

MINDO-Forces Study of Methyl Substituted Allyl Cations

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MINDO-Forces calculations have been performed on methyl substituted allyl cations with complete energy minimization. It was found that the methyl substitution on the terminal carbon atoms of the allyl cation stabilizes the cation more than that at the center carbon atom. Also, the stability of the cation depends on the conformation of the cation and not on the number of methyl substituents.

Introduction

Recently [1], we have studied the allyl and crotyl systems, using the MINDO-Forces MO method [2]. Here we would like to extend this study to methyl substituted allyl cations which are of considerable importance in organic chemistry [3] such as Diels-Alder cycloaddition reactions [4].

The methyl substituted allyl cations have been investigated by semiempirical methods [5, 6] and ab initio calculations [7, 8] without comprehensive studies of the geometries and electron densities. Therefore, the aim of the present work is to give full geometry optimization in order to assess and augment experimental data.

Results and Discussion

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

1. Effect of One Methyl Group

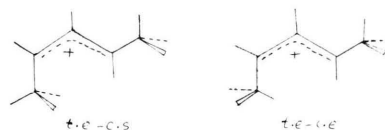
From the calculated heats of formation (Table 1) it was found [1] that the substitution on the terminal carbon atom of the allyl cation increases the stability more than that at the center carbon atom, which is in agreement with experiment [9] and theory [8].

Part of the M.Sc. thesis, H. M. Jarjis, University of Mosul 1986.

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2. Effect of Two Methyl Groups

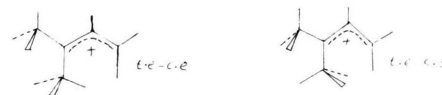
There are six possibilities for the substitution of two methyl groups on the allyl cations which are represented by cations 5, 6, 7, 8, 9 and 10 as shown in Figure 1. Besides that, there are also different possibilities for some of these cations. For example, cation 6 has the trans eclipsed–cis staggered (t.e.–c.s.) form beside the trans eclipsed–cis eclipsed (t.e.–c.e.) form.



The calculated heats of formation show that the most stable cation is (t.e.–c.e.). Also, cation 7 has the (c.s.–c.e.) form as well as the (c.s.–c.s.) one,



and it was found that the latter is more stable than the former. For cation 8, it was found that the (t.e.–c.s.) form is more stable than the (t.e.–c.e.) form.



Also, it can be seen from Table 1 that the most stable cation out of these six cations is the cation 5.

On rotating one of the methyl groups of the cation 5 to a cis form to obtain cation 6, the heat of formation increases due to steric strain. The cation 7 can be obtained by rotating the second methyl group of cation 6 to a cis form. In this case the steric

