Substitutent Effects on the Geometrical Properties of 1-Phenylallyl Alcohol

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Optimized geometrical parameters, electron densities, heats of formation and stabilization energies have been obtained on X-substituted phenylallyl alcohols, where X is H, OCH_3, NH_2, CN, F and CH_3 at *ortho*, *meta*, and *para* positions, using MINDO-Forces SCF-molecular orbital calculations. The substituent effects on the geometrical parameters and the electron density are discussed.

Key words: Phenylallyl Alcohols; Substituent Effects; Allyl System; MINDO-Forces.

1. Introduction

Pyrolysis of unsymmetrically substituted allyl alcohols involving migration of the hydroxyl group is known as oxotropy rearrangement [1]. Much attention has been paid to the chemistry of phenylally alcohols because of their utilities [2]. Approximate molecular orbital theories are based on a scheme developed within the molecular orbital theory, but with several simplifications. Often experimental data on atoms and prototype molecules are used to estimate values of quantities entering the calculations as parameters, and for this reason the procedures are known as semiempirical methods [3]. There are various approximation methods in the literature, which differ mainly in the degree of approximation [3].

The present work deals with the electronic structure of substituted 1-phenylallyl alcohols (Fig. 1), using MINDO-Forces SCF-molecular orbital calculations [4], whereby the molecular energy of the alcohols was completely minimized by the Murtagh-Sargent technique [5]. The derivative of the energy was calculated according to Pulay's force method. The program allows the variation of the β-parameter with the geometrical change in a consistent way. A full description of the program and its application is given in [4]. The substituent effects on the calculated results is discussed by means of the correlation analysis.

2. Calculations

The MINDO-Forces program was carried out on a HYUNDAI personal computer Model No. HCM-1420. Cartesian coordinates are obtained from polar coordinates. Final geometrical parameters are obtained from an improved set of Cartesian coordinates (MINDO-Forces) using the Dewar program on a Hewlett-Pakard 9830 A calculator. Standard bond lengths and angles are used as initial input data. For CH_3-group substituents different conformations were completely optimized and the most stable conformation data are recorded, in which one hydrogen atom of CH_3-group was placed in the phenyl ring plane, similarly for the OCH_3-group where the most stable conformation data are recorded.

3. Results and Discussion

The complete optimized geometrical parameters, electron densities, heats of formation and stabilization energies of substituted 1-phenylallyl alcohols (Fig. 1) are listed in Tables 1, 2, 3 and 4, respectively.

3.1. Stabilization by Substituent Groups

The effect of substituents on the energy of substituted 1-phenylallyl alcohols has been assessed from the depicted isodesmic reaction [6, 7].

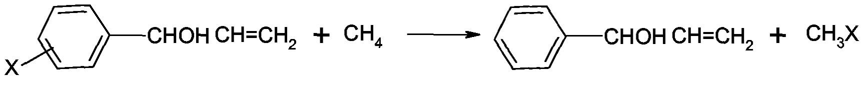

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Table 1. The bond lengths (Å), of selected bonds for substituted 1-phenylallyl alcohols. The atom numbers are as shown in Figure 1.

Substitutent X	Bond lengths (Å)* 1-2	2-3	3-4	4-5	6-1	7-1	7-8	8-9	C-X**
H	1.43	1.41	1.40	1.41	1.44	1.46	1.48	1.31	1.10
o-F	1.42	1.40	1.40	1.41	1.44	1.48	1.49	1.32	1.38
m-F	1.43	1.40	1.40	1.41	1.44	1.49	1.49	1.32	1.38
p-F	1.43	1.41	1.40	1.40	1.44	1.46	1.48	1.31	1.37
o-CH_3	1.45	1.42	1.40	1.40	1.44	1.49	1.49	1.32	1.49
m-CH_3	1.42	1.42	1.42	1.40	1.44	1.47	1.48	1.31	1.48
p-CH_3	1.43	1.40	1.42	1.42	1.43	1.49	1.49	1.32	1.48
o-CN	1.45	1.42	1.40	1.40	1.43	1.49	1.49	1.32	1.46
m-CN	1.42	1.42	1.42	1.40	1.44	1.47	1.48	1.31	1.45
p-CN	1.43	1.40	1.42	1.42	1.44	1.48	1.49	1.31	1.44
o-NH_2	1.45	1.43	1.40	1.41	1.43	1.49	1.49	1.32	1.35
m-NH_2	1.42	1.43	1.42	1.40	1.44	1.48	1.49	1.32	1.36
p-NH_2	1.43	1.40	1.43	1.43	1.43	1.48	1.49	1.32	1.35
o-OCH_3	1.44	1.42	1.40	1.41	1.43	1.51	1.49	1.32	1.35
m-OCH_3	1.41	1.41	1.41	1.40	1.44	1.48	1.49	1.31	1.34
p-OCH_3	1.43	1.40	1.42	1.42	1.43	1.48	1.49	1.32	1.34

