MINDO – Forces Calculation of Some Substituted Phenylallyl Cations

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MINDO-Forces SCF-molecular orbital calculations with complete geometry optimization have been performed on x-substituted phenylallyl cations, where x is H, OCH_3, NH_2, NO_2, CN, F and CH_3, in ortho, meta, or para positions. Optimized geometrical parameters, electron densities, heats of formation and stabilization energies were obtained. The substitutent effect on the geometrical parameters and the electron density are discussed by correlation analysis.

Key words: Phenylallyl Cations; Substituted Allyl System; MINDO-Forces.

1. Introduction

The molecular orbital theory provides a precise description of the electronic structure not only of one – electron molecules. The calculation of the molecular orbitals of most systems of interest can be reduced to a purely mathematical problem [1].

In molecular orbital theories some simplifications are introduced. Therefore the procedures are known as semi empirical methods [1, 2]. They differ mainly in the degree of approximation [3].

The present work presents calculations of the electronic structure of substituted phenyl allyl cations (Scheme 1) by the MIDO-Forces SCF-molecular orbital [4], whereby the molecular energy of the cations obtained from semiempirical MINDO/3 MO, was minimized by the Mutargh-Sargent technique. The derivative of the energy was calculated by Pulay's force method. The program allows the variation of the beta-parameter with geometrical change in a consistent way. A full description of the program and it's application is given in [4].

The substituent effects on the calculated results is discussed by means of the correlation analysis.

2. Experimental

The MINDO-Forces program was carried out on a HYUNDAI personal computer Model No. HCM-1420. Cartesian coordinates were obtained from the polar coordinates. Final geometrical parameters were obtained from an improved set of cartesian coordinates (MINDO-Forces) using the Dewar program on a Hewlett-Packard 9830 A calculator.

Standard bond lengths and bond angles are used as input data. After complete optimization of the energy, the geometrical parameters of substituted phenylallyl cations are shown in Scheme 2.

For CH_3 as substituent, different conformations were completely optimized. The most stable conformation data were those of the CH_3 group, where one hydrogen was placed in the phenyl ring plane, and also of the OCH_3 group.

3. Results and Discussion

The completely optimized geometrical parameters, electron densities, heats of formation and stabilization energies of the substituted phenylallyl cations (Scheme 1) are shown in (Scheme 2) and listed in Tables 1 and 2, respectively.

3.1. Effect of the Amino Substituent Group

Introduction of the NH_2-group into the ortho-, meta- or para position of the phenyl ring causes a decrease in the electron density on the carbon atom directly attached to the substituent, and increase the electron density on adjacent carbon atoms (Table 1) i.e. it acts as

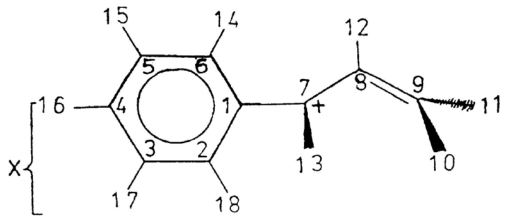
Table 1. Electron density distribution for substituted phenylallyl cations.