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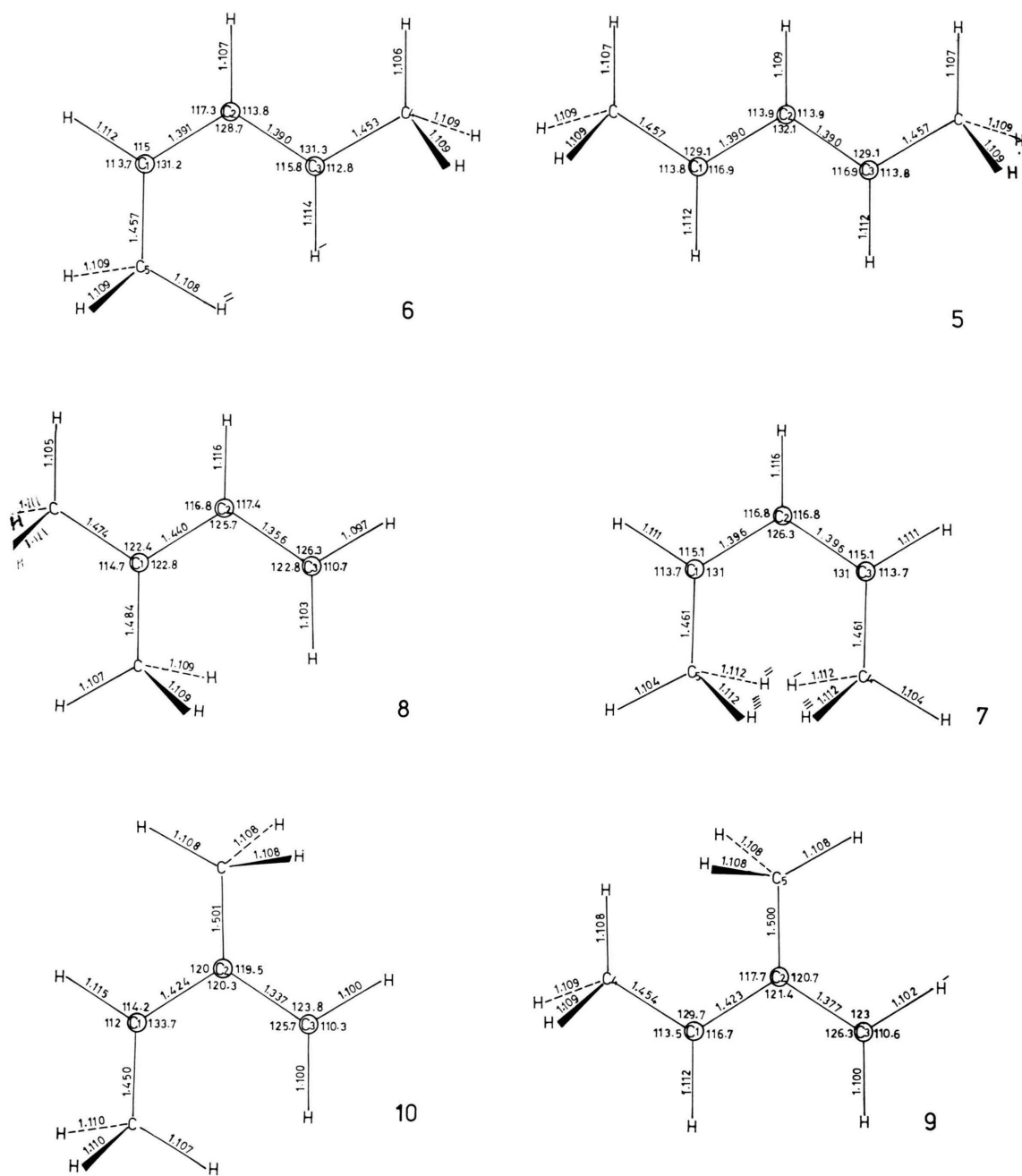


Fig. 1. Optimized geometries for two methyl substituted allyl cations.

strain becomes more pronounced, which gives rise to an increase in the heat of formation.

It can be seen from the heats of formation in Table 1 that the stability decreases from cation 5 to 7 in agreement with experiment [8] and theory [10, 7]. It was found experimentally [11] that the difference in the heats of formation between cations 6 and 7 is 6.5 kcal/mole, which is in very good agreement with the present calculations (6.4 kcal/mole) and in disagreement with *ab initio* calculations [7] (31.4 kcal/mole). Also it was found experimentally [12] that on substitution of two methyl groups on the terminal carbon atoms, cation 5 is obtained and not cations 6 or 7. This suggests that cation 5 is the most stable one, which is in agreement with the present calculations.

For the substitution of two methyl groups on one of the terminal carbon atoms of the allyl cation to obtain cation 8 (Fig. 1), the stability increases in comparison with that of cation 2. In the case of cation 9, the increase in the heat of formation in comparison with cation 8 is due to the substitution of a methyl group on the center carbon atom of the allyl cation [1]. The repulsion between the methyl groups in the cation 9 increases the angle C2C1C4 in comparison with that of C2C3H' (Figure 1).

