MINDO-Forces Calculations of Allyl and Crotyl Systems. Part 1. Theoretical Study with Complete Optimization of Geometry

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MINDO-Forces calculations have been performed on the allyl and crotyl systems. For the allyl system it was found that the stability and the $\widehat{CCC}$ angle increase from the allyl cation, to the radical, to the anion. Calculations predict no $(1,3)\pi$ interaction for allyl cation. The heat of formation and the rotation barrier for the allyl system are in fairly good agreement with the experimental values and theoretical calculations. In the case of the crotyl system, the stability increases from the cation, to the radical, to the anion. The methyl group is electron-releasing in the case of crotyl cation and electron-withdrawing in the case of crotyl anion.

Allyl cation, radical, and anion (**1**) are of central importance in organic chemistry because they are intermediates in a large number of chemical reactions.[1,2] Also, they represent the simplest possible examples of conjugated π-electron systems. Because of their high reactivity, experimental investigation is difficult and thus theoretical calculations are needed to yield reliable information. This theoretical interest is reflected in various *ab initio* and semiempirical MO studies which have appeared.[3–14]

The crotyl (1-methylallyl) system (**2**) shows a marked geometrical sensitivity to π-electron occupancy.[15–20] Experimental evidence indicates that the *trans*-crotyl cation (2 π electrons in the allyl system) is more stable than the *cis*-isomer.[18] The crotyl free radical (3 π electrons in allyl) also prefers to be *trans*.[20] Various experiments[21] have indicated that for allyl anion in alkali-metal salts in solution the *cis* isomer is more stable than the *trans*. On the other hand, studies[22] by ion cyclotron resonance (i.c.r.) spectroscopy have shown that the reverse is true. In the gas phase several attempts have been made to explain this discrepancy by theoretical calculations.[23,24] *Ab initio* molecular orbital,[24] CNDO/2,[25] and extended Hückel calculations[20] indicate that in the case of crotyl anion the *cis*-isomer is more stable than the *trans*. But the MNDO method[7] found that the *trans*-isomer is more stable than the *cis*, which is in agreement with experimental results in the gas phase.[22]

In the case of crotyl cation and free radical both CNDO/2[25] and *ab initio* MO calculations[24,26] have shown that the *trans*-isomer is predicted to be more stable than the *cis*.

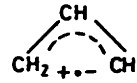
This paper refers to the geometry, heat of formation, and electron density of allyl and crotyl systems from calculations by the MINDO-Forces MO method.[27] In this method, the molecular energy of the allyl and crotyl systems obtained from the semiempirical MINDO/3 MO method[28] was completely minimized according to the Murtagh–Sargent technique.[29] The derivative of the energy was calculated according to Pulay's Forces method.[30] The program allows variation of the β parameter with geometrical change in a consistent fashion. A similar basis set is used for the three possible ion states, because we are concerned with comparisons between similar systems. A full description of the program and its application is given in ref. 27*a*.

Results and Discussion

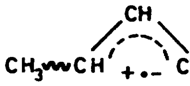
Three series of calculations were carried out for the allyl system (see Figure 1 for the co-ordinate system). In the first, denoted (0,0), both methylene groups are coplanar with the carbon atoms (planar C_{2v}); in the second, (90,0), one CH_2 group is 90° out of the CCC plane (perpendicular C_s); while in the third (90,90) both are rotated by 90° (C_{2v}).

Table 1. MINDO-Forces calculations of bond lengths (in Å) and bond angles (in degrees) of allyl system

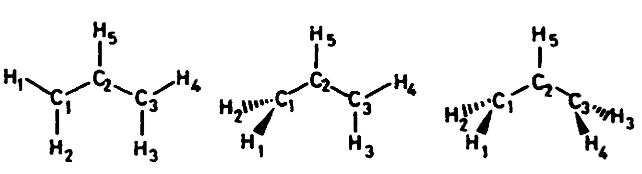
	Cation		Radical		Anion	
	(0,0)	(90,0)	(0,0)	(90,0)	(0,0)	(90,0)
C(1)–H(1)	1.100	1.104	1.096	1.095	1.099	1.094
C(1)–H(2)	1.102	1.104	1.099	1.095	1.099	1.094
C(1)–C(2)	1.375	1.401	1.373	1.416	1.371	1.397
C(2)–C(3)	1.375	1.334	1.373	1.329	1.371	1.335
C(2)–H(5)	1.109	1.114	1.116	1.123	1.135	1.169
C(3)–H(4)	1.100	1.095	1.096	1.098	1.098	1.105
C(3)–H(3)	1.102	1.100	1.099	1.100	1.099	1.106
H(1)–C(1)–H(2)	111.6	110.9	111.4	113.0	111.0	114.2
C(2)–C(1)–H(2)	123.5	124.5	123.6	123.5	123.7	122.9
H(1)–C(1)–C(2)	124.9	124.5	124.9	123.5	125.2	122.9
C(1)–C(2)–C(3)	124.3	130.6	129.1	131.4	134.7	132.6
C(1)–C(2)–H(5)	117.8	105.1	115.4	112.0	112.6	117.5
C(3)–C(2)–H(5)	117.8	124.3	115.4	116.8	112.6	109.9
H(4)–C(3)–C(2)	124.9	125.1	124.9	125.8	125.2	129.0
H(4)–C(3)–H(3)	111.6	113.4	111.4	110.9	111.0	108.2
H(3)–C(3)–C(2)	123.5	121.4	123.6	123.3	123.7	122.8



