A Theoretical Study of 2-Substituted Allyl Cations and Anions

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MINDO-Forces calculations are reported, after complete geometry optimization, for 2-X-allyl cations and anions, where X is O^-, OH, NH_2, CH_3, NO_2, CN, CF_3, F, CHO. In the case of the allyl cation, it was found that the substituents O^-, OH, NH_2 are stabilizing, CH_3 is slightly stabilizing and all other substituents are destabilizing. In the case of the allyl anions, all the substituents are stabilizing. It was found that the substituents CH_3, O^-, CN show the amphielectronic behaviour. Calculations predict no (1,3) π interaction in 2-substituted ally cations and anions.

Introduction

Recently [1], we have shown that there is no (1,3) π-interaction in the parent allyl cation, while the substitution of a methyl group on the center carbon atom of the allyl cation causes a little tendency for (1,3) π-interaction [1–3].

Much experimental [4–6] and theoretical [7, 8] work has been devoted to determining the importance of (1,3) π-interaction in the allyl cation. Also, there has been recent interest in substituent resonance effects [9–23]. A major concern is the form of the substituent response as the electron demand is altered in the attached pi-system [9–18].

The aim of the present work is to study the effect of the substituents O^-, OH, NH_2, CH_3, NO_2, CN, CF_3, F and CHO on the 2-position allyl cation and anion.

This paper reports the geometry, heat of formation and electron density of 2-substituted allyl systems from calculations by the semiempirical MINDO-Forces method [24]. The molecular energy of the 2-substituted allyl system obtained from the semiempirical MINDO/3 method [25] was completely minimized according to the Murtagh-Sargent minimization technique [26]. The derivative of the energy was calculated according to Pulay's Force method [27]. The program allows for a variation of the β parameter with geometry in a consistent fashion. A similar basis set is used for the two possible ion states because we are concerned with comparisons between similar systems. A full discription of the program and its application is given in ref. [24a].

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Results and Discussion

The calculated heats of formation and electron densities of the 2-substituted allyl system after complete geometry optimization are given in Tables 1, 2 and 3. The geometrical parameters of the system are given in Figures 1 and 2.

1. Effect of substituents on the allyl cation

Structural details:

The OH substituted on the centeral carbon atom of the allyl cation may be perpendicular to or in the plane of the cation. It was found that the latter position is more stable (Fig. 1), similar by to the hydroxypyridine structure [24d].

The 2-amino allyl cation was found to be the most stable when the angle between the plane of the allyl cation and the plane determined by the NH_2 is 15° and the amino N is in the plane of the cation.

Introduction of a substituent into the 2-position of the allyl cation has little effect on the carbon-carbon bond lengths and produces a small decrease in $\widehat{CCC}$ (Fig. 1) apart from F substituent, which is in agreement with ab initio calculations [20].

Stabilization by substituents:

The stabilizing effect of substituents is often assessed by using isodesmic reactions (conserve bond type) [20]. A positive heat of formation (Ta-

