.383	1.801	2.113
97.738	1.503	1.478	1.500	1.432	1.393	1.722	2.099
95.372	1.506	1.479	1.501	1.432	1.404	1.660	2.089
93.177	1.505	1.480	1.501	1.432	1.417	1.600	2.069
91.055	1.499	1.482	1.501	1.433	1.435	1.541	2.033
89.988	1.494	1.483	1.501	1.433	1.442	1.520	1.986
88.717	1.492	1.484	1.502	1.433	1.440	1.508	1.901
87.572	1.492	1.485	1.502	1.433	1.436	1.503	1.823
86.469	1.492	1.485	1.501	1.433	1.432	1.500	1.753
85.534	1.491	1.483	1.500	1.437	1.430	1.499	1.698
84.488	1.493	1.487	1.500	1.431	1.424	1.494	1.639
83.613	1.493	1.488	1.500	1.430	1.422	1.493	1.584
82.664	1.494	1.489	1.499	1.429	1.421	1.490	1.504
82.388	1.494	1.490	1.498	1.428	1.423	1.489	1.474

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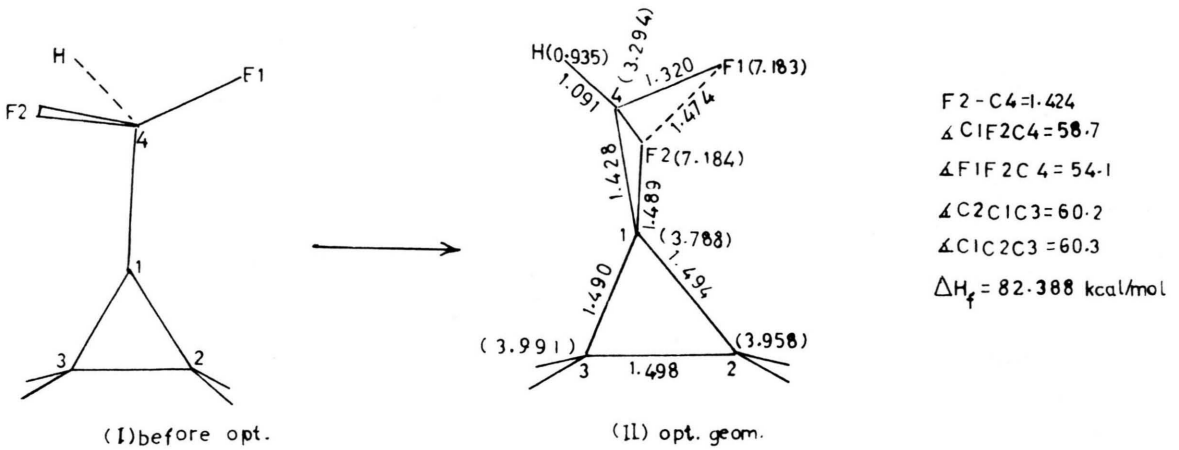

Fig. 1. Calculated geometrical parameters and electron density distributions of α-CF_2H-cyclopropyl cation.

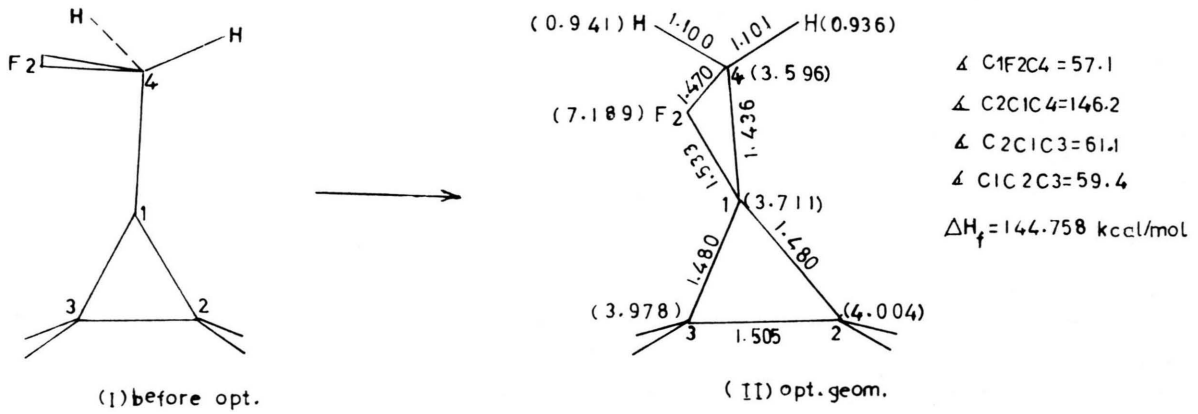

Fig. 2. Calculated geometrical parameters and electron density distributions of α-CFH_2-cyclopropyl cation.

