MINDO-Forces Study of Phenyl and Cyclopropyl Substituted Allyl Cations and Anions

Hayfa M. Jarjis and Salim M. Khalil
Chemistry Department, College of Science, University of Mosul, Mosul, Iraq

Z. Naturforsch. **42a**, 297–304 (1987); received December 1, 1986

MINDO-force calculations have been performed on phenyl and cyclopropyl substituted allyl cations and anions with complete energy minimization. It is found that the phenyl ring destabilizes the allyl cations when substituted at the terminal and at the center carbon atom of the cation, while the cyclopropyl ring stabilizes the allyl cation when substituted at the terminal carbon atoms, but destabilizes the cation when substituted at the center carbon atom of the cation. These results agree with the experimental ones. In the case of the allyl anions, it is found that the phenyl ring destabilizes the allyl anions when substituted on the terminal and on the center carbon atoms of the allyl anions, while the cyclopropyl ring stabilizes the allyl anion when substituted on the terminal carbon atom but destabilizes the anion when substituted on the center carbon atom. Also, it is found that both the phenyl and cyclopropyl rings are electron withdrawing when substituted on the allyl anions, while they are electron donating when substituted on the allyl cations.

Introduction

Having studied the effect of methyl on the allyl systems [1], we have extended our work to calculate the effect of phenyl and cyclopropyl on the allyl cations and anions using MINDO-forces [2]. Experimentally it was found that the methyl group [3] and the cyclopropyl ring [4, 5] stabilize the allyl cation to a degree greater than the phenyl ring.

Allylic anions are supposed to be intermediates in the base-catalysed isomerisation of olefins [6–9]. Their high reactivity renders difficult the experimental investigation of these anions and therefore calculations on them are of considerable interest.

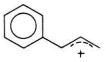
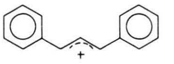
There exist no advanced calculations on these cations and anions. We have used the MINDO-forces method [2], minimizing completely the molecular energy obtained from the semiempirical MINDO/3 MO method [10] according to Murtagh and Sargent's [11] minimization technique. The derivative of the energy was calculated according to Pulay's [12] force method. A full description of the program and its application is given in reference [2a].

Results and Discussion

1. Effect of the Phenyl Ring on the Allyl Cations

The calculated heats of formation and electron densities of phenyl substituted allyl cations after complete optimization of the geometry are given in Tables 1 and 2, respectively.

Table 1. Calculated heats of formation (ΔH_f in kcal/mole) for phenyl substituted allyl cations.

Cation		ΔH_f
	1	222.7*
	2	253.5
	3	258.2
	4	246.8

* Results from Ref. [13].

Reprint requests to Prof. S. M. Khalil, Department of Chemistry, College of Science, University of Mosul, Mosul, Iraq.

0340-4811 / 87 / 0300-0297 $ 01.30/0. – Please order a reprint rather than making your own copy.

