A Theoretical Study of Monosubstituted Cyclopropenyl System

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MONDO-Forces calculations have been performed, with complete optimization of geometry on X-cyclopropenyl system (cations, radicals and anions), where X is H, O^-, OH, CH_3, CN, NO_2, F and CF_3. All substituents prefer planar structure when substituted on both cations and radicals, while they prefer pyramidal structure in the case of anions except CF_3. The substituents O^-, OH and F act as electron releasing, while CHO, NO_2 and CF_3 act as electron withdrawing when substituted on cyclopropenyl system. CH_3 and CN show amphielectronic behaviour. They act as electron releasing on the cations and withdrawing on both radicals and anions depending on electron demand. In the case of cations and radicals, all substituents were found to increase the vicinal bonds and decrease the distal bonds and bond angles to which the substituent is attached. For anions the substitutents show no such regularity because the substituents are out of the three-membered ring plane. All substituents increase the stability of the cyclopropenyl system except CF_3 in the case of the cation.

The cyclopropenyl cation is the smallest aromatic molecule which has two π-electrons and satisfies the Hückel $4n + 2$ rule. The electronic structure is of great interset since the molecule is highly strained but despite of this the ion is stable in the form of salts, e.g. $C_3H_3 \cdot SbCl_6^-$, and also in polar solvents [1]. D_{3h} configuration of the ion is indicated by its IR and NMR spectra [1]. Allen has reported a structural analysis for two cyclopropenyl cation derivatives based upon X-ray crystallographic data [2]. Clark carried out ab initio LCAO SCF MO Calculations on both $C_3H_3^+$ and $C_3H_3^-$ and discussed the aromaticitiy and antiaromaticity [3]. Ha et al. reported an ab initio LCAO SCF MO investigation on $C_3H_3^+$, $C_3H_3^{\cdot}$ and $C_3H_3^-$ and discussed the geometry and stability of these species [4]. Random et al. also carried out ab initio calculations on $C_3H_3^+$ using STO-3G and 6-31G and obtained the equilibrium structure of the ion [5]. Takada and Ohno also published an ab initio CI calculation on the electronic structure of $C_3H_3^+$ [6]. The most recent ab initio calculations on the molecular structure and vibrational spectrum of $C_3H_3^+$ were performed by Xie et al. [7], and Lee et al. [8].

Cyclopropenyl free radical, the simplest member of the series of fully conjugated cyclic radicals, has been the subject of experimental [9–13] and theoretical studies [4, 14–20].

The theoretical work by Chipman and Miller [20] predicts an ethylenic structure of C_s symmetry as the lowest energy form. The hydrogen atom at the apex of the isoceles triangle is bent substantially out of the ring plane. The allylic structure, which satisfies the Jahn-Teller theorem, is predicted to be 5 kcal/mole higher in energy. Experimental work by Closs and Redwine [13] support the C_s structure and rules out the allylic structure. There is no experimental information on the properties of the neutral radical, so it is necessary to resort to theoretical studies.

The cyclopropenyl anion, having 4π electrons, is the smallest antiaromatic species. The high pka value for cyclopropene in solution [9] indicates instability of the anion. On the other hand, there have been numerous molecular orbital calculations using either semiempirical [14, 16, 21–23] or ab initio [3, 4, 17, 24, 25] methods. Among these calculations, the latest results [24, 25] indicate that the structure with lowest energy has C_S symmetry with one hydrogen being out of the plane and the other two being out of plane in the opposite direction. This structure is supported by a recent ab initio study [26, 27].

There has been an interest in substituent resonance effects [28–42]. A major concern is the form of substituent response as the electron demand is altered in the attached pi-system [28–37].

The aim of the present work is to utilize quantum chemical calculations to provide predictions of heat of formation, geometry, electron density distribution and stability of the cyclopropenyl system (cation, radical and anion) and to study the effect of the substituents O^-, OH, CH_3, CHO, CN, NO_2, F, and CF_3 on this system.

