A Theoretical Study of Methyl Substituted Phenylallyl Cations

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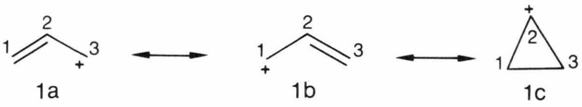
Z. Naturforsch. **43a**, 868–872 (1988); received July 11, 1988

MINDO-Forces calculations are performed, after complete optimization of geometry, on α, β, γ-methylphenylallyl cations. It is found that the substituents affect only the geometrical parameters of the allyl and show no influence on the phenyl ring. The positive charges at the carbon atoms of the phenyl ring decrease on methyl substitutions. A methyl substituent at carbon atom C9 (E, E and E, Z isomers) stabilizes the phenylallyl cation, while all other substituents al C1 and C8 are destabilizing. The calculations predict no (1,9) π-interaction in the methyl substituted phenylallyl cations.

Reaction of phenylallyl cations in acid-catalysed aqueous dioxane are well documented [1–6], however there exist no advanced calculations on methyl substituted phenylallyl cations, apart from our previous work on β-methylphenylallyl cation [7].

The charge distribution in allyl cations has been the subject of some controversy, particularly regarding the importance of 1,3 overlap (1 c) relative to the two classical resonance structures 1 a and 1 b [8, 9],



1a 1b 1c

Recently [10, 11] we have suggested that there is no (1,3) π-interaction in the parent allyl cation and in the 2-substituted allyl system. Previous molecular orbital calculations have shown that 1,3 overlap is not significant for acyclic cations [12]. The ^{13}C NMR spectra of a series of 1,3-substituted and 1,1-substituted alkenyl cations have shown that 1,3-orbital overlap does not appear to contribute significantly to the total resonance structure of these ions [13]. But experimental observation on the parent cyclobutenyl cation indicates very strong 1,3 overlap in this species, resulting in a comparable charge density at C1, C2, and C3 [14].

The charge distribution will clearly be dependent on substituents at C1, C2, and C3, and the relative delocalization caused by the substituents should give additional insight into the charge distribution in these systems.

This paper refers to the geometry, heat of formation and electron density of at the carbon atoms C1, C8 and C9 methyl substituted phenylallyl cations from calculations by the MINDO-Forces MO method [15]. In this method, the molecular energy of the cation obtained from the semiempirical MINDO/3 MO method [16] was completely minimized according to the Murtagh-Sargent technique [17]. The derivative of the energy was calculated according to Pulay's forces method [18]. The program allows variation of the β-parameter with geometrical change in a consistent fashion. A full description of the program and its application is given in [15 a].

Results and Discussion

The calculated heats of formation are given in Table 1, and the geometrical parameters and the calculated electron densities are given in Tables 2 and 3, respectively.

Structural Details

Methyl substitution at carbon atom C1 (cation 1 in Table 2) has no effect on the geometrical parameters of the phenyl ring as compared with phenylallyl cation [7], but produces a small increase in the bond lengths of C1–C8, C1–C2, C8–C9 and small decrease in the bond angles C1–C8–C9 and C2–C1–C8 of the allyl.

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

Cation	ΔH_f
1	231.548
2	206.096
3	211.208
4	203.700
5	233.784
6	213.245

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

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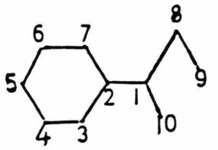
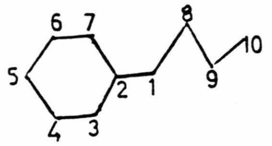
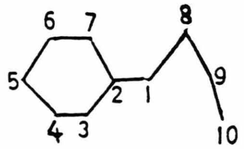
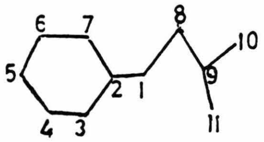
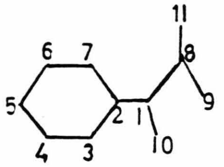
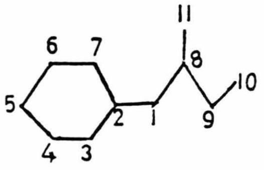
Table 2. Calculated molecular geometry of methyl substituted phenylallyl cations.