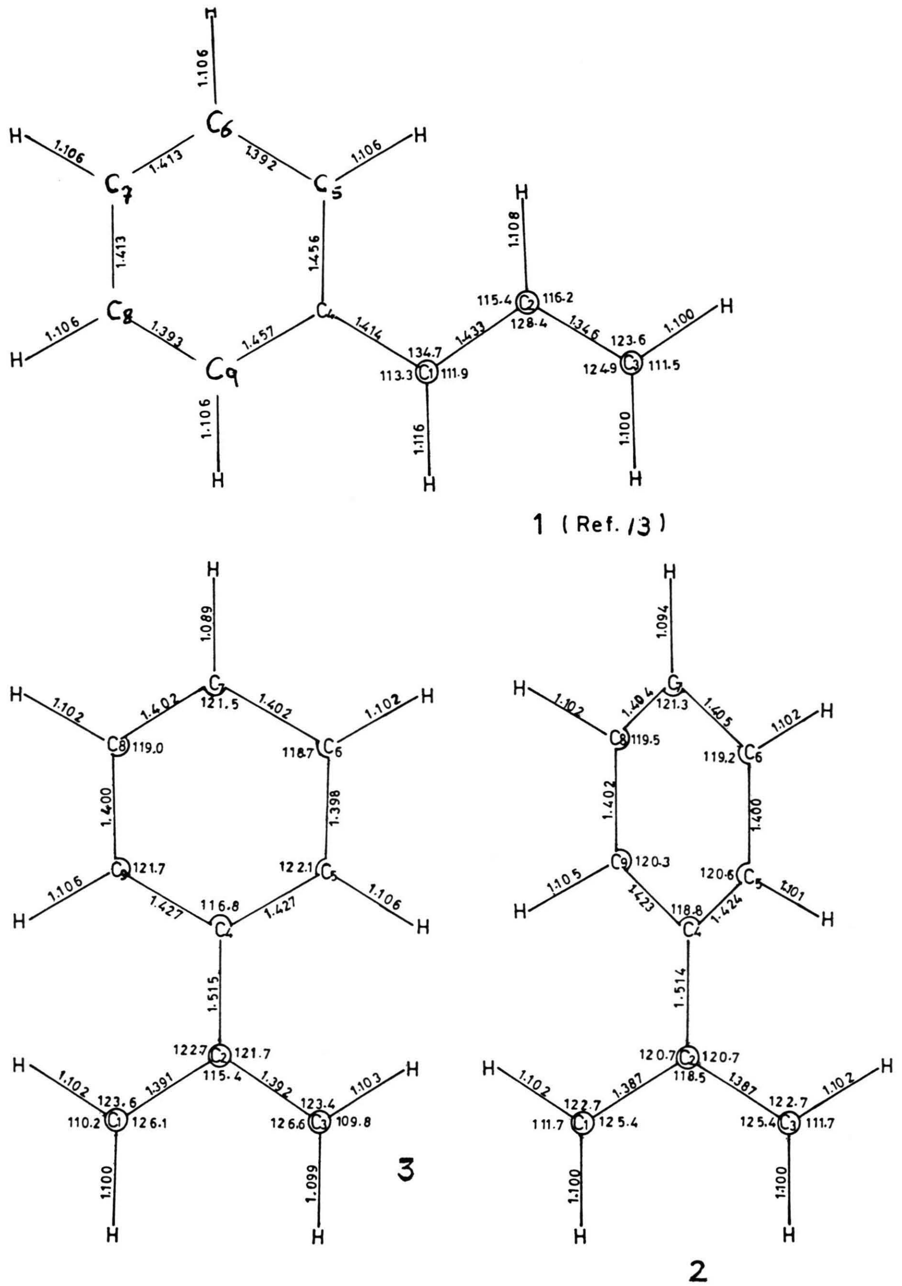


Fig. 1. Optimized geometries for one phenyl substituted allyl cations.

The phenyl substitution on the center carbon atom of the allyl cation gives rise to two possibilities; the first (cation 2) when the phenyl ring is perpendicular to the plane of the allyl carbon atoms and the second (cation 3) when the phenyl ring is in the plane of the allyl cation as shown in Figure 1.

The phenyl substitution on the terminal carbon atom of the allyl cation is expected to increase the stability of the cation due to resonance. But it was found theoretically [13] that there is a little destabilizing effect on the cation, which agrees with experimental observation [3].

Table 2. MINDO-forces calculations of electron densities for phenyl substituted allyl cations.

	Cation			
	1*	2	3	4
C1	3.657	3.665	3.681	3.699
C2	4.108	4.055	4.039	4.172
C3	3.799	3.665	3.679	3.699
C4	4.053	4.038	4.033	4.096
C5	3.856	3.984	3.972	3.897
C6	4.057	3.978	3.982	4.027
C7	3.818	3.954	3.943	3.880
C8	4.053	3.978	3.982	4.031
C9	3.854	3.981	3.970	3.908
C10				4.092
C11				3.909
C12				4.027
C13				3.881
C14				4.029
C15				3.902

* Results from Ref. [13].