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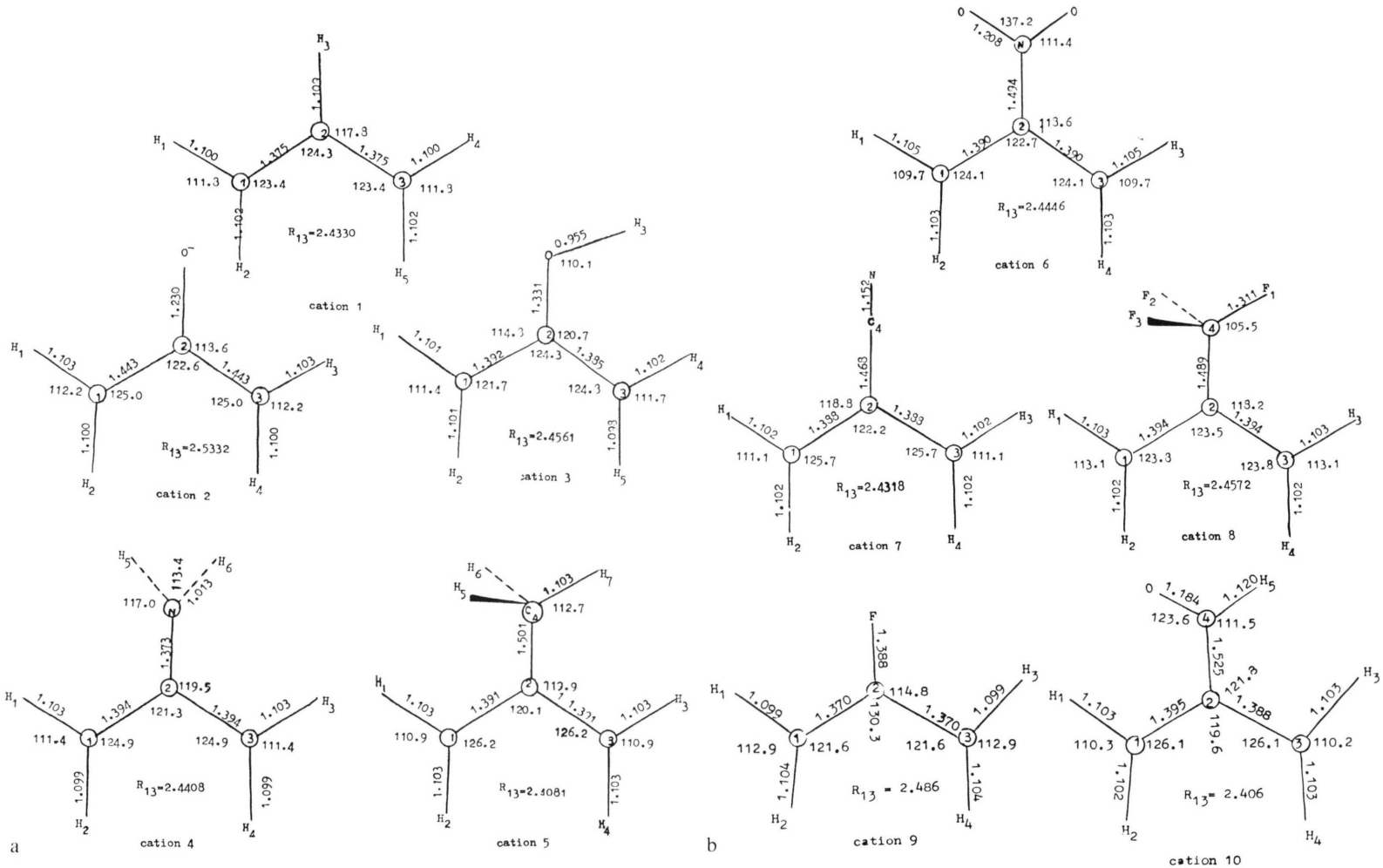

Fig. 1. Optimized geometries for 2-substituted allyl cations. Bond lengths are in Ångströms, and bond angles are in degrees.