(**1**)



(**2**)



(0,0) (90,0) (90,90)

Figure 1. Co-ordinate system adopted for allyl system

MINDO-Forces calculations for the molecular geometries resulting from the (0,0) and (90,0) conformations after allowing the geometrical parameters to vary until the energy is completely minimized are given in Table 1. The (0,0) conformation was calculated without restriction on minimization but point group symmetry was imposed, while in the (90,0) conformation the rotated CH_2 group was maintained at 90° throughout the minimization (C_s). The energy of the (90,90) conformation was calculated by allowing the geometrical parameters to vary until the energy is completely minimized without any assumptions. It was found, after about 400 geometric iterations, that the two CH_2 groups become coplanar with the plane of CCC, *i.e.* resulting in a (0,0) conformation. This strongly indicates that the allyl system is planar.

It can be seen from Table 1 that the $C\hat{C}C$ angle for the cation [124.3° for (0,0), 130.6° for (90,0)] is in good agreement with that of Peyerimhoff and Buenker[3] [123° for (0,0), 132° for (90,0)] and Kolmar and Smith[13] [123° for (0,0)]. Upon adding an electron to the system, the $C\hat{C}C$ angle changes to 129.1° for (0,0) and to 131.4° for (90,0) in fairly good agreement with the results of Peyerimhoff and Buenker for the (0,0) conformation ($C\hat{C}C$ 127°), but not with those for the (90,0) conformation ($C\hat{C}C$ 123°). By adding a second electron to the system (allyl anion) the $C\hat{C}C$ angle changes to 134.7° for the (0,0) conformation and to 132.6° for the (90,0) conformation, which is also in good agreement with Peyerimhoff and Buenker for the (0,0) conformation ($C\hat{C}C$ 134°). No theoretical calculation for the (90,0) conformation of the allyl anion is available to compare with the present results.

The calculated heats of formation for the allyl system after complete energy minimization are given in Table 2. It was found that the ground state of the system has completely planar geometry. On rotating a CH_2 group out of the plane to obtain the (90,0) conformation for the allyl cation the conjugation decreases and the bond length C(1)–C(2) increases from 1.375 to 1.40 Å and C(2)–C(3) decreases from 1.375 to 1.334 Å (essentially double bond).

The rotation barrier [energy difference between (0,0) and (90,0) conformations] is 13.8 kcal mol^{-1}, in agreement with that of Shanshal[12] (14.15 kcal mol^{-1}) and Kollmar and Smith[13] (11 kcal mol^{-1}). No experimental value has been found for the rotational barrier of allyl cation. For the substituted allyl cation the experimental measured rotation barrier is 15.7 kcal mol^{-1}.[31]

For the allyl radical, on rotating a CH_2 group to obtain the (90,0) conformation the bond length C(1)–C(2) increases from 1.373 to 1.416 Å and C(2)–C(3) decreases from 1.37 to 1.329 Å. The rotation barrier is 4 kcal mol^{-1}, in good agreement with that of Dewar[8] (4.3 kcal mol^{-1}). No experimental value has been found for the barrier to rotation of the unsubstituted and substituted allyl radical.

This result is also consistent with previous observations[32] that the addition of an electron to allene (isoelectronic with allyl cation) greatly reduces the barrier of this system toward rotation of its methylene group into a coplanar arrangement.

For allyl anion, when rotating the CH_2 group to obtain (90,0) conformation, the barrier to rotation was found to be 17.186 kcal mol^{-1}. No experimental value has been found for the barrier to rotation of the unsubstituted and substituted allyl anion apart from one theoretical calculation of Dewar *et al.*[8] (10.5 kcal mol^{-1}).

The calculated electron densities for the allyl system are given in Table 3. It can be seen that the electron densities on the terminal carbon atoms increase from the cation to the anion (cation 3.619, radical 4.056, and anion 4.503). This increase in the electron density from cation to anion suggests that repulsion between the terminal carbon atoms increases from cation to anion which in turn suggests that the angle should increase from cation to anion. This is indeed what we found in the present calculations (Table 1).