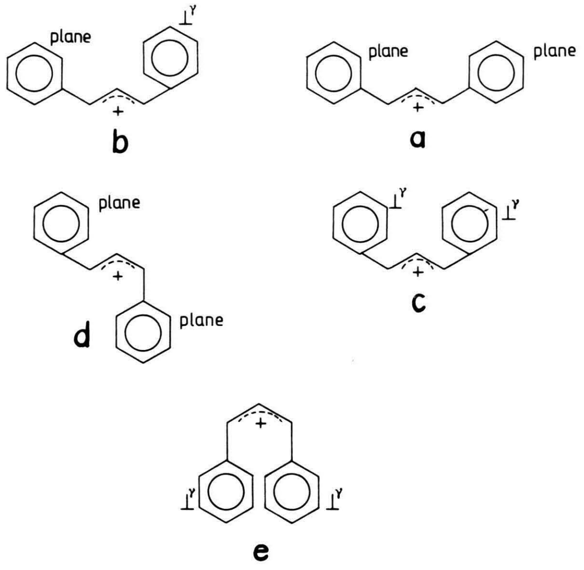


Fig. 2. Possible structures for two phenyl rings substituted allyl cations.

From this figure it is seen that both angles C1 C2 C3 and C5 C4 C9 decrease from cation 2 to cation 3 due to steric strain in cation 3. Therefore cation 2 should be more stable than cation 3, which agrees with calculations [14]. According to the calculated heats of formation (Table 1) cation 2 is more stable than cation 3, difference amounting to 4.7 kcal/mole. This difference represents the rotational barrier of the phenyl ring, which is in good agreement with that calculated by MINDO/3 [14] (4 kcal/mole). Phenyl substitution at the center carbon atom of the ally cation (cation 2) is more destabilizing than that at the terminal (cation 1). This may be due to the 6 electrons in the phenyl ring which repel the negative charge on the center carbon atom of the allyl cation [1 a].

Substitution of two phenyl rings on the terminal carbon atoms of the allyl cation gives rise to four possibilities as shown in Figure 2. The calculation of the heats of formation for these cations show that the most stable one is the cation a (cation 4 in Table 1). The calculated heat of formation of cation 4 ($\Delta H_f = 246.8$ kcal/mole) shows that the two phenyl rings destabilize the allyl cation. This is in fairly good agreement with Π-SCF calculation [15] ($\Delta H_f = 230$ kcal/mole) and indicates that there are no resonance states. This is confirmed by the bond lengths C1−C10 and C3−C4 (Fig. 3), which are longer than C1−C4 of cation 1. This means that the charge on the carbon atoms C1 and C3 has difficulty to delocalize into the phenyl rings in order to stabilize the cation (Table 2). Also the charges on the carbon atoms of the phenyl rings are small in comparison with that of cation 1 (Table 2).

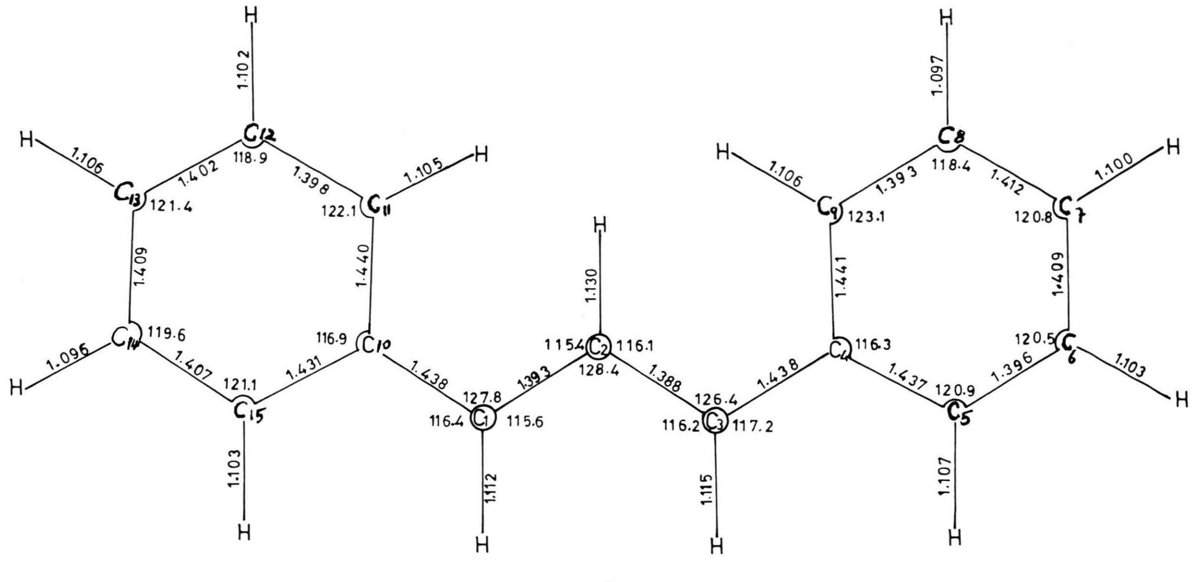
Thus it can be concluded that the substitution of the penyl ring on the terminal carbon atom has little effect on decreasing the stability, and the effect becomes more pronounced on the substitution of two phenyl rings on the terminal carbon atoms of the allyl cation. Also, the substitution of the phenyl ring on the center carbon atom of the allyl cation destabilizes the cation.