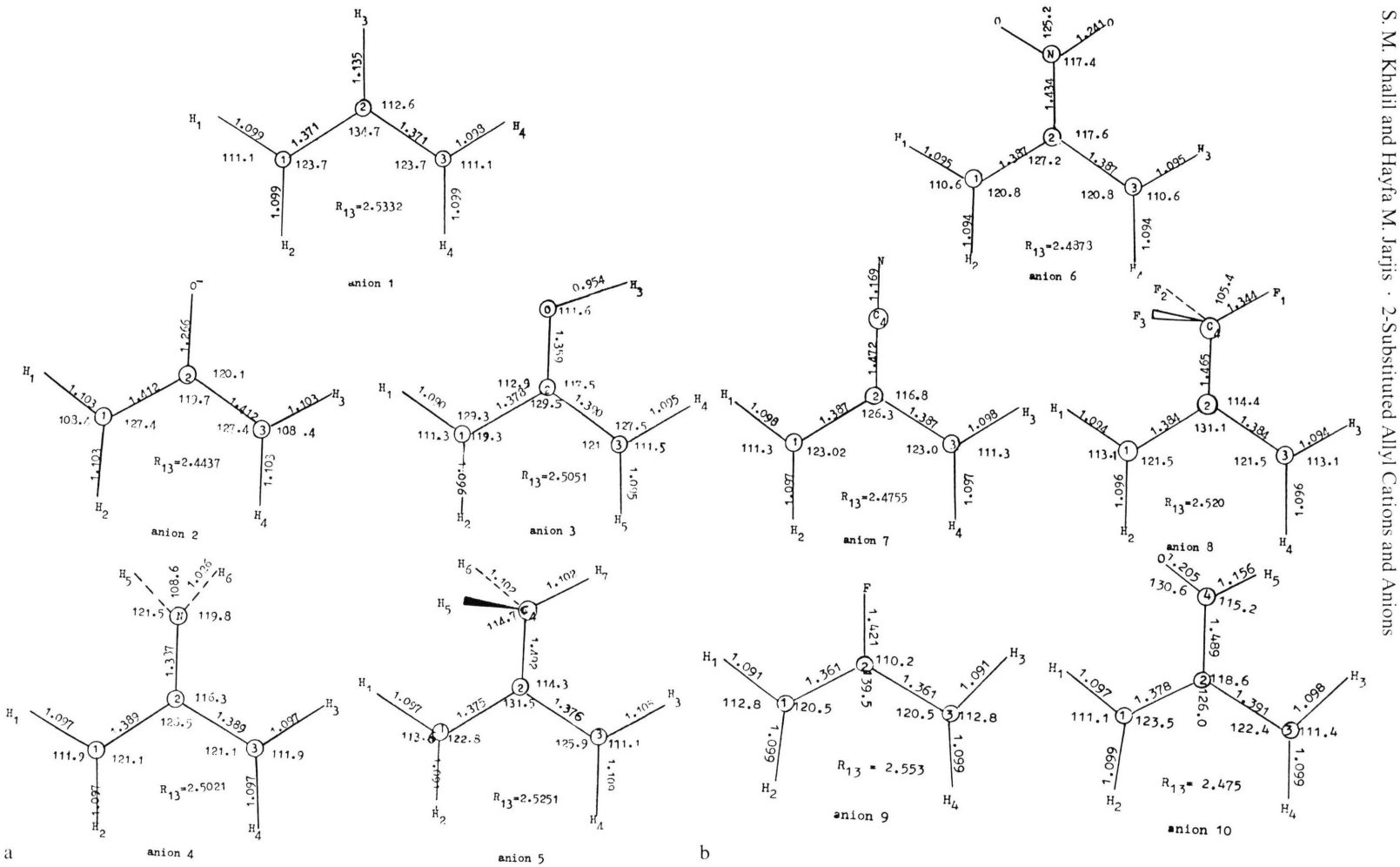

Fig. 2. Optimized geometries for 2-substituted allyl anions. Bond lengths are in Ångströms, and bond angles are in degrees.

Table 1. Calculated heats of formation (ΔH_f in kcal/mole) for parent allyl and 2-substituted allyl cations and anions.

No.	Substituent	ΔH_f	
		Cation	Anion
1	–	222.261*	40.565*
2	O^-	237.543	– 2.758
3	OH	174.246	– 18.863
4	NH_2	215.906	33.723
5	CH_3	216.560	36.431
6	NO_2	226.506	9.322
7	CN	246.336	56.247
8	CF_3	48.565	−174.311
9	F	179.558	– 32.336
10	CHO	197.971	0.814

* Results for parent allyl cation and anion from [1].

ble 4) indicates stabilization of the reactant by the substituent. The results show that the substituents O^-, OH and NH_2 are stabilizing, CH_3 is slightly stabilizing, and all other substituents are destabilizing.

Electron densities:

It can be seen from Table 2, that the substituents O^-, OH, NH_2, CH_3, CN and F decrease the electron densities on the central carbon atom of the allyl cation and increase the electron densities on its terminal carbon atoms. That is, act as electron releasing.

For the OH substituent, the electron densities on the three carbon atoms (Fig. 1) are almost equal, which may suggest that there is a little interaction between the terminal carbon atoms. But from the distance between the terminal carbon atoms (R_{13}), as indicated in Fig. 1, the possibility of the (1,3) π-interaction can be neglected.

In the case of the electrons withdrawing substituents CF_3, NO_2 and CHO the electron densities decrease on the terminal carbon atoms and increase on the central carbon atom, opposite to the effect found for O^-, OH, NH_2, CH_3, CN and F.

2. Effect of substituents on the allyl anion

Structural details:

Introduction of a substituent at the 2-position of the allyl anion has little effect on the carbon-carbon bond lengths and produces a small decrease in $\widehat{CCC}$ (Fig. 2) apart from F substituent. This is similar to the result calculated in the case of the allyl cation.

Stabilization by substituents:

The stabilizing effect of substituents is also assessed by using isodesmic reactions in a similar manner to that of 2-substituted allyl cations. The results (Table 4) show that all the substituents are stabilizing [19].

