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The structural distortion by a Substituent : Monosubstituted Benzene Derivative cases

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The substituent dependence of geometric distortion through the two independent electronic substituent effects is analyzed for mono-substituted benzene derivatives of C_{2v}. Based on resonance structures, quantitative relationships expressing the resonance and field/inductive contribution terms in bond distortions are derived. The calculated field-effect parts of C_{ipso}—C_{ortho} ring bonds increase and decrease compared to benzene for electropositive and electronegative substituents respectively. The nonbonded axial distance, $C_{ipso} \cdots C_{para'}$ decreases for electronegative substituents and increases for electropositive substituents. As the electronegativity increases, the distance $C_{ortho} \cdots C_{ortho'}$ increases. With the π-donors, $C_{meta} \cdots C_{meta'}$ nonbonded distances are shorter compared to the ones of benzene, and for π-acceptors, they are longer. Our model based on valence bond approach predicts that the average bond length determines the area of ring, and the sum of the angles $\angle C_{ortho}$—C_{ipso}—$C_{ortho(}$ and $\angle C_{meta}$—C_{para}—$C_{meta(}$ determines the axial distance.

1. Introduction

The electronic parameters have been used to study various chemical[1] and biochemical[2] problems. The relation between the geometrical structure and electronic structure has been a subject of long-standing interest for chemists. The substituent effects are of considerable interest to organic

chemists and have been the subject of many theoretical studies.[3,4] The distortion of the benzene ring brought about by the electronic properties of the substituent is very important to understand the chemical properties and reactivities of molecules and hence, is worth investigating. There are just two independent electronic effects that a substituent may exert on the angles (α, δ) (Figure 1) of the benzene ring and these can be interpreted in terms of the field/inductive effect and resonance effect of the substituent. In an extensive analysis of the experimental geometries of a large number of selected monosubstituted benzene derivatives, it has been found that substituents on the benzene ring can cause significant in-plane distortions of the carbon skeleton from D_{6h} symmetry. Experimentally it is observed that significant deviations usually occur at the ipso position to which the substituent is attached, mainly because of variations in the lengths of the r_a bonds and in the α and δ angles. The values of the ipso angle are largely related to the field/inductive effect of the substituent.[5] Smaller angular distortions in the angle δ were attributed to the resonance effects caused by the substituents in the (-electron system of the ring.[6] Due to thermal motions, the ring bonds are not precisely determined by X-ray or neutron diffraction. Moreover, structural data from microwave and electron diffraction experiments[7] are very limited on suitable systems for analysis. As a result, quantitative analysis of substituent effects on ring bonds based on experimental data is non-existent. Hence, the theoretical prediction of substituent effects on ring bonds of monosubstituted benzene derivatives plays a unique role, and is very informative and useful.

In general, a substituent may cause different distortions in all six ring angles and all six bonds, but many monoatomic or highly symmetrical substituents distort the benzene ring such that it retains C_{2v} symmetry. In that case there are seven structural parameters: the four different angles and three different bonds. Invoking the conditions of planarity and ring closure, only five structural parameters can be independent[6]. Because of these two constraints, the variation in the geometrical parameters may have a relationship with each other. For example, angles α and β have a good relationship as revealed in the experiment[6]. Hence, the analysis of nonbonded distances (d_1, d_2, d_3) across the ring will provide further insight into the kinds of distortion induced by substitution. The patterns of the ring distortion could be classified in terms of substituent properties[8].

We explore here the relationship of ring distortion with the field and resonance effects. The resonance effect affects the ring distortion pattern differently. We study the substituent effects for the monosubstituted benzene derivatives belonging to C_{2v} symmetry by our model. Our main objective is to find the relation between the pattern of the ring distortion and the electronic properties of the substituents.

The substituents according to their electron demand are divided into four different types:

Type **I** : electropositive and π-donor : S^-, O^-, NMe_2, NH_2

Type **II** : electropositive and π-acceptor : BH_2, BCl_2, BF_2

Type **III** : electronegative and π-donor : F

Type **IV** : electronegative and π-acceptor : CN, NC, NO_2, N_2^+

The ipso angle α is mainly determined by the field effect of the substituent,[5] while r_a bond length is controlled by both field and resonance effects. As a result, the bond length and the angle are not expected to have a good correlation to each other, especially for the type **IV** (Figure 2).