2. Effect of Cyclopropyl Ring on the Allyl Cations

The calculated heats of formation and electron densities of cyclopropyl substituted allyl cations are given in Tables 3 and 4, respectively.

In order to check that the phenyl ring destabilizes the allyl cation, i.e. no resonance phenomenon, we have studied the effect of cyclopropyl, which has no Π electrons to give resonance states, in other words that the driving force for the stability is not necessarily an electronic delocalization [16] that results from Π electrons.

Cyclopropyl substitution on the terminal carbon atom of the allyl cation gives two conformations,



4

Fig. 3. Optimized geometries for two phenyl rings substituted allyl cations.

Table 3. Calculated heats of formation (ΔH_f in kcal/mole) for cyclopropyl substituted allyl cations.

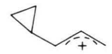
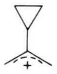
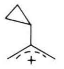
Cation		ΔH_f
	5	205.6
	6	211.2
	7	236.4
	8	236.7
	9	201.5

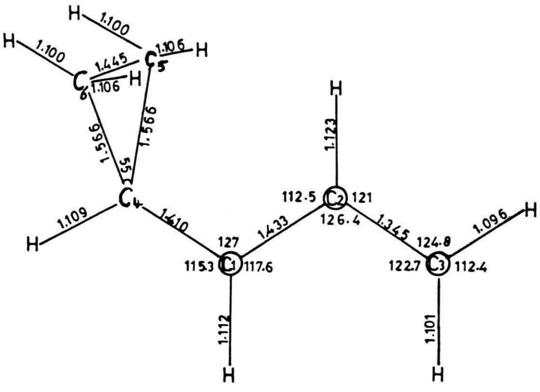
Table 4. MINDO-forces calculations of electron densities for cyclopropyl substituted allyl cations.

	Cation				
	5	6	7	8	9
C1	3.646	3.661	3.662	3.767	3.671
C2	4.113	4.119	4.058	4.045	4.176
C3	3.779	3.783	3.662	3.676	3.671
C4	4.087	4.083	4.027	4.017	4.069
C5	3.885	3.888	3.960	3.958	3.918
C6	3.885	3.888	3.961	3.958	3.918
C7					4.069
C8					3.918
C9					3.918

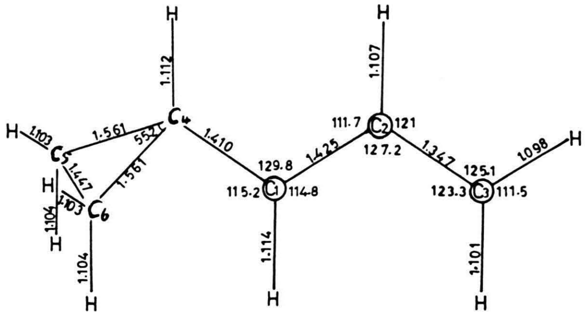
anti (cation 5) and syn (cation 6), as shown in Figure 4. The experimental results [17] could not show which of these is more stable. The calculated heats of formation (Table 3), however, did show that cation 5 is more stable than cation 6 by 5.6 kcal/mole. Also it was found that, in agreement with the experimental data [4, 5], the cyclopropyl ring increases the stability of the allyl cation.

The electron density of cation 5 (Table 4) shows that the charge increases on the substituted carbon atom and that this charge is smaller than that of cation 2 (crotyl cation [1 a]) and greater than that of cation 1. Thus increase of the charge on the substituted carbon atom of the allyl cation increases the stability of the cation. According to this, cation 5 should be more stable than cation 6, since the charge on C1 of cation 5 is greater than that on C1 of cation 6 (Table 4).