* Bond length of the bonds 5-6, 7-14, C-H, and O-H are 1.40, 1.36, 1.10, and 0.95 Å, respectively, in all compounds.

** Represents an atom directly attached to the phenyl ring.

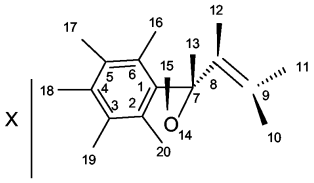

Fig. 1. Substituted 1-phenylallylalcohols, where X = H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *o*-NH_2, *m*-NH_2, *p*-NH_2, *o*-OCH_3, *m*-OCH_3, *p*-OCH_3, *o*-CN, *m*-CN, *p*-CN, *o*-F, *m*-F, and *p*-F.

The positive reaction energy indicates that the X-group stabilizes the reactant relative to the product [6, 8–10].

It can be seen from the values of the stabilization energy (Table 4) that NH_2, F, OCH_3 and CH_3 at *para* position are stabilizing groups, while CH_3 at *ortho* and *meta* positions and CN at different positions are destabilizing groups. The CH_3-group at *ortho* position was the most destabilizing group; this may be due to steric factors.

3.2. Effect of the Fluoro Substituent Group

Introduction of a fluorine atom into the *ortho*, *meta* or *para* positions of the phenyl ring causes a decrease in the electron density on the carbon atom at which the substituent is attached, and an increase in the electron density on the adjacent carbon atoms (Table 3); i.e. it acts as electron donating group, as agrees with similar published results [6, 8–10].

The calculated heats of formation indicate that *ortho-*, *meta-* and *para*-substituted isomers have almost the same stability (Table 4).

The C_1-C_2 bond length is not affected by the substituent at different positions, the C_1-C_7, C_7-C_8, and C_8-C_9 bond lengths are not affected by the substituent at *para* position, while bond lengthenings were observed on substitution at *ortho* and *meta* positions. The $C_6C_1C_2$ bond angle was decreased by the substituent group at the *ortho* position, while substitution at the *meta* or *para* position did not affect the angle. The $C_1C_7C_8$ bond angle was not affected by the substituent, while the $C_7C_8C_9$ bond angle was increased by the substituent group at *ortho* and *meta* positions, and not affected by *para* substituents (Tables 1 and 2).

3.3. 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 slightly increases the electron density on the adjacent carbon atoms (Table 3), i.e. it acts as a weak electron donating group, in agreement with similar published results [6, 8–10].

The calculated heats of formation (Table 4) indicate that the *para*-substituted isomer is the most stable isomer.

The C_1-C_2, C_7-C_8 and C_8-C_9 bond lengths are not affected by the substituent at different positions, while substituents at different positions cause lengthening of the C_1-C_7 bond length. The $C_6C_1C_2$ bond angle was not affected by the substituent group. The $C_1C_7C_8$ bond angle was slightly increased by the substituent group at *ortho* and *para* positions, and not affected by *meta* substitution, while the $C_7C_8C_9$ bond angle was increased by the substituent group (Tables 1 and 2, Fig. 2).