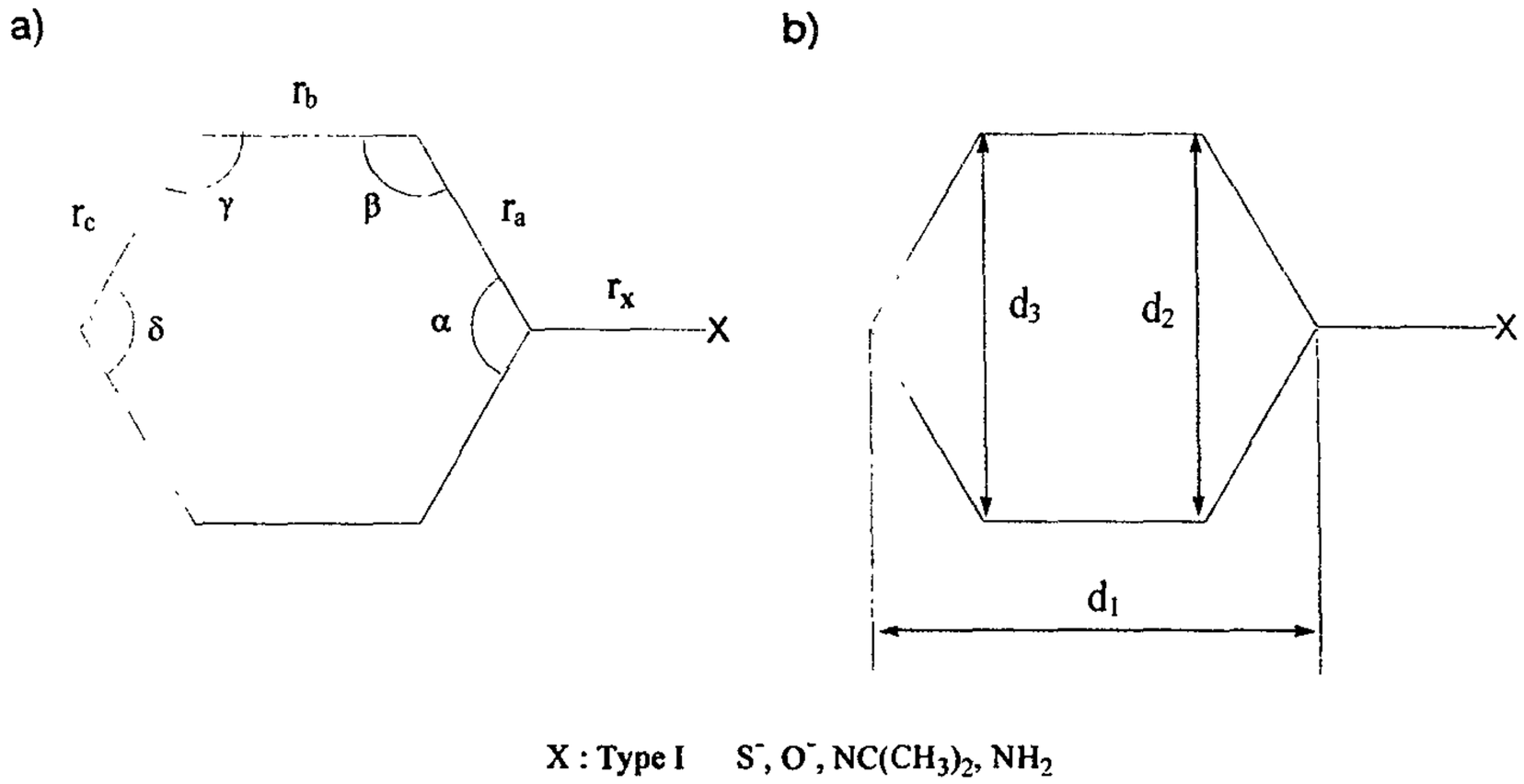
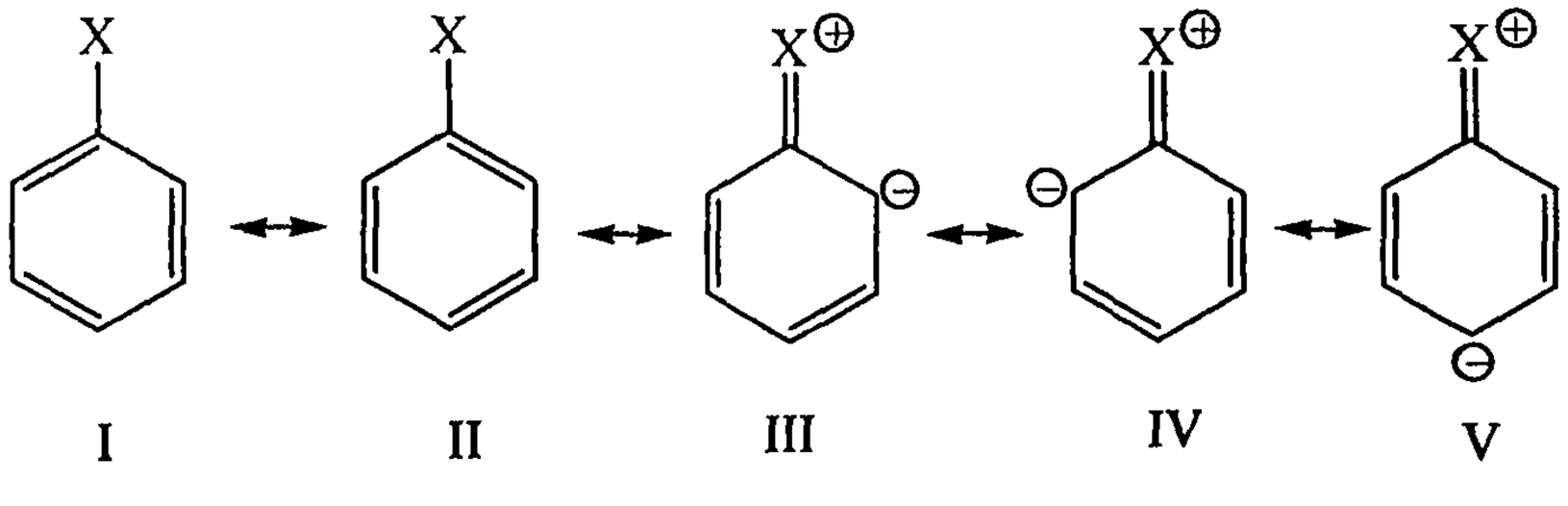