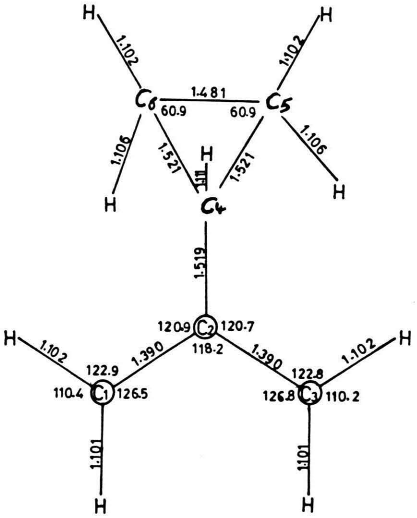
Cyclopropyl on the center carbon atom of the allyl cation also gives rise to two possibilities: either the cyclopropyl ring is not perpendicular to the plane of the allyl cation (cation 7) or it is (cation 8),



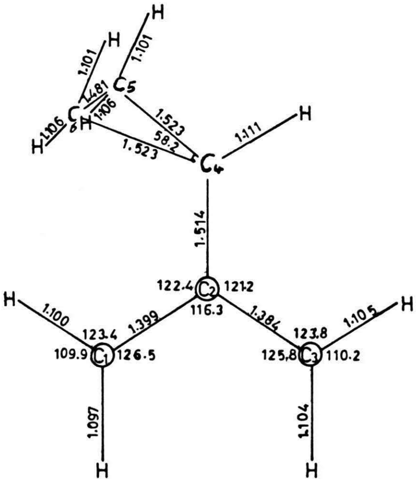
6



5

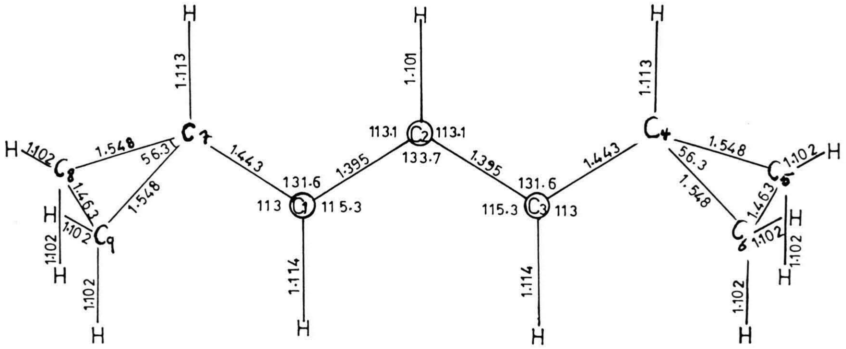


7



8

Fig. 4. Optimized geometries for cyclopropyl substituted allyl cations.



9

Fig. 5. Optimized geometries for two cyclopropyl rings substituted allyl cations.

as shown in Figure 4. The heats of formation (Table 3) show that cyclopropyl substitution at the center of the allyl cation decreases its stability. This may be due to the three electrons in the Walsh orbital [18], which cause a repulsion between the cyclopropyl ring and the negative charge on the center carbon atom of the allyl cation [1].

The difference in the heats of formation between cations 7 and 8 ($\Delta H_f = 0.3$ kcal/mole) is smaller than that between cations 2 and 3 (4.6 kcal/mole), which may be due to the ring size.

Substitution of two cyclopropyl rings on the terminal carbon atoms of the allyl cation (cation 9) is found to increase the stability of the cation more than that of one cyclopropyl ring (cation 5). From Fig. 5, it can be seen that the angle C1C2C3 of cation 9 is greater than that of cation 5 (Fig. 4), which indicates that there is less strain cation 9. This means that cation 9 should be more stable than cation 5. This situation is similar to that with cations 2 and 5 [1b].

Thus the cyclopropyl ring conjugates intensely with the allyl cation and stabilizes it more than the phenyl substituents.

3. *Effect of the Phenyl Ring on the Allyl Anions*

The calculated heats of formation and electron densities of phenyl substituted allyl anions after complete optimization of geometry are given in Tables 5 and 6, respectively.