The calculated heat of formation of monosubstituted cyclopropenyl system is obtained by the semiempirical MINDO-Forces MO method [43]. The

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Table 1. Calculated geometrical parameters of monosubstituted cyclopropenyl system. Bond lengths are in Ångstroms and bond angles in degrees

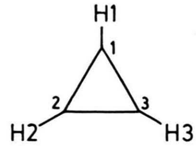
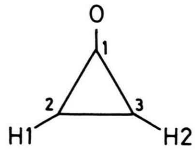
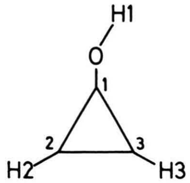
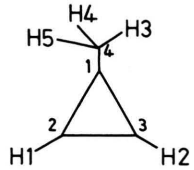
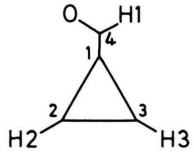
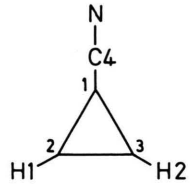
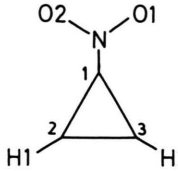
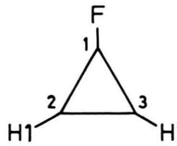
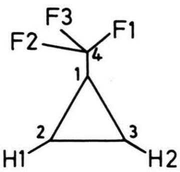
Compounds	Cations	Radicals	Anions
1 	C1 – C2, 1.386; C1 – H, 1.088 C2C1C3, 59.9	C1 – C2, 1.453; C2 – C3, 1.345 C1 – H, 1.104; C2C1C3, 55.4	C1 – C2, 1.514; C2 – C3, 1.309 C1 – H, 1.175; C2C1C3, 51.2
2 	C1 – C2, 1.501; C2 – C3, 1.303 C1 – O, 1.161; C2C1C3, 51.5	C1 – C2, 1.458; C2 – C3,1.340 C1 – O, 1.194; C2C1C3, 55.1	C1 – C2, 1.460; C2 – C3, 1.429 C1 – O, 1.232; C2C1C3, 60.1
3 	C1 – C2, 1.401; C2 – C3, 1.371 C1 – O, 1.263; C2C1C3, 58.3	C1 – C2, 1.460; C2 – C3, 1.339 C1 – O, 1.296; C2C1C3, 57.0	C1 – C2,1.535; C2 – C3, 1.313 C1 – O, 1.389; C2C1C3, 50.8
4 	C1 – C2, 1.408; C2 – C3, 1.369 C1 – C4, 1.452; C2C1C3, 58.2	C1 – C2, 1.457; C2 – C3, 1.335 C1 – C4, 1.415; C2C1C3, 55.0	C1 – C2, 1.534; C2 – C3, 1.304 C1 – C4, 1.476; C2C1C3, 50.7
5 	C1 – C2, 1.404; C2 – C3, 1.377 C1 – C4, 1.494, C2C1C3, 58.8	C1 – C2, 1.457; C2 – C3, 1.329 C1 – C4, 1.412; C2C1C3, 55.2	C1 – C2, 1.512; C2 – C3, 1.312 C1 – C4, 1.390; C2C1C3, 51.9
6 	C1 – C2, 1.408; C2 – C3, 1.371 C1 – C4, 1.427; C2C1C3, 58.3	C1 – C2, 1.460; C2 – C3, 1.334 C1 – C4, 1.385; C2C1C3, 54.7	C1 – C2, 1.532; C2 – C3, 1.307 C1– C4, 1.442; C2C1C3, 50.7
7 	C1 – C2, 1.400; C2 – C3, 1.385 C1 – N, 1.471; C2C1C3, 59.4	C1 – C2, 1.456; C2 – C3, 1.337 C1 – N, 1.361; C2C1C3, 55.1	C1 – C2, 1.506, C2 – C3, 1.314 C1 – N, 1.348; C2C1C3, 52.0
8 	C1 – C2, 1.391; C2 – C3, 1.386 C1 – F, 1.314; C2C1C3, 59.8	C1 – C2, 1.461; C2 – C3, 1.339 C1 – F, 1.332; C2C1C3, 56.7	C1 – C2, 1.494; C2 – C3, 1.322 C1 – F, 1.453; C2C1C3, 52.5
9 	C1 – C2, 1.410; C2 – C3, 1.376 C1 – C4, 1.467; C2C1C3, 58.4	C1 – C2, 1.456; C2 – C3, 1.327 C1 – C4, 1.509; C2C1C3, 56.8	C1 – C2, 1.506; C2 – C3, 1.311 C1 – C4, 1.448; C2C1C3, 51.9

Table 2. Calculated heats of formation (ΔH_f in kcal/mol) for parent cyclopropenyl and monosubstituted cyclopropenyl cation (planar), radical (planar and pyramidal), and anion (planar and pyramidal).