Substituent (x)	Electron density on atom number (see Scheme 1)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	X**
H*	4.116	3.854	4.053	3.818	4.057	3.856	3.657	4.108	3.799						
o-F	4.217	3.390	4.188	3.792	4.081	3.861	3.642	4.114	3.801	0.961	0.941	0.955	0.998	0.978	7.305
m-F	4.069	4.017	3.597	3.963	4.002	3.907	3.649	4.117	3.777	0.956	0.939	0.946	1.011	0.979	7.273
p-F	4.150	3.815	4.183	3.368	4.182	3.818	3.673	4.105	3.815	0.964	0.943	0.957	1.013	0.980	7.276
o-CH3	4.128	3.826	4.078	3.815	4.053	3.863	3.671	4.103	3.813	0.965	0.945	0.953	1.024	0.990	3.984
m-CH3	4.107	3.882	4.015	3.845	4.045	3.865	3.658	4.109	3.801	0.965	0.944	0.950	1.016	0.991	3.936
p-CH3	4.117	3.844	4.081	3.783	4.077	3.856	3.674	4.104	3.816	0.965	0.945	0.956	1.017	0.987	3.816
o-CN	4.118	3.819	4.060	3.827	4.045	3.869	3.663	4.108	3.803	0.962	0.940	0.956	1.017	0.988	3.980
m-CN	4.107	3.876	4.000	3.843	4.044	3.863	3.653	4.114	3.794	0.962	0.940	0.954	1.015	0.990	3.940
p-CN	4.112	3.853	4.066	3.783	4.064	3.858	3.668	4.107	3.808	0.963	0.942	0.956	1.016	0.988	3.973
o-NH2	4.151	3.683	4.151	3.815	4.061	3.899	3.742	4.075	3.868	0.970	0.944	0.968	1.042	0.978	5.049
m-NH2	4.051	4.022	3.824	3.949	3.994	3.919	3.660	4.110	3.797	0.963	0.942	0.953	1.016	0.987	5.157
p-NH2	4.131	3.827	4.151	3.674	4.149	3.830	3.746	4.077	3.873	0.969	0.951	0.976	1.016	0.982	5.038
o-NO2	4.047	4.120	3.944	3.882	4.003	3.872	3.682	4.112	3.759	0.951	0.940	0.957	0.932	0.981	3.900
m-NO2	4.130	3.792	4.252	3.775	4.064	3.833	4.644	4.118	3.779	0.959	0.938	0.947	1.010	0.986	3.873
p-NO2	4.087	3.885	3.978	4.054	3.995	3.876	3.639	4.118	3.769	0.960	0.938	0.941	1.011	0.985	3.907
o-OCH3	4.205	3.745	4.181	3.798	4.975	3.875	3.657	4.106	3.822	0.965	0.943	0.959	1.018	0.984	6.408
m-OCH3	4.065	4.012	3.676	3.961	4.001	3.912	3.655	4.113	3.791	0.962	0.940	0.953	1.015	0.985	6.382
p-OCH3	4.143	3.819	4.174	3.458	4.173	3.825	3.693	4.097	3.835	0.966	0.946	0.964	1.016	0.987	6.393

* Values taken from [5]. ** Represents atom directly attached to the phenyl ring.

Table 2. The heats of formation ($\Delta H_f kj$/mole) and stabilization energies (S. E kj/mole) for substituted phenylallyl cations.

Substituent	ΔH_f	S. E	Substituent	ΔH_f	S.E
H	932.12 [5]	0	o-F	699.14	45.07
o-CH_3	922.24	−46.62	m-F	734.59	9.62
m-CH_3	908.85	−33.22	p-F	701.36	42.85
p-CH_3	902.49	−26.86	o-CN	1051.35	−53.10
o-NH_3	850.68	45.86	m-CN	1039.88	−41.64
m-NH_3	896.34	0.20	p-CN	1030.84	−32.60
p-NH_3	819.38	77.17	o-NO_2	973.51	−58.54
o-OCH_3	770.50	15.98	m-NO_2	912.66	2.30
m-OCH_3	785.94	0.54	p-NO_2	939.90	−24.94
p-OCH_3	744.13	42.35			



Scheme 1: x = H, o-OCH_3, m-OCH_3, p-OCH_3, o-NH_2, m-NH_2, p-NH_2, o-NO_2, m-NO_2, p-NO_2, o-CN, m-CN, p-CN, o-F, m-F, p-F, o-CH_3, m-CH_3, and p-CH_3.

electron donating group, in agreement with other theoretical results [6–9].

The calculated heats of formation (Table 2) indicate that the para-substituted isomer is most stable.