In general, phenyl substitution increases the stability of the anions [19], due to resonance structures. But according to the present calculations, the phenyl substituent (anion 2) destabilizes the allyl anion (anion 1) by 5.8 kcal/mole as shown in Table 5. The present calculations are similar to those on phenyl substituted allyl cations [3, 13]. Thus, there is no point of carrying out a complete energy minimization for two phenyl rings substituted on the terminal carbon atoms of the allyl anion.

From Table 6, it can be seen that the phenyl ring acts as a electron withdrawing substituent (anion 2), while it was found to be electron-donating when attached to the allyl cation. This means that the electron density increases on the phenyl ring of anion 2, which causes a little decrease in the bond lengths of the phenyl ring and the bond length C1C4 (anion 2, Fig. 6) in comparison with phenyl substituted allyl cations.

Anion	ΔH_f
1	40.5
2	46.3
3	73.3
4	38.1
5	56.5

Table 5. MINDO-forces calculations of heats of formation (ΔH_f in kcal/mole) of allyl anion, phenyl and cyclopropyl substituted allyl anions.

Table 6. Calculated electron densities of allyl anion and phenyl substituted allyl anions.

	Anion		
	1	2	3
C1	4.053	4.362	4.487
C2	3.708	3.790	3.752
C3	4.503	4.292	4.487
C4		3.779	3.919
C5		4.169	4.026
C6		3.917	3.997
C7		4.178	4.039
C8		3.915	3.997
C9		4.172	4.029
H1	1.038	1.026	1.028
H2	1.027	1.093	1.008
H3	1.027	1.027	1.028
H4	1.036	1.018	1.008
H5	1.154	1.027	1.022
H6		1.075	1.049
H7		1.047	1.049
H8		1.077	1.050
H9		1.036	1.024

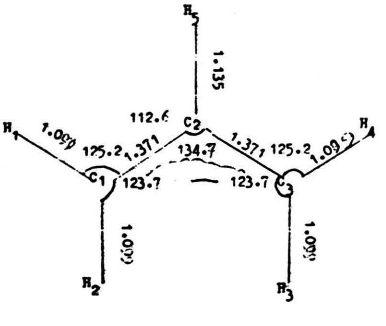
The substitution of the phenyl ring on the center carbon atom of the allyl anion can occur in two ways: the phenyl ring can be perpendicular to the plane of the allyl anion (anion 3) or in the plane of it. The calculated heats of formation show that the former (anion 3, Fig. 6) is more stable. This is similar to the case of the phenyl substituted allyl cations. From Table 5, it can be seen that the phenyl ring on the center carbon atom (anion 3) of the allyl anion destabilizes the anion by 32.8 kcal/mole.

Also the phenyl ring on the center carbon atom of the allyl anion (Table 6) acts as electron-donating substituent. Fig. 6 shows that the angle C1C2C3 of anion 3 (126.4 degree) is smaller than that of the allyl anion (134.7). This indicates that there is a strain in the anion 3 which destabilizes the anion.

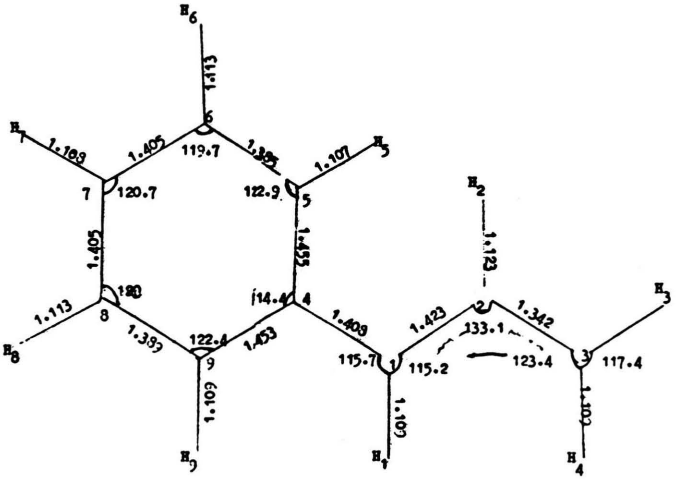
Thus phenyl ring destabilizes both the allyl anion and the allyl cation.