Cation		Bond lengths in Å and bond angles in degrees
1	 R_{19} = 2.535	C1C2, 1.432; C2C3, 1.5483; C3C4, 1.390; C4C5, 1.412; C5C6, 1.412; C6C7, 1.395; C2C7, 1.448; C1C8, 1.468; C8C9, 1.355; C1C10, 1.509; C2C1C8, 131,8; C2C1C10, 119.4; C3C2C7, 114.7; C2C3C4, 122.3; C3C4C5, 119.0; C4C5C6, 120.8; C5C6C7, 120.0; C2C7C6, 122.3; C1C8C9, 127.7.
2	 R_{19} = 2.521	C1C2, 1.422; C2C3, 1.451; C3C4, 1.395; C4C5, 1.411; C5C6, 1.411; C6C7, 1.393; C2C7, 1.451; C1C8, 1.416; C8C9, 1.369; C9C10, 1.462; C2C1C8, 134.3; C3C2C7, 115.1; C2C3C4, 122.3; C3C4C5, 119.6; C4C5C6, 120.6; C5C6C7, 119.7; C2C7C6, 122.5; C1C8C9, 129.6; C8C9C10, 128.0;
3	 R_{19} =2.476	C1C2, 1.422; C2C3, 1.452; C3C4, 1.394; C4C5, 1.411; C5C6, 1.412; C6C7, 1.393; C2C7, 1.451; C1C8, 1.423; C8C9, 1.372; C9C10, 1.465; C2C1C8, 134.0; C3C2C7, 115.2; C2C3C4, 122.5; C3C4C5, 119.5; C4C5C6, 120.7; C5C6C7, 119.7; C2C7C6, 122.4; C1C8C9, 124.7; C8C9C10, 125.7;
4	 R_{19} = 2.545	C1C2, 1.425; C2C3, 1.455; C3C4, 1.394; C4C5, 1.412; C5C6, 1.411; C6C7, 1.392; C2C7, 1.542; C1C8, 1.413; C8C9, 1.414; C9C10, 1.457; C9C11, 1.484; C2C1C8, 135.4; C3C2C7, 114.4; C2C3C4, 122.7; C3C4C5, 120.6; C4C5C6, 120.0; C5C6C7, 120.0; C2C7C6, 122.9; C1C8C9, 128.4; C8C9C10, 123.5; C8C9C11, 123.0;
5	 R_{19} = 2.475	C1C2, 1.458; C2C3, 1.459; C3C4, 1.392; C4C5, 1.409; C5C6, 1.409; C6C7, 1.398; C2C7, 1.449; C1C8, 1.488; C8C9, 1.366; C8C11, 1.506; C1C10, 1.498; C2C1C8, 128.9; C2C1C10, 122.5; C3C2C7, 112.2; C2C3C4, 125.2; C3C4C5, 118.8; C4C5C6, 119.8; C5C6C7, 120.4; C2C7C6, 123.5; C1C8C9, 120.2; C1C8C11, 122.9.
6	 R_{19} = 2.490	C1C2, 1.429; C2C3, 1.451; C3C4, 1.398; C4C5, 1.411; C5C6, 1.409; C6C7, 1.394; C2C7, 1.453; C1C8, 1.441; C8C9, 1.388; C9C10, 1.471; C8C11, 1.494; C2C1C8, 129.9; C3C2C7, 113.9; C2C3C4, 122.7; C3C4C5, 120.1; C4C5C6, 120.3; C5C6C7, 119.1; C2C7C6, 123.9; C1C8C9, 123.3; C1C8C11, 117.6; C8C9C10, 129.0.

The repulsion between the phenyl ring and the methyl group increases the bond angle C2–C1–H from 113.3° in phenylallyl cation to 119.4° in cation 1 (C2–C1–C10).

Methyl substitution at carbon atom C9 gives rise to the cations 2 and 3. The methyl group in the E, E form (cation 2) increases the carbon-carbon bond lengths of C1–C2, C8–C9, decreases C1–C8 and produces a small increase in the bond angle C1–C8–C9, while the methyl group in E, Z form (cation 3) has also same effect on the carbon-carbon bond lengths of C1–C8, C1–C2, C8–C9 but produces a decrease in the bond angle C1–C8–C9, as compared with phenylallyl cation [7]. These results are in agreement with those of methyl substituted allyl cations when the methyl group is in the trans and cis forms [10, 19–21].