Figure 1. Geometrical parameters for monosubstituted benzene derivatives of C_{2v} symmetry; (a) bonds and angles of benzene (b) nonbonded distances.

We split the bond distortion into two contributing terms, field term due to field effect and resonance term due to resonance effect. The resonance term could be described by the valence structures such as I-V (Scheme 1), and the bond lengths r_b and r_c are determined by the resonance effect. In the valence bond approach the resonance structures I-V are contributing to the ground state structure. Structures I and II imply no interaction between the substituent and benzene ring. Structures III - V imply some distortion of the aromatic ring from its regular geometry of benzene; Structures III and IV imply that r_a bond distance increases, while r_b and r_c bond distances decrease. Structure V is a quinonoid structure and implies that r_a and r_c increase and r_b decreases. The relative contribution of the structures to the ground state geometry i.e. the optimized geometry is not known. However, the optimized geometrical parameters have the necessary information for the individual contribution. Based on resonance structures, we derive empirical relationships from which the individual bond length changes due to field/inductive(F) effect and resonance(R) effect are obtained:

$$\Delta r_a = \Delta r_a(F) + \Delta r_a(R)$$

$$\Delta r_a(R) = 4/3[\Delta r_c(R) - \Delta r_b(R)]$$



Scheme 1. Resonance Structures of Substituted Benzene

II. Computational Method

Optimized geometries are obtained at three levels of theory, HF/DZ, HF/DZP, B3LYP/6-31+G*. All the ab initio calculations have been carried out using the Gaussian 98 suite of programs[9]. The

relation between the individual geometrical parameter and the electronic properties of the substituents is investigated, and the pattern of ring distortion with the nonbonded C—C distances along and across the ring is discussed.

Ⅲ. Results and Discussion

The geometrical parameters along with the field/inductive and resonance contribution terms for the monosubstituted benzene derivatives are presented in Table 1. The geometrical parameter that is most affected by the substituent is the ipso angle (α). The values of α are approximately in the gap of 10°, ranging from 124.1°(HF/DZP 125.5°) in benzene diazonium ion to 113.9°(HF/DZP 113.9°) in phenolate anion at B3LYP/6-31+G*, and are associated with β. The other important angular parameter δ, which is related with the resonance effect (R), have values ranging from 117.4° to 121.2°. We have explored the correlation between $\Delta\alpha$ and $\Delta\beta$. These two angles are related well by a negative correlation (in accord with the previous results[6]. From the factor analysis it was contended that $\Delta\gamma$ is the best single angular parameter for describing independent resonance effect, because it has the lowest correlation coefficient with $\Delta\alpha$[6], which is in disagreement with our results. A less pronounced distortion of the benzene ring occurs in the bond lengths. Though the bond lengths do not chGange much compared to the unsubstituted benzene ring, they, particularly r_a, are of great importance in understanding the subsituent effects. The ring area change (ΔA), already probed as a substituent effect parameter in the literature[10], has a good correlation with the average CC bond length (R^2=0.999). When the substituent is an effective π-electron acceptor such as N_2^+, the correlation between the angle α and length r_a is poor as expected (Figure 2). The bond length r_a is controlled by two independent effects, field/inductive effect (F) and resonance effect(R). We decompose Δr_a into Δr_a(F) and Δr_a(R) terms. We have calculated the two contributing terms using our obtained expressions. It is found that these two calculated values have a quite good correlation with the Hammett substituent constants (Table 1). In Figure 2 (Δr_a and Δr_a(F) vs. $\Delta\alpha$), it is observed that Δr_a(F) linearly