4. *Effect of the Cyclopropyl Ring on the Allyl Anions*

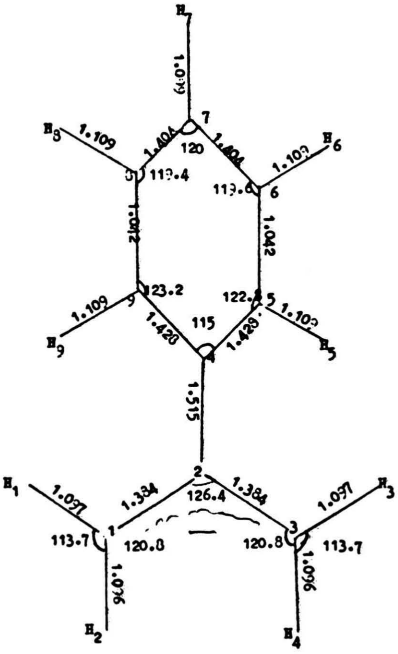
The calculated heats of formation and electron densities of cyclopropyl substituted allyl anions



anion 1



anion 2



anion 3

Fig. 6. Optimized geometries of the allyl anion and phenyl substituted allyl anions.

Table 7. Calculated electron densities of cyclopropyl substituted allyl anions.

	Anion	
	4	5
C1	4.465	4.485
C2	3.734	3.750
C3	4.418	4.483
C4	3.763	3.918
C5	4.044	4.000
C6	4.044	4.000
H1	1.018	1.035
H2	1.130	1.014
H3	1.030	1.035
H4	1.017	1.015
H5	1.104	1.074
H6	1.048	1.062
H7	1.069	1.033
H8	1.048	1.062
H9	1.069	1.033

after complete optimization of geometry are given in Tables 5 and 7, respectively.

The substitution of the cyclopropyl ring on the terminal carbon atom of the allyl anion (anion 4) increases the stability by 2.4 kcal/mole (Table 5). This increase in the stability is smaller than that when cyclopropyl is attached to the allyl cation. This may be due to the weaker conjugation [18] of the cyclopropyl ring with the allyl anion: the bond length C1C4 (1.451 Å, cf. Fig. 7) of the anion 4 is greater than that of the cation (1.410 Å). Also the angle C1C2C3 of anion 4 decreases by 4 degrees relative to anion 1 in comparison with that of the cyclopropyl substituted allyl cation, where the angle C1C2C3 increases by 3.2 degrees relative to allyl cation. This indicates that there is a strain in the anion 4 which may cause its destabilization.

From Table 7 it can be seen that the cyclopropyl ring is electron-withdrawing when substituted on the allyl anion (anion 4), while it was found to be electron donating when substituted on the allyl cation.

The substitution of the cyclopropyl ring on the center carbon atom destabilizes both the allyl anion (anion 5, Table 5) and the allyl cation.