On rotating the methyl group at the terminal carbon atom of the cation 9 to the *cis* form to obtain cation 10 (Fig. 1), a slight decrease in the heat of formation with that of cation 9 suggests a decrease in the repulsion between the two methyl groups.

It was found experimentally [13] that the heat of formation for an allyl cation which has one methyl group at the terminal carbon atom and one at the center is 192 kcal/mole, which is approximately equal to that of cations 9 or 10 (Table 1).

It can be seen from Table 1 that cation 5 is the most stable one in comparison with cations 6, 7, 8, 9 and 10, which is in agreement with the experimental observation [12].





















3. Effect of Three Methyl Groups

The substitution of three methyl groups on the allyl cation gives rise to a six different forms of cations, represented by 11, 12, 13, 14, 15 and 16 (Figure 2). It can be seen from Table 1 that there is a small difference in the heat of formation between cations 13 and 14, which may be due to the crowding between the three methyl groups in cation 13.

The increase in the heat of formation and the angle C1C2C3 in the case of cation 15 in comparison with that of cation 14 are due to the two methyl groups in the *cis* form. The cation 11 (Fig. 2) is similar to that of cation 8 (Fig. 1) apart from the extra methyl group on the terminal carbon atom which causes an increase in the stability of the cation (Table 1). On rotating the methyl group on the cation 11 to the *cis* form to obtain cation 12 (Fig. 2), the stability decreases due to the repulsion between the two methyl groups in the *cis* form. The case of cation 16 (Fig. 2) is similar to that of cation 8 (Fig. 1) apart from the extra methyl group on the center carbon atom, which decreases the heat of formation (Table 1), i.e. increase the stability of the cation.

From the comparison between cations 8, 11 and 16 it can be seen that the addition of a methyl group on the terminal carbon atom of the cation 8 to obtain cation 11, causes a decrease in the heat of formation by 20.1 kcal/mole while addition of a methyl group at the center carbon 8 causes a decrease

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

Cation	ΔH_f	Cation	ΔH_f
	1 222.2		11 171.3
	2 198.4		12 176.2
	3 200.4		13 178.6
	4 216.6		14 178.1
	5 177.4		15 182.4
	6 179.2		16 190.9
	7 185.6		17 172.7
	8 191.4		18 175.4
	9 196.3		19 178.3
	10 196.1		20 178.9