It interesting to determine the importance of 1,3 π interactions in allyl cation. The electron deficiency in allyl cation (Figure 2) may be distributed equally between the terminal centres as in (**1a**) or the central carbon atom may also be electron deficient due to 1,3 π interactions as in (**1b**). Our

Table 2. Comparison of the calculated heats of formation (ΔH_f) with the observed values and other theoretical calculations

	ΔH_f/kcal mol^{-1}		
Compound	Calcd.	Obsd.	Previous calculations
Allyl cation			
(0,0)	222.261	216[a]	222.2[b]
(90,0)	236.003		
Allyl radical			
(0,0)	44.063	39.40 ± 1.5[c] 44.2[b] 41.5 ± 2[d]	35.3[e]
(90,0)	48.803		
Allyl anion			
(0,0)	40.565		26[e]
(90,0)	57.751		

[a] $C_3H_5^+$ give wide range of values of ΔH_f ($C_3H_5^+$) from 216 to 260 kcal mol^{-1} (J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, 'Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' National Standards Bureau, Washington, 1969); F. P. Lossing, *Can. J. Chem.*, 1971, **49**, 357. [b] Ref. 8. [c] M. Rossi and D. M. Golden, *J. Am. Chem. Soc.*, 1979, **101**, 1230. [d] R. J. Field and P. I. Abell, *J. Am. Chem. Soc.*, 1969, **91**, 7226. [e] M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 748.

(**1a**) (**1b**)

Figure 2. Types of electron distribution for allyl cation

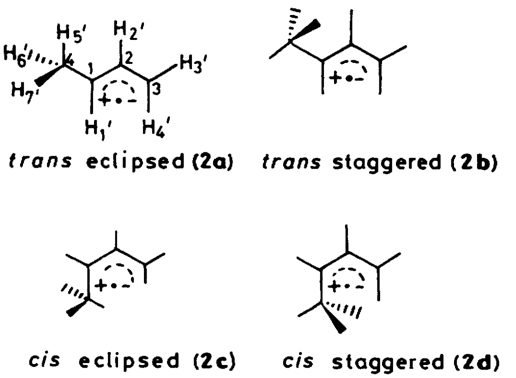
Table 3. MINDO-Forces calculations of electron densities for the allylic system

Compound	H(1)	H(2)	C(1)	C(2)	C(3)	H(3)	H(4)	H(5)
Allyl cation								
(0,0)	0.923	0.951	3.619	4.121	3.619	0.951	0.923	0.891
(90,0)	0.945	0.945	3.433	4.173	3.833	0.942	0.908	0.821
Allyl radical								
(0,0)	0.984	0.988	4.056	3.923	4.056	0.988	0.984	1.021
(90,0)	0.975	0.975	4.082	3.918	4.048	0.991	0.988	1.022
Allyl anion								
(0,0)	1.038	1.027	4.503	3.708	4.503	1.027	1.038	1.154
(90,0)	1.005	1.005	4.711	3.638	4.249	1.048	1.063	1.280

Table 4. MINDO-Forces calculations of heats of formation (ΔH_f/kcal mol^{-1}) and optimized bond lengths (in Å) and bond angles (in degrees) for the crotyl system

	Cation	Radical	Anion
ΔH_f	198.3	29.5	17.2
1 2[a]	1.405	1.398	1.399
2 3	1.361	1.362	1.360
1 4	1.449	1.452	1.438
1 1′	1.113	1.110	1.109
2 2′	1.110	1.116	1.132
3 3′	1.090	1.096	1.098
3 4′	1.101	1.099	1.100
4 5′	1.107	1.111	1.122
4 6′	1.110	1.115	1.134
4 7′	1.110	1.115	1.134
1 2 3	127.8	129.7	133.0
1 2 2′	113.8	113.4	112.6
3 2 2	118.2	116.7	114.2
4′ 3 3′	111.5	111.1	110.3
4′ 3 2	124.1	123.5	123.4
3′ 3 2	124.3	125.3	126.1
4 1 1′	114.6	113.5	112.9
4 1 2	129.1	130.0	130.9
1′ 1 2	116.2	116.4	116.0
6′ 4 7′	106.0	104.3	100.1
6′ 4 5′	107.9	105.7	102.7
6′ 4 1	110.4	112.8	116.5
7′ 4 5′	107.9	105.7	102.7
7′ 4 1	110.4	112.8	116.5
5′ 4 1	113.7	114.2	115.7

[a] See Figure 3 for numbering.