Electron densities:

For the O^- substituent the electron densities decrease on the three carbon atoms (Table 3), which may be due to the high electronegativity of O^-. This strongly suggests that the phenomenon of electron releasing depends on the system to which the substituent is attached, which is another support for our previous work [1]. The CHO substituent behaves as O^-, i.e. it decreases the electron densities on the three carbon atoms of the allyl anion.

For OH, NH_2 and F substituents the electron densities increase on the terminal carbon atoms of the allyl anion and decrease on its central carbon atom. That is, they behave as electron releasing groups.

For the rest of the substituents, it was found that there is a decrease in the electrons density on the terminal carbon atoms of the allyl anion and an increase on the central one. That is, they behave as electron withdrawing. Therefore CN, O^-, CH_3 show the amphielectronic behaviour. They thus act as electron releasing and withdrawing depending on the electron demand [1], [18], [28–30].

The distances R_{13} between the terminal carbon atoms of the allyl anion and 2-substituted allyl anions (Fig. 2) are large enough to rule out the possibility of (1,3) π-interaction.

It can be concluded from this work that the phenomenon of electron releasing or withdrawing depends on the systems to which the substituent is attached and that the possibility of (1,3) π-interaction between the terminal carbon atoms in 2-substituted allyl system is not significant.

Acknowledgements

We would like to thank our project students for running the MINDO-Forces program and their help during the preparation of this work. Thanks are also to the Mosul University Computer Centre for computer time.

Table 2. Calculated electron densities of 2-substituted allyl cations.

Atom	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6	Cat. 7	Cat. 8	Cat. 9	Cat. 10
C1	3.619	3.712	3.721	3.748	3.652	3.570	3.639	3.580	3.719	3.585
C2	4.121	3.620	3.736	3.912	4.072	4.321	4.063	4.282	3.717	4.224
C3	3.619	3.712	3.794	3.748	3.652	3.570	3.639	3.580	3.719	3.614
C4					3.948		3.954	2.640		
H1	0.923	0.883	0.891	0.922	0.934	0.907	0.929	0.904	0.880	0.921
H2	0.951	0.934	0.935	0.934	0.950	0.946	0.953	0.944	0.929	0.957
H3	0.891	0.883	0.710	0.923	0.934	0.902	0.929	0.903	0.880	0.937
H4	0.923	0.934	0.911	0.933	0.951	0.948	0.953	0.944	0.929	0.950
H5	0.951		0.921	0.867	0.966					1.054
H6				0.871	0.966					
H7					0.973					
O		6.321	6.381			6.480				6.370
O						6.480				
N				5.455		3.850	4.940			
F1								7.398	7.226	
F2								7.413		
F3								7.413		

See Fig. 1 for numbering.

Table 3. Calculated electron densities of 2-substituted allyl anions.

Atom	An. 1	An. 2	An. 3	An. 4	An. 5	An. 6	An. 7	An. 8	An. 9	An. 10
C1	4.503	4.305	4.575	4.566	4.501	4.420	4.470	4.430	4.605	4.410
C2	3.708	3.441	4.434	3.605	3.756	3.914	3.757	3.901	3.325	3.386
C3	4.503	4.305	4.624	4.566	4.501	4.420	4.470	4.430	4.605	4.455
C4					3.874		3.876	2.714		
H1	1.038	1.024	1.008	1.026	1.030	0.993	1.032	0.995	0.983	1.017
H2	1.027	1.052	1.008	1.009	1.019	1.004	1.018	1.006	1.003	1.022
H3	1.154	1.024	0.801	1.026	1.040	0.989	1.032	0.995	0.983	1.029
H4	1.038	1.052	1.019	1.009	1.025	1.007	1.018	1.000	1.003	1.014
H5	1.077		1.002	0.988	1.094					1.226
H6				0.988	1.094					
H7					1.096	6.660				
O		6.797	6.528			6.660				6.572
O						3.936				
N				5.217			5.380			
F1								7.519	7.494	
F2								7.508		
F3								7.508		

See Fig. 2 for numbering.

Table 4. Evaluation of substituent effects using MINDO – Forces calculations (energies are in kcal/mole).

	O^-	OH	NH_2	CH_3	NO_2	CN	CF_3	F	CHO
2-allyl cations  $+CH_3CH_3 \rightarrow$  $+CH_3CH_2X$	7.315	6.715	13.355	2.001	−2.563	−0.002	−12.629	−1.597	−3.110
2-allyl anions  $+CH_3CH_3 \rightarrow$  $+CH_3CH_2X$	65.915	18.158	14.842	0.434	5.969	10.275	28.551	28.601	12.351

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