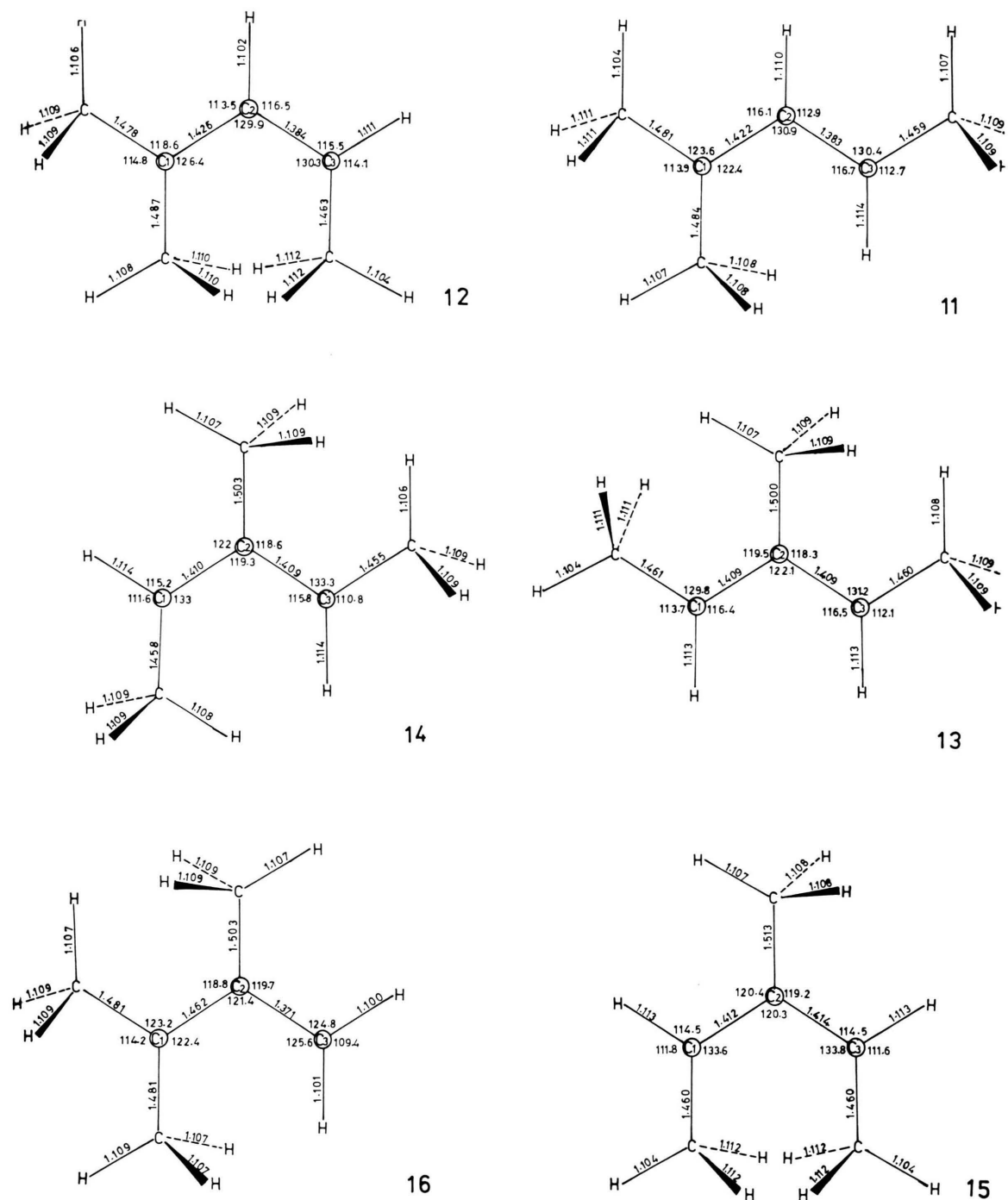


Fig. 2. Optimized geometries for three methyl substituted allyl cations.