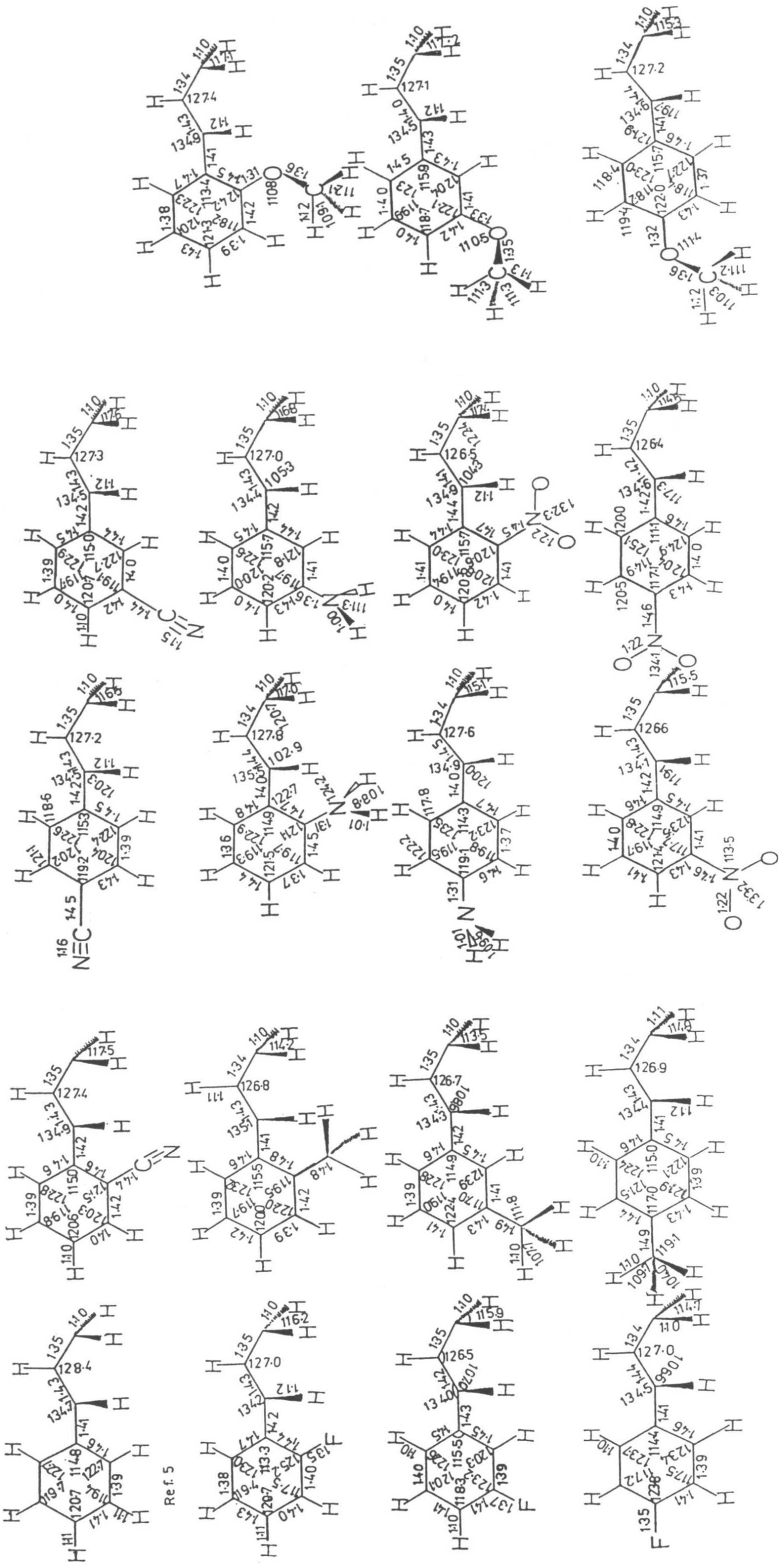
The C_1-C_2 bond is slightly lengthened by the substitution at the ortho- and para-position, while meta-substitution causes a small shortening; the C_1-C_7 bond length is slightly affected by the substituent group; the C_7-C_8 and C_8-C_9 bonds length are not affected by the meta-substituent, while substitution at the ortho- and para-positions causes small lengthening and small shortening in the bond lengths, respectively. The bond angles $\angle C_6C_1C_2$ and $\angle C_1C_7C_8$ are slightly affected by the substituent, while $\angle C_7C_8C_9$ decreased by the substituent (Scheme 2).

