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Ab Initio Investigation of the Electronic Properties of Cyclopropyl, α-Fluorocyclopropyl, and α-Chlorocyclopropyl Anions

J. Tyrrell,* V. M. Kolb, and C. Y. Meyers

Contribution from the Department of Chemistry and Biochemistry,
Southern Illinois University at Carbondale,
Carbondale, Illinois 62901. *Received December 26, 1978*

Abstract: Electronic structure calculations using a 4-31G basis set have been carried out on cyclopropyl and α-halocyclopropyl anions. The results show substantial barriers to inversion of the X atom in the species $C_3H_4X^-$ about the plane of the cyclopropyl ring. Substitution of halogens for hydrogen in the α position does not appear to stabilize the anion.

Introduction

Meyers et al.[1a-g] have shown that α-halo ketones may follow a variety of reaction pathways when treated with powdered potassium hydroxide in *tert*-butyl alcohol, depending on the nature of the α-halo ketone. A striking example is the contrast between α-haloisopropyl ketones and α-halocyclopropyl ketones. At 25 °C α-bromo- and α-chloroisopropyl phenyl ketone are rapidly converted into α-hydroxyisopropyl phenyl ketone. Under identical conditions α-chlorocyclopropyl phenyl ketone is quantitatively cleaved within 2.5 h into chlorocyclopropane and potassium benzoate, and α-bromocyclopropyl phenyl ketone with 2 h quantitatively undergoes 50% cleavage into bromocyclopropane and potassium benzoate and 50% dehydrobromination. Likewise, mono- and bis(α-chlorocyclopropyl) ketone are quantitatively cleaved into chlorocyclopropane and, respectively, potassium cyclopropanoate and potassium α-chlorocyclopropanoate. On the other hand, cyclopropyl phenyl ketone and α-methylcyclopropyl phenyl ketone were quantitatively *recovered* after similar treatment even after many hours under reflux (82 °C). Meyers suggested that the facile cleavage reactions reflect the low transition energy associated with the substantial stability of the α-chloro- and α-bromocyclopropyl anions (or the metal-anion pairs) formed in this process. This suggestion has been supported by preliminary calculations.[1c,e,h]

It has also been shown[2,3] that cleavage of optically active cyclopropanes involves the chiral anion as an intermediate but that the resulting cyclopropanes retain their original configuration. This would suggest the possibility of a significant barrier to inversion about the plane of the cyclopropyl ring for the anion. Koeppl[4] has used valence force field methods to estimate a barrier to inversion for the cyclopropyl anion of 19 kcal/mol. On the other hand, Clark and Armstrong[5] using a small Gaussian-type basis set have determined the energy difference between the bent and planar cyclopropyl anion to be only 1.66 kcal/mol.

The purpose of the present study is to determine the relative energies of the planar and bent $C_3H_4X^-$ anions where X is H, F, or Cl and thus to determine the barrier to inversion in these anions. We further wish to determine the stabilizing effect, if any, of substitution of fluorine or chlorine for hydrogen at the α position. For this purpose we use the method of "isodesmic" reactions and also compare the electron population distributions in the three anions.

Method and Results

Calculations were first carried out using the semiempirical MINDO/3 program[6] to obtain optimized geometries for the α-halocyclopropyl anions. For comparative purposes similar calculations were carried out on the related halocyclopropanes and cyclopropane and the geometries obtained compared, where possible, with experimental data. The MINDO/3 program was also used to optimize the geometries of the species $CH_3\bar{C}XCH_3$ where again X is hydrogen, fluorine, or chlorine.