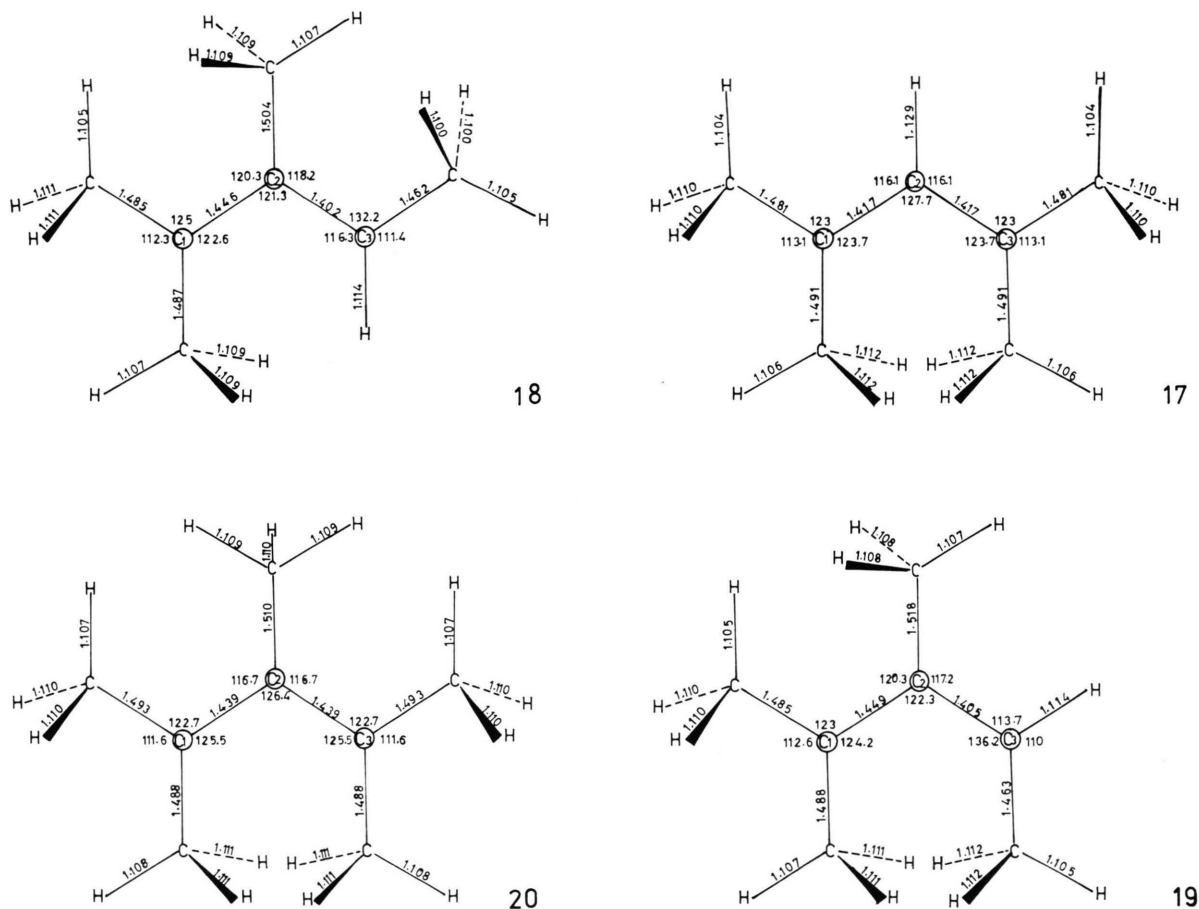


Fig. 3. Optimized geometries for four and five methyl substituted allyl cations.

in the heat of formation by 0.5 kcal/mole. This indicates that methyl substitution at the terminal carbon of the cation increases the stability more than that at the center carbon atom, which is in agreement with our recent results [1] (see Table 1 for comparison between cations 2 and 4).

4. Effect of Four Methyl Groups

The substitution of four methyl groups on the allyl cation gives rise to three different forms, which are represented by cations 17, 18 and 19 (Figure 3).

The cation 17 is obtained by substitution of a methyl group on the 11 in the cis form (Figure 2). It was expected that the addition of this methyl group will cause an increase in the stability of cation 17 due to an increase in the number of the methyl

groups. But because of the repulsion between the two methyl groups in the cis form the stability of cation 17 decreases by 1.4 kcal/mole in comparison with that of cation 11 (Table 1).

The addition of one methyl group on the center carbon atom of cation 11 (Fig. 2) to obtain cation 18 (Fig. 3) causes an increase in the heat of formation by 4.1 kcal/mole (Table 1), which may be due to crowding. This is a similar case to that when a methyl group is substituted on the center carbon atom of cation 5 (Fig. 1) to obtain cation 13 (Figure 2).

On rotating the methyl group at carbon C3 of the cation 18 to obtain cation 19 (Fig. 3), the heat of formation increases by 2.9 kcal/mole (Table 1), which may be due to the repulsion between the two methyl groups in the cis form.

5. Effect of Five Methyl Groups

There is only one form for this kind of substitution which is represented by cation 20 as shown in Figure 3. This cation can be obtained by substitution of a methyl group at the center carbon atom of cation 17. This kind of substitution causes a decrease in the bond angle C1C2C3. This decrease in the bond angle causes an increase in the repulsion between the two methyl groups in the cis form of the cation 20, which results an increase in the heat of formation (Table 1), i.e. a decrease in the stability.