3.2. Effect of the Methoxy Substituent Group

Introduction of the CH_3O-group into the ortho-, meta-, or para-positions of the phenyl ring causes decrease in the electron densities on the carbon atoms directly attached to the substituent, and increase of the electron densities on the adjacent carbon atoms (Table 1), i.e. they acts as electron donating group, in agreement with other theoretical results [2, 10].

The calculated heats of formation (Table 2) indicate that the para-substituted isomer is the most stable isomer.

The C_1-C_2 and C_1-C_7 bond lengths were not affected by the substituent group at the ortho and para-position, while substitution at the meta-position causes shortening and lengthening of the bonds, respectively. The C_7-C_8 and C_8-C_9 bonds lengths were almost not affected by the substituent groups. $\angle C_6C_1C_2$ is not affected by substitution at the meta- and para-positions,



Scheme 2. Optimized geometry of substituted phenylallyl cations. Bond length are in angström and bond angles in degrees.

while substitution at the ortho-position causes a small decrease.

Substitution at different positions have almost no effect on $\angle C_1C_7C_8$, while substitution at different positions causes a decreases in $\angle C_7C_8C_9$ (Scheme 2).

3.3. Effect of the Fluoro Substituent Group

Introduction of fluorine at the ortho-, meta- or para-positions of the phenyl ring was found to acts as electron donating in a similar way to that of NH_2 and OCH_3 (Table 1).

The calculated heats of formation (Table 2) indicate that ortho- and para-substituted isomers are the more stable ones. The C_1-C_2 bond length is slightly affected by the substituent; ortho- and meta-positions of the substitution cause a small shortening while substitution at the para-position has no effect; the C_1-C_7 bond length is not affected by substitution at para-position while substitution at ortho- and meta- causes small lengthening; C_7-C_8 is slightly affected by the substituent, while C_8-C_9 was not affected. $\angle C_6C_1C_2$ and $\angle C_1C_7C_8$ were lightly affected by the substituent; while $\angle C_7C_8C_9$ was slightly decreased by the substituent group (Scheme 2).

3.4. Effect of the Methyl Substituent Group

Introduction of the CH_3 group into the ortho-, meta- or para-positions of the phenyl ring causes a slight decrease in the electron density on the carbon atom directly attached to the substituent, and in slight increases in the electron densities on the adjacent carbon atoms: i.e they act as weak electron donating group (Table 1).

The calculated heats of formation (Table 2) indicate that the para-substituted isomer is the most stable one.

The C_1-C_2 bond was slightly lengthened by ortho-substitution, and slightly shortened by meta- and para-substitutions.

The C_1-C_7, C_7-C_8 and C_8-C_9 bond lengths were slightly affected by the substituents group. $\angle C_6C_1C_2$ and $\angle C_1C_7C_8$ were slightly affected by the substituents, while $\angle C_7C_8C_9$ decreased by the substituent (Scheme 2).

3.5. Effect of the Cyano Substituent Group

The results in [6 – 9] suggested amphielectronic behaviour of π-electron acceptor groups such as CF_3, CN, CHO …; thus these groups donate π-electrons when attached to a system that has electron demand, such as CH_2X, but accept it in other cases.

Introduction of the CN into the ortho-, meta- or para-positions of the phenyl ring was found to act as a weak electron donating group in a similar fashion to that found in the case of the CH_3 group, and in agreement with [6 – 9] (Table 1).

The calculated heat of formation (Table 2) indicates that the para-substituted isomer is the most stable one. The C_1-C_2 bond length is not affected by substitution at the ortho-position while a small shortening is observed on substitution at meta and para-positions. The substituent at different positions causes small lengthening of the C_1-C_7 bond. While the C_7-C_8 and C_8-C_9 bond lengths were not affected by the substituent groups. $\angle C_6C_1C_2$ and $\angle C_1C_7C_8$ were not affected by substituents, while $\angle C_7C_8C_9$ decreased by the substitution at different positions (Scheme 2).