No.	Subst.	ΔH_f				
		cat.	rad.		ani.	
		plan.	plan.	pyr.	plan.	pyr.
1	H	240.494	100.582	98.994	104.545	112.667
2	O^-	213.083	15.175	15.473	23.326	22.943
3	OH	170.975	31.041	34.720	74.630	44.877
4	CH_3	216.272	79.311	85.236	105.084	97.127
5	CHO	204.857	46.260	57.943	204.859	39.834
6	CN	249.631	105.302	109.716	118.047	116.724
7	NO_2	233.174	59.944	66.635	29.344	28.716
8	F	193.597	23.017	25.237	36.427	28.012
9	CF_3	59.603	– 115.874	– 109.276	– 146.882	– 138.913

molecular energy of the monosubstituted system obtained from the MINDO/3 method [44] was completely minimized according to the Murtagh-Sargent minimization technique [45]. The derivative of the energy was calculated according to Pulay's Force method [46]. The program allows for variation of the parameters with geometry in a consistent fashion. A similar basis set is used for the system because we are concerned with comparisons between similar systems. A full description of the program and its application is given in [43a].

Results and Discussion

The calculated geometrical parameters, heats of formation and electron density distributions of the monosubstituted cyclopropenyl system after complete optimization of the geometrical parameters are given in Tables 1, 2, 3, 4, and 5.

1. Effect of substituents on the cyclopropenyl cations

Structural details:

The geometry of $C_3H_3^+$ has not been determined experimentally, so predictions of the geometry may be helpful for future experimental work. The geometry of $C_3H_3^+$ (Table 1) is in fair agreement with theoretical calculations of Takada et al. [6] (C–C = 1.383 Å and C–H = 1.095 Å), and Random et al. [5] (C–C = 1.377 Å and C–H = 1.095 Å). The geometry optimization using the STO-3G basis set, which was performed in [5], must be considered as rough because of its very small basis set. The experimental C–C bond length for the 1,2,3-trisdimethylaminecyclopropenyl cation is 1.363 ± 0.007 Å [47], and 1.373 Å for the sym-triphenylcyclopropenyl cation [48]. The experimental C–C bond value for 1,2,3 trisdimethylaminecyclopropenyl cation may not be precise because of the interaction of the amino groups with three-membered ring. The C–C bond lengths (1.386 Å in Table 1) in the three-membered ring are significantly shorter than those in benzene (1.397 Å) [49]. This effect may be interpreted as due to the bent C–C bond in the three-membered ring.

All the substituents on the cyclopropenyl cations are found to lie in the plane of the cyclopropenyl cations. The vicinal bounds are longer than the distal bond for all substituents except for F, which is in agreement with ab initio calculations [50]. Also, it was found that the C–X bond in cyclopropenyl cation is longer than that in C–X cyclopropyl cation [51] especially for electron donating substituents. This may be due to the interaction between the localized empty *P* orbital on the Cl atom in the cyclopropyl cation [51] and the substituent, which decreases the C–X bond.

Stabilization by substituents:

The stabilizing effect of substituents is often assessed by using isodesmic reactions (conserved bond type) [39]. A positive heat of formation (Table 6) indicates stabilization of the reactant by the substituent. The results show that the substituents O^-, OH, CH_3, CHO, CN and NO_2 are stabilizing, F is slightly stabilizing, and CF_3 is destabilizing. This is in agreement with ab initio calculations [50] for OH, CH_3, and F substituents.

Electron densities:

It can be seen from Table 3 that the substituents O^-, OH and F decrease the electron densities on Cl and increase the electron densities on C2 and C3. That is, they act as electron releasing. CH_3 and CN act as weak electron releasing.

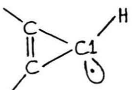
For CF_3 and NO_2 substituents, the electron densities increase on Cl and decrease on C2 and C3. That is, they act as electron withdrawing. The CHO substituent acts as weak electron withdrawing.

2. Effect of substituents on the cyclopropenyl radical:

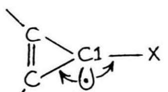
Structural details:

The present calculation of geometrical parameters of parent cyclopropenyl radical show that the hydrogen atom at the apex of the isoceles triangle is bent substantially out of the ring plane by 56.6° which is in agreement with Chipman and Miller [20]. The calculated heat of formation is 98.994 kcal/mole, in a good agreement with the experimental value (105.1 ± 4.1 kcal/mole) [52] and that of Bischof (96.8 kcal/mole) [53]. The calculated pseudorotation barrier height is 1.588 kcal/mole, in better agreement with the experimental value (0.57 kcal/mole) established by Gunthard et. al. [54] and Bischof (0.515 kcal/mole) than that obtained by ab initio calculations (3–4 kcal/mole) [20].