3.4. Effect of the Cyano Substituent Group

The published results [6, 8–10] suggested amphielectronic behavior 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 and acceptors in the case of electron rich systems.

Introduction of the CN-group into the *ortho*, *meta* or *para* positions of the phenyl ring was found to have

Table 2. The bond angles (°) of selected angles of substituted 1-phenylallyl alcohols. The atom numbers as shown in Figure 1.

Substitutent	Bond angles (°)													
X	< 1,2,3	< 2,3,4	< 3,4,5	< 4,5,6	< 5,6,1	< 6,1,2	< 8,7,1	< 7,8,9	< 15,14,7	< 13,7,8	< 10,9,11	< 20,2,1	< 19,3,2	< 18,4,3
H	123.1	119.7	120.2	119.1	123.7	114.1	109.2	126.7	101.0	111.3	119.6	119.5	120.6	119.4
o-F	125.8	117.9	120.6	118.7	124.5	112.5	109.3	127.4	105.7	110.0	117.9	117.6	121.2	119.6
m-F	120.6	124.2	116.6	120.4	123.7	114.5	109.7	128.0	106.5	110.0	117.7	121.3	118.3	121.7
p-F	123.9	117.3	123.7	116.8	124.4	114.0	109.2	126.6	100.8	117.7	119.8	119.4	119.4	121.7
o-CH_3	120.7	122.0	118.9	119.5	124.3	114.6	110.4	128.0	107.9	110.6	117.4	120.3	118.2	120.2
m-CH_3	124.0	118.3	120.5	119.1	124.1	114.0	109.3	127.3	104.1	110.3	119.0	120.2	119.6	118.8
p-CH_3	122.4	122.07	116.6	120.9	123.5	114.5	110.5	129.2	109.2	109.4	116.2	120.9	119.7	121.3
o-CN	120.5	121.9	119.0	119.5	124.2	114.8	110.4	128.3	108.0	110.1	117.1	120.2	118.6	120.5
m-CN	123.5	118.8	120.3	119.1	124.1	114.1	109.3	127.2	103.2	110.4	119.1	120.3	121.3	118.7
p-CN	123.0	120.7	118.2	120.0	123.8	114.4	109.5	127.5	104.4	110.3	118.7	120.2	120.7	121.8
o-NH_2	121.4	120.6	120.2	118.8	124.9	114.1	110.9	128.5	108.7	109.9	116.6	119.5	119.2	119.8
m-NH_2	123.2	119.1	119.5	120.0	123.7	114.4	109.6	127.7	105.1	110.1	118.3	120.3	120.6	119.5
p-NH_2	123.7	120.1	118.5	119.3	124.6	113.8	109.8	128.1	105.8	110.5	117.9	119.9	120.8	121.2
o-OCH_3	123.4	119.8	119.6	119.4	125.0	112.8	111.0	128.9	111.6	110.0	115.3	120.7	120.0	119.8
m-OCH_3	120.5	123.0	117.4	119.8	124.2	115.0	109.5	127.5	104.6	110.3	118.6	121.6	118.6	120.1
p-OCH_3	123.6	119.2	120.3	118.3	124.6	114.0	109.7	128.0	106.1	109.9	118.0	120.2	121.0	119.5

Table 3. Electron density distributions in substituted 1-phenylallyl alcohols. For atom numbers see Figure 1.