Using the optimized geometries for the cyclopropyl anions obtained using the MINDO/3 program a series of calculations were carried out for each anion using the GAUSSIAN 70 ab initio program[7] and a 4-31G basis set. In these calculations the dihedral angle XCCC was varied from 90° through 180° op-

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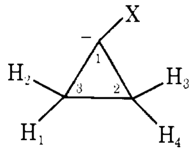
Table I. MINDO/3 Optimized Geometries of Cyclopropyl Anions[a]



	cyclopropyl anton	fluorocyclopropyl anion	chlorocyclopropyl anion
R C_1-C_2	1.483	1.507	1.500
R C_2-C_3	1.488	1.489	1.489
R H_1-C_3	1.125	1.122	1.120
R H_2-C_3	1.129	1.117	1.115
R H_3-C_2	1.129	1.117	1.115
R H_4-C_2	1.125	1.122	1.120
R X-C_1	1.122	1.444	1.890
$\angle C_3C_2C_1$	59.9	60.5	60.3
$\angle H_1C_3C_2$	122.7	120.9	121.8
$\angle H_2C_3C_2$	118.8	118.4	118.3
$\angle H_3C_2C_3$	118.8	118.4	118.3
$\angle H_4C_2C_3$	122.8	120.9	121.8
$\angle XC_1C_2$	117.0	112.5	114.9
$\angle H_1C_3C_2C_1$	109.0	108.1	105.9
$\angle H_2C_3C_2C_1$	−121.2	−121.3	−122.1
$\angle H_3C_2C_3C_1$	121.1	121.2	122.1
$\angle H_4C_2C_3C_1$	−109.1	−108.1	−106.0
$\angle XC_1C_2C_3$	107.3	103.5	105.5
Total energy, eV	−452.2898	−916.0243	−785.9597

[a] Bond lengths are in ångstroms and angles in degrees.

timizing the XCC angle for each dihedral angle considered but allowing the rest of the geometry to remain constant. This allowed us to observe the variation in the energy of the various cyclopropyl anions for a range of angles θ where θ is the angle between the C–X bond and the extension of the plane of the cyclopropyl ring.

A further set of ab initio calculations, using the 4-31G basis set, was carried out for the cyclopropyl anions $C_3H_4X^-$ and the propyl anions $C_3H_6X^-$ using the MINDO/3 optimized geometry of the fluorocyclopropyl anion and the fluoropropyl anion, respectively, except for the C–X bond lengths in the cases X = H or Cl. These latter bond lengths were taken from the MINDO/3 optimized geometries of the appropriate cyclopropyl and propyl anions.

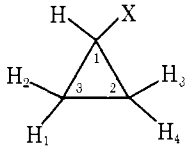
Table I lists the optimized geometries and total energies obtained for the cyclopropyl, fluorocyclopropyl, and chlorocyclopropyl anions using the MINDO/3 method with no restraints placed on the optimization procedure. The comparable optimized geometries and total energies for cyclopropane, fluorocyclopropane, and chlorocyclopropane obtained using the MINDO/3 program are given in Table II. The ab initio results for the energies of the various cyclopropyl anions, $C_3H_4X^-$, as a function of the angle, θ, between the C–X bond and the extension of the plane of the cyclopropyl ring are presented in Table III. Table IV lists the total electron populations at the atoms for both the bent and planar configurations of the cyclopropyl anions obtained using the ab initio method. Finally, Table V gives the energies for the various cyclopropyl and propyl anions obtained using the ab initio program, the geometries used being obtained as described previously.

Discussion

The results of the geometry optimization for all three cyclopropyl anions using the MINDO/3 method indicate that the X atom in $C_3H_4X^-$ is significantly out of the plane of the cyclopropyl ring. In other words, the bent configuration is the minimum energy one. Comparison of the optimized geometries obtained for cyclopropane and chlorocyclopropane with experimental data[8,9] indicates that the MINDO/3 optimization procedure gives very good agreement for the C–H bond lengths and only slightly short (0.01–0.03 Å) C–C and C–Cl bond lengths. A comparison of the cyclopropane geometries with those of the appropriate cyclopropyl anions shows that the C–H bonds lengthen slightly in going to the latter. The C–F and C–Cl bonds also lengthen by approximately 0.06 and 0.12 Å, respectively, on forming the anion. Also notable is the significant increase in the dihedral angles $H_2C_3C_2C_1$ and $H_3C_2C_3C_1$ in the anions where H_2 and H_3 are on the same side of the plane of the cyclopropyl ring as the X atom. The XC_1C_2 angle is also observed to decrease slightly on formation of the anion.