From the calculated heats of formation (Table 1) the most stable cation out of these cations (1, 2, 3) is cation 2, which is in agreement with that of methyl substituted allyl cations [10, 19, 21]. The high heat of formation, in the case of cation 1, is due to the repulsion between the methyl group and the phenyl ring.

Substitution of two methyl groups at C9 (cation 4) has no effect on the bond angle C1–C8–C9 but produces small changes in the carbon-carbon bond lengths of C1–C8, C1–C2 and an appreciable increase in the C8–C9 length.

Introduction of two methyl groups into positions 1 and 8 (cation 5) produces a small increase in the carbon-carbon bond lengths of C1–C8, C1–C2, C8–C9 and a large decrease in the bond angle C1–C8–C9. The large decrease in the bond angle C1–C8–C9 is due to the substitution of the methyl group at C8 [7].

Substitution of two methyl groups at C8 and C9 (cation 6) produces a small increase in the carbon-carbon bond lengths of C1–C8, C1–C2, C8–C9 and decrease in the bond angle C1–C8–C9. It can be seen from the calculated heats of formation (Table 1) that the most stable cation out of these cations (4, 5, 6) is cation 4, which is in agreement with previous calculations on the methyl substituted allyl cations [19, 21].

Therefore calculations predict that methyl substituents produce almost no effect on the geometrical parameters of the phenyl ring and have only an appreciable effect on the geometrical parameters of the allyl.

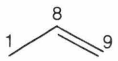
Table 3. Calculated electron densities of methyl substituted phenylallyl cations. See Table 2 for numbering.

Atom no.	Electron densities					
	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6
1	3.663	3.657	3.664	3.672	3.671	3.676
2	4.121	4.114	4.114	4.109	4.125	4.019
3	3.872	3.868	3.867	3.879	3.883	3.868
4	4.049	4.045	4.046	4.041	4.044	4.046
5	3.832	3.839	3.837	3.853	3.838	3.839
6	4.047	4.044	4.045	4.040	4.046	4.004
7	3.891	3.870	3.868	3.879	3.866	3.877
8	4.111	4.153	4.144	4.177	4.082	4.120
9	3.821	3.732	3.751	3.718	3.845	3.754
10	4.045	4.001	4.003	4.009	4.035	3.966
11				4.015	3.927	3.924

Electron Densities

Substitution of methyl group at carbon atom C1 (cation 1) causes a small increase in the electron densities on the carbon atoms C1, C8, C9 and C2. It decreases the positive charges (increasing the electron densities) at C3, C5, C7 and decreasing the electron densities at C4, C6 (Table 3), in agreement with ^{13}C NMR observations [13]. Experimentally, it was found that the addition of water to phenyl allenes gave cinnamyl alcohol only [22]. i.e. addition of water at C9 and not at C1. This may be due to a relative by localized charge at the terminal carbon atom C9, whereas the charge on C1 is delocalized into the phenyl ring.

The distance C1–C8 is 1.468 Å and the distance C8–C9 is 1.355 Å (Table 2), which suggests a localized bond existing between C8 and C9 and a partial single bond between C1 and C8:



Also, C9 is relatively less hindered than C1 toward the approach of a molecule of water. Therefore, the present calculation is in agreement with the experimental work [22].

In the case of cation 2, the methyl substituent decreases the electron density at C9 and increases it at C8. It thus increases the positive charge at C9 and hence acts as electron releasing. This methyl substituent has the same effect on the carbon atoms of the phenyl ring as that of the methyl substituent in cation 1, in agreement with the ^{13}C NMR observation [13].

For cation 3, the methyl substituent decreases the electron density at C9 and increases it at C8, but not as much as in cation 2. That is, the methyl group in the E, E isomer (cation 2) has more effect than in the E, Z isomer (cation 3) [10, 19, 21]. The methyl substituent in the E, E and E, Z isomers has the same effect on the phenyl ring as in the case of cations 1 and 2.