Substitutent	Electron density on atom number														
X	1	2	3	4	5	6	7	8	9	10	11	12	13	14	X*
H	4.056	3.969	4.006	3.979	4.020	3.988	3.569	4.066	3.998	0.985	0.991	0.992	1.117	6.478	1.003
o-F	4.180	3.524	4.143	3.925	4.063	3.937	3.537	4.069	3.993	0.987	0.990	0.999	1.210	6.472	7.351
m-F	3.993	4.120	3.547	4.127	3.940	4.057	3.571	4.065	3.991	0.988	0.987	0.996	1.110	6.479	7.352
p-F	4.115	3.912	4.152	3.524	4.144	3.928	3.550	4.067	3.992	0.989	0.998	0.989	1.120	6.483	7.352
o-CH_3	4.073	3.964	4.014	3.977	4.003	3.982	3.561	4.060	3.995	0.989	0.990	0.998	1.118	6.488	3.923
m-CH_3	4.052	3.960	3.998	3.990	3.998	3.989	3.568	4.065	3.997	0.987	0.990	0.994	1.117	6.480	3.914
p-CH_3	4.058	3.968	4.013	3.974	4.009	3.984	3.560	4.061	3.993	0.993	0.990	1.001	1.118	6.487	3.918
o-CN	4.052	3.965	3.997	3.986	3.990	3.992	3.564	4.063	3.992	0.989	0.989	0.999	1.114	6.484	3.898
m-CN	4.056	3.967	3.991	3.977	4.004	3.979	3.568	4.066	3.995	0.986	0.998	0.995	1.115	6.478	3.904
p-CN	4.045	3.975	4.000	3.970	3.997	3.992	3.569	4.065	3.994	0.987	0.988	0.995	1.115	6.479	3.910
o-NH_2	4.190	3.765	4.131	3.910	4.087	3.915	3.538	4.059	3.996	0.992	0.992	0.999	1.131	6.494	5.161
m-NH_2	3.995	4.091	3.802	4.107	3.935	4.067	3.574	4.062	3.998	0.990	0.990	0.993	1.115	6.481	5.170
p-NH_2	4.139	3.901	4.133	3.779	4.128	3.917	3.548	4.063	4.000	0.991	0.992	0.999	1.127	6.486	5.166
o-OCH_3	4.175	3.632	4.119	3.934	4.054	3.940	3.532	4.059	3.991	0.990	0.993	1.005	1.121	6.493	6.413
m-OCH_3	4.004	4.094	3.657	4.109	3.948	4.049	3.575	4.064	3.996	0.988	0.989	0.994	1.114	6.478	6.408
p-OCH_3	4.100	3.921	4.127	3.636	4.122	3.938	3.554	4.065	3.995	0.990	0.989	0.998	1.122	6.483	6.406

* Represents atoms directly attached to the phenyl ring.

almost no effects on the electron density distribution (Table 3).

The calculated heats of formation (Table 4) indicate that *ortho*-, *meta*- and *para*-substituted isomers have nearly the same stability.

C_1-C_2, C_7-C_8 and C_8-C_9 bond lengths are not affected by the substituent at different positions, while the substituent causes lengthening of the C_1-C_7 bond. The $C_6C_1C_2$ bond angle was not affected by substituents. The $C_1C_7C_8$ bond angle was slightly increased by the substituent group, while the $C_7C_8C_9$ bond angle increases by substitution at different positions (Tables 1 and 2, Fig. 2).

3.5. *Effect of the Amino Substitutent 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 an increase in the electron density on the adjacent carbon atoms (Table 3), i.e. it acts as electron donating group, in agreement with similar published results [6, 8 – 10].

The calculated heats of formation (Table 4) indicate that the *para*-substituted isomer is the most stable isomer.

The C_1-C_2 bond is lengthened by substitution at *ortho* position. *Meta* substitution causes a small short-