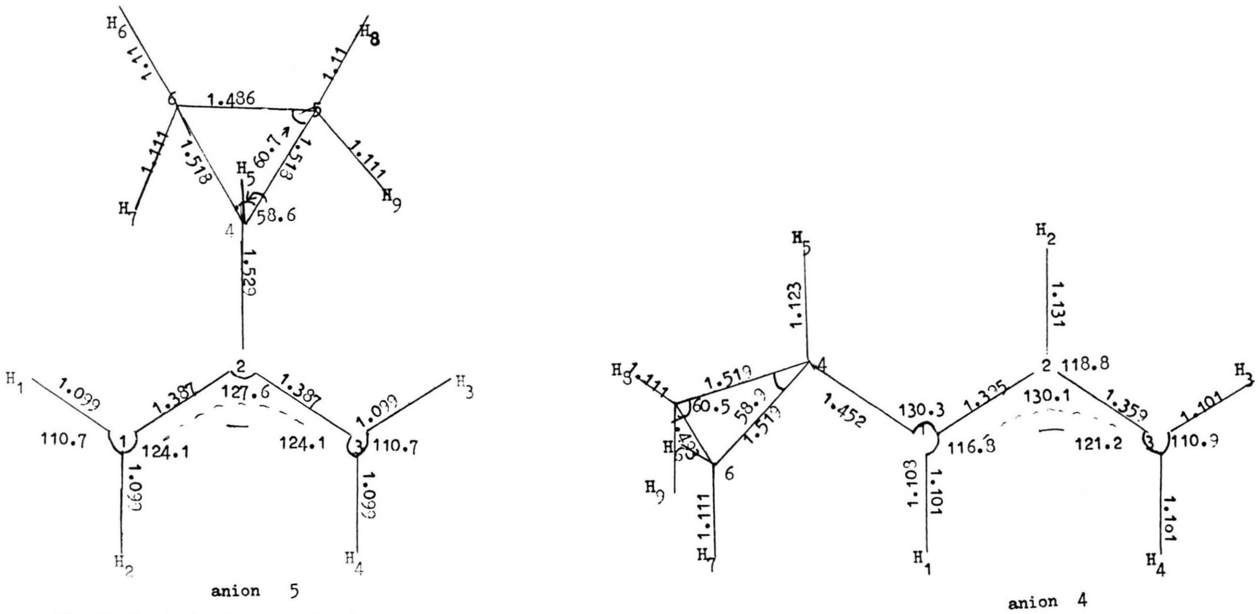


Fig. 7. Optimized geometries for cyclopropyl substituted allyl anions.

The angle C1C2C3 of the anion 5 (Fig. 7) is decreased by 7.1 degrees realtive to anion 1 (Fig. 6), which indicates that there is a strain in the anion 5. Thus it is to be expected that anion 5 is less stable than anion 1.

Therefore, it can be concluded that the cyclopropyl ring stabilizes the allyl anion when substituted on its terminal carbon atom and destabilizes it when substituted on its center atom, in a similar way to that when it is substituted on the allyl cation. Also it can be concluded that the efficiency of phenyl and cyclopropyl rings in either electron donating or electron withdrawing depends on the magnitude of the charge on the carbon atom to which the phenyl or cyclopropyl is attached. This is similar to the case when methyl is substituted on the allyl and crotyl systems [1].

Acknowledgement

The continued generousity of computer time of the Mosul University Computer Centre is gratefully acknowledged.

[1] a) H. M. Jarjis and S. M. Khalil, J. Chem. Soc., Perkin II (in press). b) H. M. Jarjis and S. M. Khalil, Z. Naturforsch. **42a** (in press).

[2] a) S. M. Khalil and M. Shanshal, Theor. Chim. Acta **46,** 23 (1977). b) S. M. Khalil and M. Shanshal, Z. Naturforsch. **33a,** 722 (1978). c) S. M. Khalil, Egypt. J. Chem. **21,** 465 (1978). d) S. M. Khalil, Z. Naturforsch. **40a,** 1278 (1985).

[3] N. C. Deno, in: Carbonium ions, Vol. 2 (G. A. Olah and P. v. R. Schleyer, eds). Wiley Interscience, New York, N.Y. 1970, Chapter 18.

[4] C. F. Wilcox, L. M. Lowe, and R. Hoffmann, J. Amer. Chem. Soc. **95,** 8192 (1973).

[5] N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, J. Amer. Chem. Soc. **87,** 4533 (1965).

[6] S. Bank, A. Schriesheim, and C. A. Rowe, J. Amer. Chem. Soc. **87,** 3244 (1865).

[7] D. Carr, J. R. P. Clarke, and M. C. Whiting, Proc. Chem. Soc. **1963,** 333.

[8] A. Atkinson, Ph.D. Thesis, Queen Mary College, London 1970.

[9] A. Stoichi and M. Piretta, La Rivista Italiana Delle Sostanze Grasse **45,** 607 (1968).

[10] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. **97,** 1298 (1975).

[11] B. A. Murtagh and R. W. H. Sargent, Comput. J. **13,** 185 (1970).

[12] P. Pulay, Molec. Phyd. **17,** 197 (1969).

[13] M. Y. Shandala, S. M. Khalil, and M. S. Al-Dabbagh, Tetrahedron **40,** 1195 (1984).

[14] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. **97,** 1294 (1975).

[15] N. C. Baird, Tetrahedron **28,** 2355 (1972).

[16] S. S. Shaik and P. C. Hiberty, J. Amer. Chem. Soc. **107,** 3089 (1985).

[17] G. A. Olah and R. J. Spear, J. Amer. Chem. Soc. **97,** 1539 (1975).

[18] A. D. Walsh, Nature London **159,** 712 (1947).

[19] D. J. Hunter and D. J. Cram, J. Amer. Chem. Soc. **86,** 5478 (1964).