The calculated heats of formation (Table 2) for all substituents on cyclopropenyl radical show that all substituents prefer the planar structure. This may be due to that fact that the unpaired electron density (Table 7) lies mainly on the apex of the isoceles triangle for parent cyclopropenyl radical, which pushes the hydrogen atom adjacent to Cl out of the plane. That is to say that the parent radical prefers the pyramidal structure 1a. For monosubstituted cyclopropenyl radicals it was found that the unpaired electron density for most of the substituents is distributed over the three carbon atoms and hence the planar structure is prefered.



1a



1b

All substituents are found to increase the vicinal bonds and to decrease the distal bonds and bond angles to which the substituent is attached (Table 1), except OH. Also it was found that the C–X bond in cyclopropenyl radical is shorter than that in cyclopropyl radical [55]. This may be due to the fact that the substituent in the cyclopropyl radical lies out of the ring and hence decreases the interaction with the unpaired electron in the P orbital. That is to say longer C–X bond.

Stabilization by substituents:

The results (Table 6) show that all the substituents are stabilizing, and O^- is strongly stabilizing as compared to the case of the cation.

Electron densities:

For O^-, OH and F substituents, it was found that there is a decrease in the electron density distributions on Cl and an increase on C2 and C3 (Table 4). That is, they act as electron releasing. For CH_3, CHO, CN, NO_2 and CF_3, the electron density distributions increase on Cl and decrease on C2 and C3. That is, they act as electron withdrawing.

3. Effect of substituents on cyclopropenyl anion:

Structural details:

The calculated geometrical parameters for the parent cyclopropenyl anion show C_S symmetry, with one hydrogen being out of the plane by 72.9°, and the other two being out of the plane by 7.7° in the opposite direction, which is in agreement with recent ab initio calculations [26, 27]. The heat of formation of pyramidal cyclopropenyl anion is 112.667 kcal/mole, in agreement with that suggested by the ab initio study (110 ± 5 kcal/mole) [25]. No experimental heat of formation exists for cyclopropenyl anion. The calculated energy barrier is 33.87 kcal/mole, in agreement with ab initio study (35.4 kcal/mole) [25]. This demonstrates the 'antiaromatic' character of the cyclopropenyl anion, that is the repulsive 4π electron interaction between the localized lone pair electrons in the P orbital in the planar structure and the double bond.

The calculated heats of formation (Table 2) for all substituents on cyclopropenyl anion show that all substituents except CF_3 prefer the pyramidal structure substituent. This may be due to the high rotational barrier (33.87 kcal/mole) of the parent cyclopropenyl anion.

Table 3. Electron density distributions of monosubstituted cyclopropenyl cations. See Table 1 for numbering.

Atom	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6	Cat. 7	Cat. 8	Cat. 9
C1	3.823	3.345	3.505	3.775	3.924	3.754	4.035	3.426	3.982
C2	3.823	3.925	3.888	3.870	3.809	3.862	3.778	3.903	3.790
C3	3.827	3.932	3.963	3.873	3.832	3.863	3.781	3.905	3.799
C4				3.988	3.408	3.960			2.673
H1	0.842	0.808	0.841	0.852	0.846	0.848	0.838	0.825	0.833
H2	0.842	0.809	0.842	0.853	0.850	0.850	0.841	0.826	0.832
H3	0.843		0.680	0.941	1.023				
H4				0.924					
H5				0.923					
N						4.863	3.858		
O1		6.181	6.281		6.309		6.434		
O2							6.434		
F1								7.116	7.366
F2									7.362
F3									7.362

Table 4. Electron density distributions of monosubstituted cyclopropenyl radicals. See Table 1 for numbering.

Atom	Rad. 1	Rad. 2	Rad. 3	Rad. 4	Rad. 5	Rad. 6	Rad. 7	Rad. 8	Rad. 9
C1	4.107	3.403	3.509	4.167	4.152	4.109	4.191	3.594	3.829
C2	3.985	4.091	4.224	3.965	3.923	3.959	3.903	4.044	3.926
C3	3.949	4.095	4.267	3.944	3.947	3.945	3.900	4.049	3.946
C4				3.818	3.428	3.881			2.917
H1	1.021	0.947	0.746	0.965	1.140	0.956	0.930	0.952	0.917
H2	0.963	0.945	0.915	0.971	0.946	0.958	0.932	0.949	0.914
H3	0.976		0.918	1.042	0.951				
H4				1.066					
H5				1.062					
N						5.188	3.915		
O1		6.518	6.421		6.514		6.615		
O2							6.615		
F1								7.413	7.522
F2									7.514
F3									7.516

Table 5. Electron density distributions of monosubstituted cyclopropenyl anion. See Table 1 for numbering.