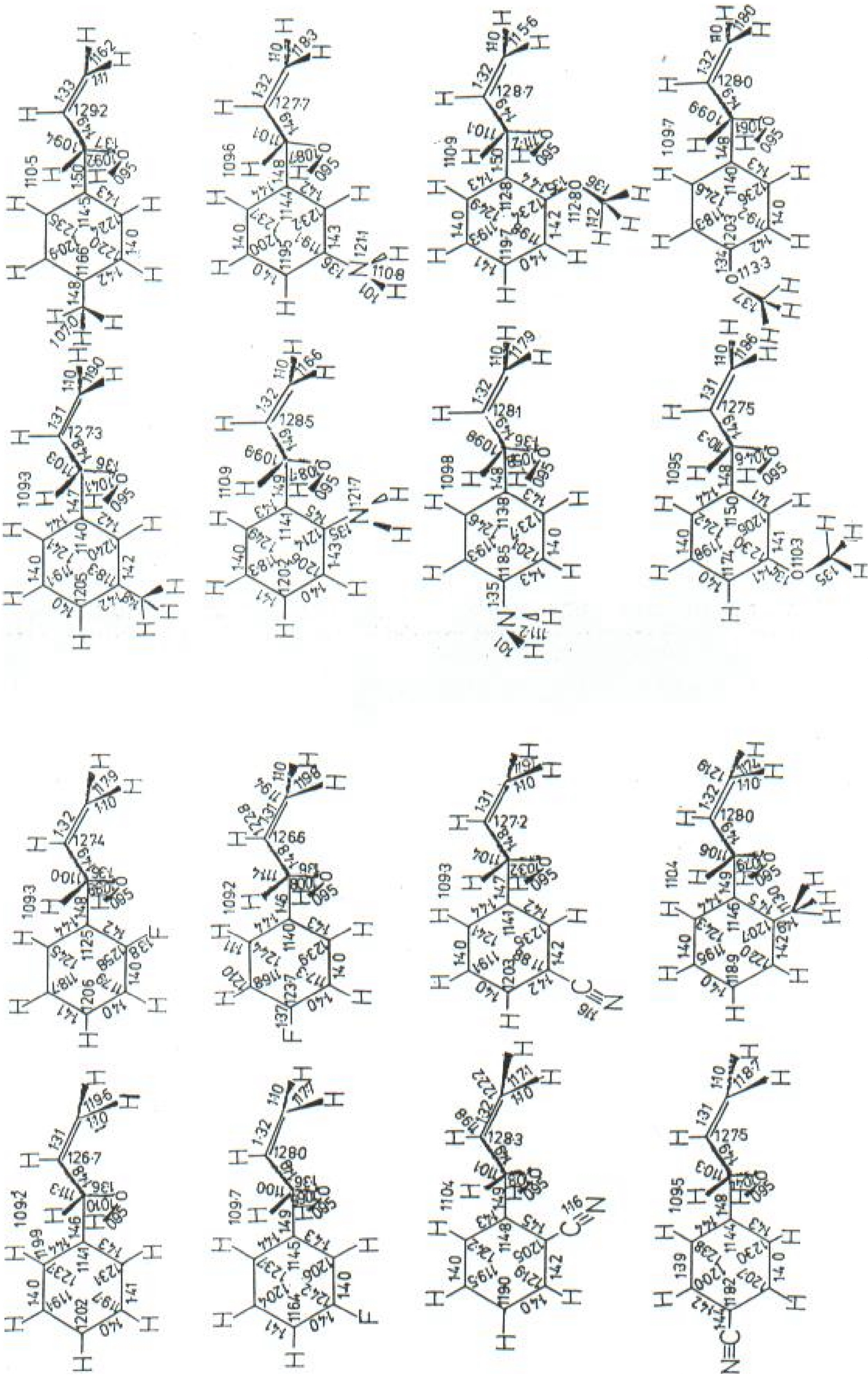

Fig. 2. Optimized geometries of substituted 1-phenylallyl alcohols; bond lenghts in Å and bond angles in degrees.

Table 4. The heats of formation (ΔH_f in kJ/mol) and stabilization energies (S. E. in kJ/mol) for substituted 1-phenylallyl alcohols.

Substituent	ΔH_f	S. E.	Substituent	ΔH_f	S. E.
H	63.23	0	*m*-OCH_3	−114.25	31.84
o-CH_3	56.33	−49.59	*p*-OCH_3	−133.16	50.76
m-CH_3	30.04	−23.31	*o*-F	−205.94	81.27
p-CH_3	2.67	4.05	*m*-F	−196.98	72.31
o-NH_3	21.05	6.61	*p*-F	−198.36	73.86
m-NH_3	4.10	23.56	*o*-CN	141.95	−12.59
p-NH_3	−4.47	32.14	*m*-CN	140.90	−11.55
o-OCH_3	−113.66	31.26	*p*-CN	135.63	−6.27

ening, while *para* substitution has no effect. Substitution at different positions causes lengthening of the C_1-C_7 bond. The C_7-C_8 and C_8-C_9 bond lengths were not affected by *meta* substitution, while substitution at *ortho* and *para* positions causes small lengthening and small shortening in bond lengths, respectively. The $C_6C_1C_2$ bond angle was not affected by *ortho* or *meta* substituents but the *para* substituent causes a small decrease. The $C_1C_7C_8$ bond angles were slightly affected by the substituent, while the $C_7C_8C_9$ bond angle increases by the substituent (Tables 1 and 2).