3.6. Effect of the Nitro Substituent Group

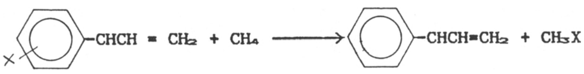
Introduction of NO_2 into the ortho, meta, or para-position of the phenyl ring causes an increase in the electron densities on the carbon atoms directly attached to the substituent and a decrease on the adjacent carbon atoms (Table 1), i. e. they acts as electron withdrawing group.

The calculated heats of formation (Table 2) indicate that meta-substituted isomer is most stable. The C_1-C_2 bond length is slightly affected by the substituent, C_1-C_7 is slightly lengthened while C_8-C_9 and C_8-C_9 were almostly constant. $\angle C_6C_1C_2$ is not affected by substitution at the meta-position, while it increased by substitution at the ortho-position and decreased by para-substitution. $\angle C_1C_7C_8$ is almostly not affected by the substituent groups, while $\angle C_7C_8C_9$ is decreased by the substituent (Scheme 2).

3.7. Stabilization by Substituents

The stabilizing effect of substituents on phenylallyl cations has been calculated from the isodesmic reaction [2, 10].

The positive reaction energy indicates that the X-group stabilizes the reactand relative to the product [6 – 9].



It can be seen from the stabilization energy (Table 2) that NH_2, F and OCH_3 were stabilizing groups, while CH_3 and CN at different positions and the NO_2 group at ortho-and para-positions are destabilizing groups. It can be concluded from the obtained results that strong electron donating groups decrease the electron demand on the allyl system, which reflects the stabilization of the molecule, while the electron withdrawing group NO_2 and the weak electron donating groups CN and CH_3 do not affect or increase the electron demand on the allyl system, which leads to destabilization of the molecule.

3.8. Correlation Analysis of Substituent Effect on Molecular Properties of Phenylallyl Cations

Among plots of the electron density (E. D.) distribution on various carbon atoms against σ, σ_I and σ_R [11], the following equations represent the best correlations (m refers to meta- and p to para-substituted compounds):

$$\text{E. D. at } (C_1)_m = 4.11 \pm 0.003 + 0.112\sigma_R \pm 0.01, \quad r = 0.97,$$

$$\text{E. D. at } (C_4)*_m = 3.83 \pm 0.01 - 0.283\sigma_R \pm 0.04, \quad r = 0.94.$$

When plotting various bond lengths and bond angles against σ, σ_R, and σ_I, the correlations are less satisfactory.

Taft's dual parameters equation [11] was applied on all molecular properties. For meta and para substituted compounds, the following correlations were best:

$$\text{E. D. at } (C_1)_m = 4.11 \pm 0.005 - 0.01\sigma_I \pm 0.01 + 0.118\sigma_R \pm 0.011, \quad r = 0.97.$$

$$\text{E. D. at } (C_4)_m = 3.81 \pm 0.015 + 0.06\sigma_I \pm 0.03 - 0.306\sigma_R \pm 0.03, \quad r = 0.95.$$

$$(C_1 - C_7)_p = 1.41 \pm 0.002 + 0.012\sigma_I \pm 0.004 + 0.018\sigma_R \pm 0.004, \quad r = 0.91.$$

Application of the Yukawa-Tsuno [11] equation results in the following best correlations:

$$\text{E. D. at } (C-7)_{m,p} = 3.66 \pm 0.003 - 0.03[\sigma + 1.92(\sigma^+ - \sigma)] \pm 0.003, \quad r = 0.92.$$

$$\text{E. D. at } (C-9)_{m,p} = 3.80 \pm 0.003 - 0.03[\sigma + 1.7(\sigma^+ - \sigma)] \pm 0.004, \quad r = 0.92.$$

On the other hand, application of Taft's equation [11] for the treatment of ortho-subtituents (Es and σ^* constants), results in poor correlations ($r \leq 0.85$).

4. Conclusion

All substituents have effects on the geometrical parameters and the electron density. For meta- and para-substituents the best correlation obtained between the electron density and σ_R or the Yukawa-Tsuno equation clearly indicates that the major affecting ability of the substituent is through resonance effects. The correlation between the geometrical properties (bond length and bond angle) and the constants of the substituent was found to be poor. Therefore there must exist parameters which measure the effects of the substituent on the geometrical properties.

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