trans eclipsed (**2a**) *trans* staggered (**2b**)

cis eclipsed (**2c**) *cis* staggered (**2d**)

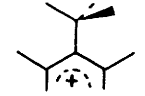
Figure 3. Possible structures for the crotyl system

calculations (see Table 3) suggest a charge distribution similar to that in (**1a**), in agreement with *ab initio* LCAO-MO SCF calculation[4] and an experimental study[33] on remote secondary isotope effects. The distance between terminal carbon atoms (2.433 Å) suggests charge distribution similar to that in (**1a**), but conflicting predictions concerning the charge distribution are given by quantum mechanical calculations of the valence type[14] and by n.m.r. spectra[34] of the allyl and 2-methylallyl cations, which suggest a charge distribution similar to that in (b).

For the crotyl systems there are four different structures adopted for the allyl system as in Figure 3. The calculations have been performed on each of the four structures (**2a**—**d**) for the crotyl cation, the free radical, and the anion. The calculated geometries and heats of formations after complete energy minimization are given in Table 4. The calculations show that the crotyl system prefers the *trans*-eclipsed isomer, which is in very good agreement with the experimental values.[18,22] In the case of crotyl cation and radical, these results are also in agreement with *ab initio*[24] and CNDO/2.[25] But for crotyl anion, both *ab initio*[24] and CNDO/2[25] calculations predict that the *cis* isomer is more stable than the *trans*, the opposite to the experimental prediction.[22]

Table 5. MINDO-Forces calculations of electron densities for the crotyl system

	Cation	Radical	Anion
C(1)	3.586	4.027	4.468
C(2)	4.142	3.939	3.729
C(3)	3.681	4.052	4.420
C(4)	4.056	3.891	3.692
H(1)	0.992	1.010	1.026
H(2)	0.917	1.023	1.134
H(3)	0.930	0.984	1.034
H(4)	0.956	0.989	1.023
H(5)	0.939	1.031	1.128
H(6)	0.901	1.027	1.173
H(7)	0.901	1.027	1.173



ΔH_f = 216·5 kcal mol^{-1}

The *ab initio* method[24] assumes that in the case of crotyl anion the methyl group donates two electrons to the system to make a total of 6 π electrons and they suggest that this system has aromatic character. According to the present results, the methyl group is electron-withdrawing and in this case there will be no aromatic character and the *cis*-isomer should not be more stable than the *trans* as suggested by the *ab initio* method.

Our calculations for crotyl anion, which suggest the *trans*-isomer is more stable, is in good agreement with experimental values[22] and the recently reported MNDO method.[7]

The calculated electron densities for the crotyl system are given in Table 5. Methyl substitution at C-1 or C-3 is electron-releasing relative to allyl cation, which results in a decrease in electron density at C-1 and an increase in electron density at C-3 and C-2 (Table 5). This suggests an elongation of the C-1–C-2 bond and shortening of the C-2–C-3 bond. This is indeed what we found in the present calculations. This is in agreement with theoretical calculations[26] and the experimental values.[35]

In the case of crotyl anion the methyl group is electron-withdrawing which decreases the electron density at C-1 and C-3. This decrease in electron density at the terminal leads to a decrease in the repulsion between C-3 and C-1 which suggests a decrease in the bond angle. The bond lengths remain almost constant as those of the crotyl cation (Table 4). The methyl group in the crotyl radical shows a weak electron-withdrawing tendency.

It can be seen from Table 4 that the angle C-1$\hat{\text{C}}$-2C-3 increases from the crotyl cation, to the radical, to the anion, which is in a good agreement with *ab initio* calculations.[24] As a result this increase in C-1$\hat{\text{C}}$-2C-3 leads to an increase in repulsion between H-2 and H-5, which in turn leads to an increase in C-2$\hat{\text{C}}$-1C-4. But *ab initio* calculations[24] give the opposite prediction; we believe that the *ab initio* method underestimates the repulsion between H-2 and H-5.

From the view point of 1,3 π interaction methyl substitution at C-1 or C-3 of allyl cation causes an increase in the angle from the allyl cation to the crotyl cation (Table 4), which suggests a charge distribution similar to that in (**1a**).

We have also studied the effect of methyl substitution at C-2 of allyl cation in order to investigate the stability and 1,3 π interactions. Our results show that methyl substitution at C-2 results in a decrease in angle from 124.3 to 120° which suggests that there is a little tendency for 1,3 π interactions in (**1b**). This is in agreement with theoretical results[10] and experimental values.[33]

From the heats of formation of 1-methylallyl and 2-methylallyl cation it can be seen that the methyl group on the terminal carbon atom stabilizes the cation more than that at the centre by 8.2 kcal mol^{-1}, which is in a good agreement with *ab initio* calculations.[26]

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