In the case of cation 4, the two methyl substituents at C9 decrease the electron densities at C9 and increase it at C1 and C8, i.e. they act as electron releasing groups, in agreement with ^{13}C NMR observation [13]. Also, they decrease the positive charges at the carbon atoms of the phenyl ring.

For cation 5, the methyl substituent at C1 increases the electron densities at C1 and C2. It was expected that this substituent should increase the electron density at C8 as seen in case of cation 1, but because of the second methyl group at C8, which acts as electron releasing, the electron densities decrease at C8 and increase at C9 [7]. These two methyl substituents also decrease the positive charges at the carbon atoms of the phenyl ring.

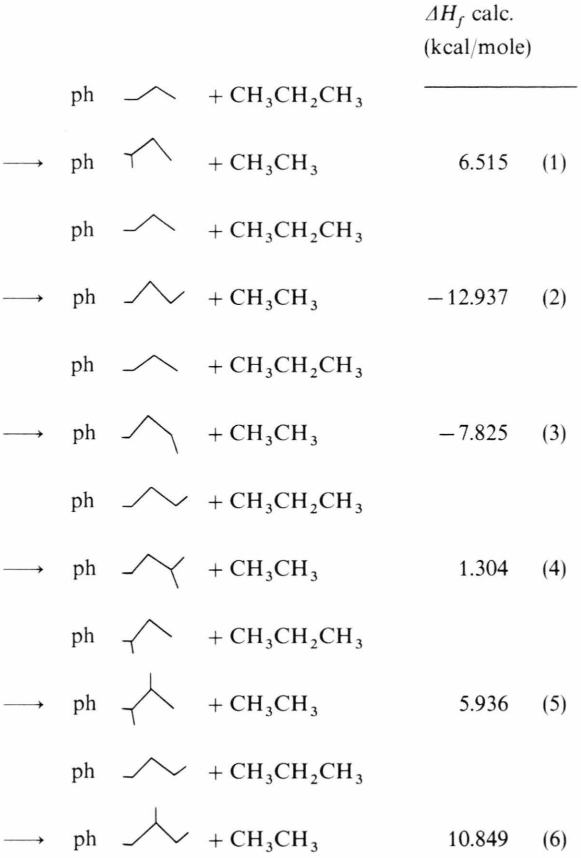
In the case of cation 6, the methyl substituent at C9, decreases the electron density at C9 and increase it at C8, but not as much as in cation 2. This is because the second methyl substituent at C8 acts as electron releasing, which decreases the electron density at C8 and increase it at C1 and C9 [7]. Also, the two methyl substituents decrease the positive charges on the carbon atoms of the phenyl ring. The ^{13}C NMR spectra of a series of 1,3-substituted alkenyl cations and 1,1-substituted alkenyl cations have demonstrated an extensive charge delocalization between C1 and C9 [13].

It can be seen from Table 3 that the carbon atoms C10 in cation 1 and C10 in cation 5 have an appreciable negative charge (− 0.045 and − 0.035, resp.) These two carbon atoms are adjacent to the phenyl ring, which is rich in π-electrons. Thus it can be said that the two methyl groups corresponding to these two carbon atoms are weakly electron withdrawing depending on the electron demand [10, 11, 23–32].

The distance R_{19} between the terminal carbon atoms of the substituted phenylallyl cations (Table 2) are large enough to rule out the possibility of (1,9) π-interaction, which is in agreement with the ^{13}C NMR chemical shifts [13].

Stabilization by Substituents

The stabilization of phenylallyl cations by methyl substituents can be evaluated from the calculated heats of formation (Table 1) on the basis of isodesmic reactions (1)–(6). A negative heat of formation indicates stabilization of the products by substituents [11, 20, 21].



It can be seen from these reactions that the methyl substituent at C9 (E, E and E, Z isomers) is stabilizing, (2), (3). The E, E isomer is more stable than E, Z isomer, in agreement with ab initio calculations [20, 21]. Two methyl substituents at C9 are slightly destabilizing, (4). The rest of the substituents are destabilizing (1), (5), (6).

It can be concluded from our calculations that the methyl substituents cause a charge delocalization in these cations, and that (1,9) π-interaction does not appear to contribute significantly to the total resonance structure of these cations.

Acknowledgement

Thanks to the Mosul University Computer Centre for computer time.

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