The results of the ab initio calculations on the cyclopropyl anions indicate the C–X bond to form an angle of 61° with the plane of the cyclopropyl ring in the cyclopropyl anion and 71 and 65°, respectively, for the fluoro- and chlorocyclopropyl

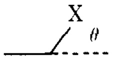
Table II. MINDO/3 Optimized Geometries of Cyclopropanes[a]



	cyclopropane		fluorocyclopropane	chlorocyclopropane	
R C_1-C_2	1.494	(1.524)[b]	1.481	1.489	(1.513)[c]
R C_2-C_3	1.494		1.508	1.501	
R H_1-C_3	1.106	(1.08)[b]	1.106	1.106	(1.105)[c]
R H_2-C_3	1.106		1.103	1.104	
R H_3-C_2	1.106		1.103	1.104	
R H_4-C_2	1.106		1.106	1.106	
R H_5-C_1	1.106		1.103	1.105	
R X-C_1	1.106		1.387	1.768	(1.778)[c]
$\angle C_3C_2C_1$	60.0		59.4	59.7	
$\angle H_1C_3C_2$	120.7		120.8	121.0	
$\angle H_2C_3C_2$	120.7		119.7	120.1	
$\angle H_3C_2C_3$	120.7		119.7	120.0	
$\angle H_4C_2C_3$	120.7		120.8	121.1	
$\angle H_5C_1C_2$	120.8		125.3	121.4	
$\angle XC_1C_2$	120.6		116.9	122.5	
$\angle H_1C_3C_2C_1$	110.0		109.8	109.0	
$\angle H_2C_3C_2C_1$	−110.0		−110.6	−110.9	
$\angle H_3C_2C_3C_1$	110.1		110.6	110.8	
$\angle H_4C_2C_3C_1$	−110.0		−109.7	−109.2	
$\angle H_5C_1C_2C_3$	−110.1		−114.8	−110.9	
$\angle XC_1C_2C_3$	109.9		107.5	111.9	
Total energy, eV	−468.8575		−931.9561	−801.6054	

[a] Bond lengths are in ångstroms and angles in degrees. [b] Reference 8. [c] Reference 9.

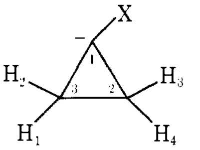
Table III. Variation of Energy with θ



cyclopropyl anion		fluorocyclopropyl anion		chlorocyclopropyl anion	
θ, deg	E_{tot}, au	θ, deg	E_{tot}, au	θ, deg	E_{tot}, au
0.0	−115.9395	0.0	−214.6593	0.0	−574.3598
11.2	−115.9428	10.6	−214.6603	11.9	−574.3683
28.8	−115.9510	31.8	−214.6730	32.0	−574.3885
48.6	−115.9632	55.45	−214.7068	52.3	−574.4132
57.6	−115.9668	63.9[a]	−214.7186	60.1	−574.4209
58.2[a]	−115.9673	64.6	−214.7192	60.9[a]	−574.4218
65.3	−115.9666	72.8	−214.7243	67.7	−574.4222
67.0	−115.9616	75.0	−214.7202		

[a] MINDO optimized geometries.

Table IV. Electron Populations for Cyclopropyl Anions[a]



	cyclopropyl anion		fluorocyclopropyl anion		chlorocyclopropyl anion	
	planar	bent	planar	bent	planar	bent
C_1	6.52	6.37	6.02	5.88	6.38	6.21
C_2	6.31	6.38	6.30	6.41	6.28	6.37
C_3	6.31	6.38	6.30	6.42	6.28	6.37
H_1	0.98	0.95	0.99	0.95	0.95	0.92
H_2	0.99	0.98	0.96	0.93	0.97	0.93
H_3	0.98	0.96	0.97	0.93	0.95	0.92
H_4	0.99	0.98	0.95	0.93	0.97	0.93
X	0.93	0.98	9.49	9.54	17.22	17.34

[a] Planar corresponds to X in plane of cyclopropyl ring; bent corresponds to minimum energy configuration.