3.6. Effect of the Methoxy Substituent Group

Introduction of the OCH_3-group into the *ortho*, *meta*, or *para* positions of the phenyl ring causes a decrease in the electron densities on the carbon atoms directly attached to the substituent, and an increase in the electron densities on the adjacent carbon atoms (Table 3), i.e. it acts as electron donating group, in agreement with similar published results [6, 8 – 10].

The calculated heats of formation (Table 4) indicate that the *para*-substituted isomer is the most stable isomer.

The C_1-C_2 bond is lengthened by the substitution at *ortho* position, *meta* substitution causes a small shortening, while *para* substitution has no effect. Substituent at different positions causes lengthening of the C_1-C_7 bond. The C_7-C_8 and C_8-C_9 bond lengths are almost not affected by the substituent groups. The $C_6C_1C_2$ bond angle is not affected by substitution at *para* position, while substitution at *ortho* and *meta* positions cause a decrease and increase, respectively. Substitution at different positions cause an increase in the $C_1C_7C_8$ and $C_7C_8C_9$ bond angle (Tables 1 and 2, Fig. 2).

3.7. Correlation Analysis of the Substituent Effect on the Molecular Properties of Phenylallyl Alcohols

The calculated geometrical parameters (bond length and bond angle) and electron densities where plotted according to the extended Hammett equations. The correlation between the substituent constants and the geometrical properties is poor ($r < 0.7$), while with the electron density (E. D.), the following equations represent the correlations (*m*, and *p* refers to *meta*-, and *para*-substituted compounds):

$$\begin{aligned}
&\text{E.D at } (C_1)_m = 4.05 \pm 0.006 + 0.127\ \sigma_R \pm 0.02, && r = 0.95,\\
&\text{E.D at } (C_4)_m = 3.98 \pm 0.015 - 0.29\ \sigma_R \pm 0.05, && r = 0.94,\\
&\text{E.D at } (C_7)_m = 3.56 \pm 0.000 - 0.012\ \sigma_R \pm 0.002, && r = 0.92,\\
&\text{E.D at } (C_1)_p = 4.05 \pm 0.001 - 0.10\ \sigma_R \pm 0.034, && r = 0.92,\\
&\text{E.D at } (C_7)_p = 3.67 \pm 0.001 + 0.037\ \sigma_R \pm 0.000, && r = 0.97.
\end{aligned}$$

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

$$\text{E. D at } (C_1)_m = 4.06 \pm 0.006 - 0.03\ \sigma_I \pm 0.01 + 0.13\ \sigma_R \pm 0.016,\ r = 0.96,$$

$$\text{E. D at } (C_4)_m = 3.97 \pm 0.01 + 0.07\ \sigma_I \pm 0.03 - 0.30\ \sigma_R \pm 0.04,\ r = 0.96,$$

$$\text{E. D at } (C_7)_p = 3.57 \pm 0.001 - 0.003\ \sigma_I \pm 0.004 + 0.04\ \sigma_R \pm 0.004,\ r = 0.96.$$

In general the Hammett and extended Hammett substituent constants (σ, σ_I and $\sigma_{R)}$ are poor parameters for measuring the substituent effects on molecule geometry.

4. Conclusion

All substituents have an effect on the geometrical parameters, and the electron density distribution. The best correlation obtained between the electron density and σ_R or the extended Hammett equation clearly indicates that the major affecting ability of substituents on the electron density distribution is through resonance effects. The poor correlation between the substituent constants and the geometrical properties (bond length and bond angle) indicates that there must be consistent parameters which measure the substituent effects on the geometrical properties.

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