Table 2. Calculated electron densities for methyl substituted allyl cations.

Cat- ion	Electron density			Cat- ion	Electron density		
	C ₁	C ₂	C ₃		C ₁	C ₂	C ₃
1	3.619	4.121	3.619	11	3.631	4.180	3.669
2	3.586	4.142	3.681	12	3.645	4.169	3.689
3	3.595	4.137	3.689	13	3.657	4.130	3.657
4	3.653	4.072	3.653	14	3.674	4.117	3.665
5	3.626	4.172	3.626	15	3.686	4.105	3.686
6	3.640	4.167	3.632	16	3.623	4.099	3.775
7	3.654	4.155	3.654	17	3.679	4.180	3.679
8	3.604	4.141	3.738	18	3.657	4.136	3.702
9	3.612	4.097	3.717	19	3.669	4.124	3.723
10	3.624	4.087	3.726	20	3.697	4.145	3.697

6. Electron Density

It can be seen from Table 2 that on substitution of a methyl group at the terminal carbon atom of the cation 2 to obtain cation 5 the electron density increases at the center carbon due to the equal effect of two methyl groups. For cation 6, the electron density at C1 is greater than that at C3 due to the inductive effect of the methyl group in the trans form. The electron densities at the terminal carbon atoms of cation 7 become equal due to the two methyl groups in the cis form.

The inductive effect of two methyl groups at C1 (cation 8), is greater than that of one methyl group at C1 (cation 2) as can be seen from the high electron density at C3 of cation 8 in comparison with that of cation 2 (Table 2). For cation 9, the electron density decreases at the center carbon in comparison with that of cation 2 because of the methyl group at the center carbon atom.

On rotating the methyl group at the terminal carbon atom of cation 9 to obtain cation 10, the electron density increases on the terminal carbon atoms and decreases on the carbon atom of cation 10, in comparison with cation 9. This is due to the methyl group in the cis form (see the electron densities of cations 3 and 2 for comparison).

For cation 11, the electron density at C3 is still greater than at C1 because of the high inductive effect of two methyl groups at C1. On rotating the methyl group at C3 of cation 11 to obtain cation 12, the electron density increases on the terminal carbon atoms and decreases on the center carbon atom in comparison with cation 11. This is due to the methyl group in the cis form, which is the same reason as given for cations 10 and 3.

For cation 13, the electron densities are equal on the terminal carbon atoms due to the two methyl groups in the trans form. On rotating the methyl group at C1 of cation 13, to obtain cation 14, the electron density decreases on the central carbon atom and increases on the terminal carbon atoms of cation 14 in comparison with that of cation 13. This is due to the same reason as given in the comparison between cations 11 and 12.

The effect of the methyl group at the center carbon atom becomes more pronounced on the comparison between cations 16 and 8. For cation 17, the four methyl groups have equal effects on the electron density at C1 and C3.

The substitution of a methyl group on the unsubstituted terminal carbon atom of cation 16 to obtain cation 18 decreases the electron densities at C3 of cation 18 in comparison with that of cation 16, which is due to the inductive effect of a methyl group. In the case of cation 19, the electron density increases at C3 in comparison with cation 18, which is due to the methyl group in the cis form. Finally, equal effect of the five methyl groups at C1 and C3 of cation 20 can be seen from Table 2.

Conclusion

It can be concluded that the effect of a methyl group at the terminal carbon atom of the allyl cation is greater than that at the center carbon atom. Also the stability of the allyl cation depends on the different forms of substitution and not on the numbers of the methyl groups. This can easily be seen from cation 11, which contains only three methyl

groups but is found to be the most stable cation out of the twenty cations, though there are cations which contain four or five methyl groups. Thus it is not possible to say that the stability of a carbonium ion increases as the number of methyl substituents increases.

Acknowledgement

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