Table V. Energy Values for the Cyclopropyl and Propyl Anions[a]

	cyclopropyl anions	propyl anions
H	−115.9611	−117.3310
F	−214.7192	−216.0964
Cl	−574.4166	−575.7894

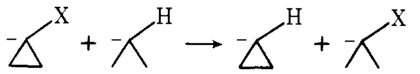
[a] Assuming fixed geometries except for C–X bond. Energies are in atomic units.

anions. These values are in quite good agreement with the angles of 58.2, 63.9, and 60.9° obtained for cyclopropyl, fluorocyclopropyl, and chlorocyclopropyl anions, respectively, in their MINDO/3 optimized geometries. In all three cyclopropyl anions, as indicated in Table III, the planar structure ($\theta = 0°$) is less stable than the optimum bent configuration. The energy difference between the two configurations is taken as the barrier to inversion of the X atom about the plane of the cyclopropyl ring. The barriers are 17.4 kcal/mol for the cyclopropyl anion, 41.8 kcal/mol for the fluorocyclopropyl anion, and 39.7 kcal/mol for the chlorocyclopropyl anion. The barrier of 17.4 kcal/mol for the cyclopropyl anion is in good agreement with the estimated value of 19 kcal/mol obtained by Koeppl[4] using a valence force field method developed by Costain and Sutherland[10] and Weston.[11] On the other hand, Clark and Armstrong[5] using a small Gaussian-type basis set determined the energies of the planar and bent configurations of the cyclopropyl anion to be −111.840 22 and −111.842 86 hartrees, respectively, giving a barrier of only 1.66 kcal/mol. Presumably the basis set used by Clark and Armstrong[5] was too limited to properly represent the anion. The barriers for the α-fluoro- and α-chlorocyclopropyl anions indicate an even greater likelihood of configuration retention in reactions involving these ions. Jaffé[12] has obtained the energies for the bent and planar forms of $C_3H_5^-$ and $C_3H_4F^-$ using an optimization procedure and the CNDO/2 program. For $C_3H_5^-$ he obtains a barrier to inversion of 36.6 kcal/mol and for $C_3H_4F^-$ a barrier of 18.7 kcal/mol, almost exactly the reverse of the ab initio results. In all three anions there is a significant increase in nuclear repulsion in the bent as opposed to the planar configuration but this is more than compensated for by an increase in the electronic energy in going to the bent configuration.

The highest occupied orbital in all three anions in the planar configuration is predominantly a 2p orbital of the carbon bound to the X atom with the 2p orbital oriented perpendicular to the plane of the cyclopropyl ring, though in the α-chlorocyclopropyl anion there is also some Cl 3p character present. In the bent configuration the highest occupied orbital, while still predominantly associated with the α carbon, has acquired some carbon 2s character and the other carbons and the X atoms also contribute. The atomic orbital electron population changes in going from the planar to the bent configuration are similar for all three anions. The largest changes are observed for the orbitals of the carbon attached to the X atom and to a lesser extent for the orbitals of the X atom itself. The electron population of the 2s orbital of the α carbon shows increases of from 0.24 e in the cyclopropyl anion to 0.46 e in the α-chlorocyclopropyl anion and a corresponding decrease in the 2p orbitals of the α carbon, particularly in the 2p orbital oriented perpendicular to the plane of the ring. There is also an increase of about 0.2 e in the 3p orbital of the chlorine oriented toward the attached carbon and similarly in the corresponding 2p orbital of the fluorine.