Table 2. Variation of ΔH_f (kcal/mol) with bond distances (in Å) during geometry optimization of α-CFH_2-cyclopropyl cation. See Fig. 2 for numbering.

ΔH_f	C1C3	C1C2	C2C3	C1C4	C4F2	C1F2
174.195	1.430	1.430	1.426	1.489	1.311	2.231
164.975	1.471	1.465	1.482	1.432	1.389	2.211
162.293	1.471	1.471	1.496	1.435	1.392	2.139
160.148	1.472	1.477	1.499	1.435	1.396	2.143
156.105	1.471	1.485	1.500	1.436	1.406	1.893
154.920	1.454	1.480	1.495	1.455	1.416	1.843
151.553	1.479	1.496	1.504	1.432	1.419	1.743
148.997	1.474	1.495	1.502	1.436	1.432	1.666
146.807	1.471	1.488	1.501	1.443	1.451	1.592
145.839	1.479	1.486	1.504	1.436	1.458	1.557
145.360	1.479	1.480	1.504	1.437	1.466	1.540
145.203	1.481	1.481	1.504	1.435	1.466	1.538
145.110	1.486	1.483	1.506	1.429	1.465	1.534
145.008	1.480	1.504	1.504	1.436	1.468	1.536
144.918	1.480	1.480	1.504	1.435	1.468	1.536
144.758	1.480	1.480	1.505	1.436	1.470	1.533

atom forms a single bridge with an angle of 57.1°, and the carbon atom C4 is by 15° below the plane of the cyclopropyl ring, as shown in Figure 2.

The calculated electron density distribution (Fig. 2) on F2 indicates that the lone pair is still in the vicinity of the fluorine atom, and the positive charge is mainly on the carbon atom C4.

In order to emphasise that the fluorine atom interacts only with the empty P-type orbital and localized positive charge, we study the effect of CF_3 on the cyclopropyl anion and CF_2H on the cyclopropenyl cation.

In the first case, no interaction was found between the fluorine atoms and the P-orbital on carbon atom C1. This is because there is a high electron density (4.610) on this carbon atom which prevents such an interaction.

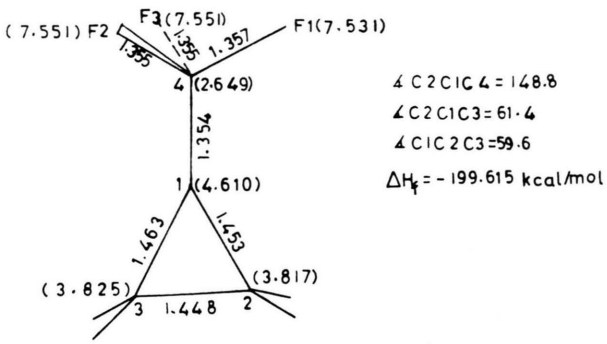

Fig. 3. Calculated geometrical parameters and electron density distributions of α-CF_3-cyclopropyl anion.

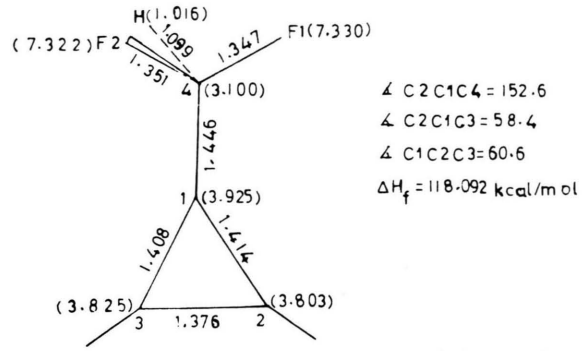

Fig. 4. Calculated geometrical parameters and electron density distributions of α-CF_2H-cyclopropenyl cation.

The calculated electron densities and the geometrical parameters of the α-CF_3-cyclopropyl anion after complete optimization are given in Figure 3.

For the CF_2H is substituted on the cyclopropenyl cation, also no interaction was found between the fluorine atom and the empty P-orbital on the carbon atom C1. This is because the positive charge is delocalized on the cyclopropenyl ring. This is in a good agreement with our recent calculations on 2-substituted allyl cations [6].

The calculated geometrical parameters and the electron density distributions of the α-CF_2H-cyclopropenyl cation are given in Figure 4.

It can be concluded from these calculations that the fluorine atom interacts strongly with the localized empty Pπ-type orbital and forms a bridge. This is another peculiarity of the fluorine atom which is first noticed in our calculations.

Acknowledgement

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