Atom	An. 1	An. 2	An. 3	An. 4	An. 5	An. 6	An. 7	An. 8	An. 9
C1	4.315	3.432	4.069	4.406	4.381	4.406	4.388	3.917	4.329
C2	4.094	4.323	4.167	4.102	4.089	4.084	4.048	4.140	4.066
C3	4.108	4.343	4.119	4.041	4.003	4.048	4.021	4.130	3.988
C4				3.763	3.413	3.845			2.793
H1	1.264	1.127	1.103	1.084	1.054	1.072	1.031	1.093	1.014
H2	1.113	1.041	1.106	1.095	1.067	1.083	1.040	1.092	1.035
H3	1.107		0.852	1.148	1.283				
H4				1.208					
H5				1.153					
N						5.463	3.931		
O1		6.735	6.584		6.711		6.764		
O2							6.778		
F1								7.627	7.576
F2									7.622
F3									7.577

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

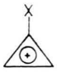
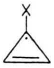
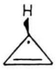
	O^-	OH	CH_3	CHO	CN	NO_2	F	CF_3
 $+ CH_3CH_3 \rightarrow CH_3CH_2X +$ 	50.008	28.219	20.522	8.237	16.825	9.002	2.597	− 5.434
 $+ CH_3CH_3 \rightarrow CH_3CH_2X +$ 	106.416	24.653	15.983	25.334	19.654	40.720	31.677	28.543
 $+ CH_3CH_3 \rightarrow CH_3CH_2X +$ 	112.321	26.490	11.840	45.433	21.905	85.633	40.355	73.224

Table 7. Calculated spin densities of monosubstituted cyclopropenyl radicals. See Table 1 for numbering.

Atom	Rad. 1	Rad. 3	Rad. 4	Rad. 5	Rad. 6	Rad. 7	Rad. 8	Rad. 9
C1	0.349	0.360	0.322	0.310	0.305	0.312	0.441	0.204
C2	0.300	0.260	0.293	0.289	0.303	0.312	0.106	0.122
C3	0.310	0.268	0.289	0.291	0.305	0.563	0.102	0.121
C4			0.064	0.068	0.055			0.144
H1	0.015	0.007	0.012	0.004	0.012	0.012	0.006	0.004
H2	0.011	0.010	0.011	0.011	0.012	0.012	0.008	0.004
H3	0.012	0.009	0.004	0.011				
H4			0.004					
H5			0.004					
N					0.004	0.030		
O1		0.082		0.013		0.003		
O2						0.003		
F1							0.335	0.117
F2								0.141
F3								0.148

The effects of substituents on the geometrical parameters (Table 1) are not consistent as in the case of the cation or radical since they lie outside the three-membered ring.

It was found that the C–X bond in the cyclopropenyl anion is longer than that in cyclopropenyl anion [51] due to the localized negative charge on the P orbital in the case of the cyclopropyl anion, which enhances the interaction.

Stabilization by substituents:

The results in Table 6 show that all substituents are highly stabilizing as compared to the cation and radical. Also it was found that O^- substituent is highly stabilizing as compared to radical and cation, probably because the O^- substituent is a relatively strong σ and π donor [56], which causes the cyclopropenyl anion to obtain aromatic character (6π electrons), as compared to the radical (5π electrons) and the cation (4π electrons).

For the electron withdrawing substituents such as CHO, CN and NO_2, the stabilizing effect is more pronounced in the case of anion than in that of both radical and cation. This may be due to the decrease of the electron densities on the three-membered ring and hence the unstabilized anion (relative to the radical and cation) becoming aromatic in character. The high dipole moments of NO_2 (11.8 D) and CF_3 (10.9 D) in the case of the cyclopropenyl anion as compared to the parent cyclopropenyl anion (8.9 D), support the high stabilizing effect of these substituents (Table 6) as compared to the cation and radical.

Electron densities:

It was found that O^-, OH and F substituents decrease the electron densities on C1 and increase on C2 and C3 (Table 5). That is, they act as electron releasing.

For CH_3, CHO, CN, NO_2 and CF_3, the electron density increases on Cl and decrease on C2 and C3. That is, they acts as electron withdrawing.

Therefore CH_3 and CN show the amphielectronic behaviour. Thus they act as electron releasing on the cations and withdrawing on both radicals and anions depending on electron demand [5, 57–63].

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