Table IV shows that the X atom gains electron population, primarily at the expense of the α carbon, in going from the planar to the bent configuration in all three anions. In particular, the cyclopropyl anion shows a much more evenly balanced electron population distribution among the carbons in the bent configuration. The bent configurations in the α-halocyclopropyl anions are characterized by a greater electron population on the halogen atom as compared to the planar anions. This additional electron population on the halogen is acquired at the expense of the hydrogens and the α carbon. In fact the α carbon ends up with a net decrease in electron population in the α-fluorocyclopropyl anion. It is notable, however, that the other two carbons in the cyclopropyl ring retain their excess electron population on α-halogen substitution. In fact there is an increasing discrepancy between the electron population on the α carbon and that on the other two carbons as X goes from hydrogen to chlorine and finally to fluorine.

In attempting to determine the relative stability of the three cyclopropyl anions we make use of the concept of the "isodesmic" reaction[13] of the type shown in eq 1. The energy of re-



(1)

action 1 represents the difference between halogen substituent stabilization of a strained ring and that of its saturated acyclic analogue. By calculating the total energies of all four species, using the same basis set (4-31G) and the same geometries for both rings and for both propanes, we obtain a reaction energy which should indicate whether the halogen has a stabilizing effect on the cyclopropyl anion or not. From the total energies listed in Table V we obtain a reaction energy of −1.8 kcal/mol when X is chlorine and −4.6 kcal/mol when X is fluorine. This suggests that substitution of hydrogen by chlorine may slightly destabilize the cyclopropyl anion whereas substitution by fluorine significantly destabilizes the anion. This pattern of increasing destabilization of the cyclopropyl anion follows the increasing discrepancy between the electron population on the α carbon and that on the other two carbons. However, the energy difference, particularly in the case of chlorine substitution, is so small that perhaps the only reasonable conclusion would be that the halogen substitution at the α carbon has little influence on the stability of the cyclopropyl anion.

In conclusion, therefore, our results show that the three cyclopropyl anions investigated all have substantial barriers to inversion of the X atom in $C_3H_4X^-$ about the plane of the cyclopropyl ring. This would certainly appear to support the idea of configuration retention in such ions. The effect of halogen substitution at the α carbon, while reducing the electron population in the ring, does so primarily at the expense of the α carbon leading to an imbalance of electron population distribution in the ring. The "isodesmic" reaction method suggests that such halogen substitution has only a small effect on the stability of the cyclopropyl anion and that the effect is a destabilizing one.

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Infrared Spectra, Structure, and Bonding in the Dihalocarbene Cations in Solid Argon

Lester Andrews* and Brian W. Keelan

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901.

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Abstract: Argon resonance photoionization of $CHFCl_2$, $CDFCl_2$, CH_2Cl_2, CD_2Cl_2, and $CHCl_3$ during condensation with excess argon at 15 K produced a new 1197-cm^{-1} infrared absorption which is assigned to CCl_2^+. Chlorine and carbon-13 isotopic data verify the molecular identity and provide a 133° valence angle calculation. The markedly increased ν_3 mode for CCl_2^+ at 1197 cm^{-1} above CCl_2 at 746 cm^{-1} is attributed to enhanced π bonding in the cation. Observation of the $CClBr^+$ and CBr_2^+ cations at 1122 and 1019 cm^{-1}, respectively, in studies with CH_2ClBr and $CHFBr_2$, $CDFBr_2$, CH_2Br_2, and CD_2Br_2 reinforces the identification of CCl_2^+.

Dihalocarbenes have been of considerable interest to physical organic chemists over the last 2 decades.[1] Dichlorocarbene has been trapped in solid argon following generation by photolysis, chemical reaction, and pyrolysis of suitable precursors.[2-4] Isotopic shifts in the matrix infrared spectrum provide a Cl-C-Cl bond angle determination[5] of 106 ± 5°, and the position of the infrared fundamentals of CCl_2 question the extent of π bonding in this intermediate.[3] π bonding should,

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