decreases with an increase in the angle α. We further explore the reasons for poor correlation of Δr_a with that angle change, $\Delta \alpha$. As the angle increases by 1°, the field induced length will decrease by about 0.004 Å. This trend is as per the useful rule of thumb[11] from experiments that the C—C single bond distance decreases by 0.04 Å when one of the participating carbon atoms changes hybridization type from sp^3 (109.5°) to sp^2 (120.0°). So when the hybridization changes from sp^3 to sp^2, the controlling factor of (r_a shifts gradually to resonance effect. The calculated $\Delta r_a(F)$ values correlate well with $\Delta \alpha$ which is a field effect parameter.

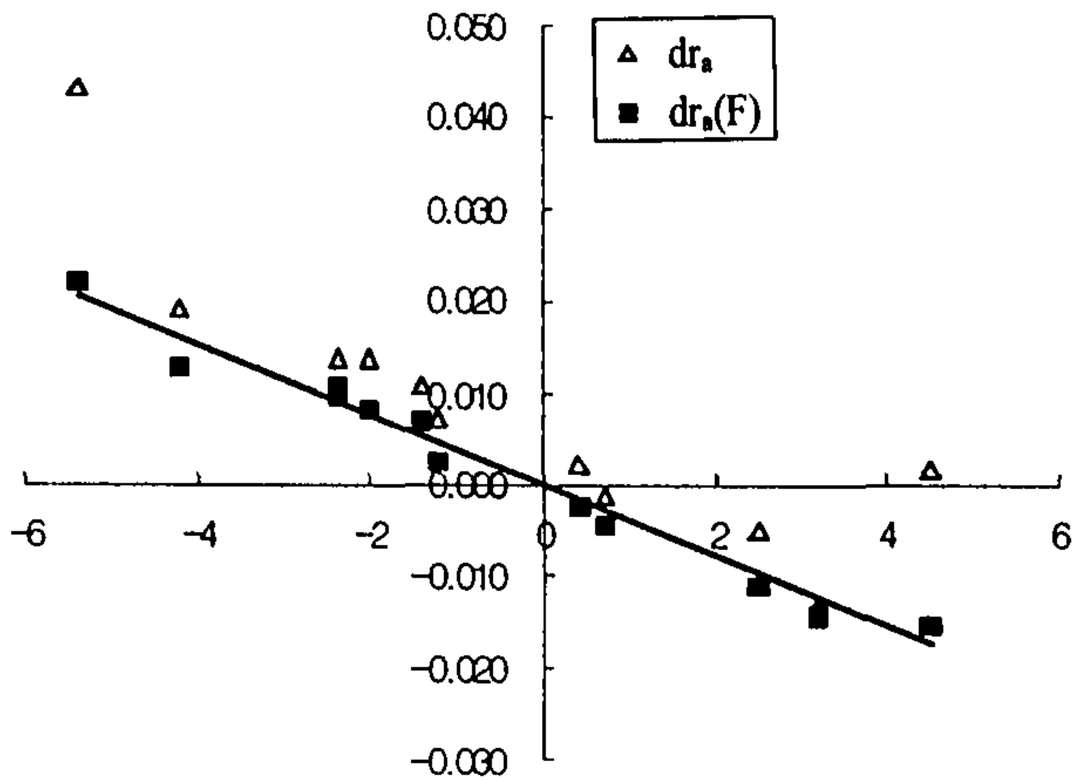


Figure 2. Plot of B3LYP/6-31+G* calculated Δr_a and $\Delta r_a(F)$ against the ipso angle α for monosubstituted benzene derivatives.

TABLE 1. HF-SCF/DZ predicted geometrical parameters and Hammett substituent constant (F,R) for monosubstituted benzene derivatives (phenyl-X) [a, b]

	Type I				Type II			Type III	Type IV			
X	S^-	O^-	$N(CH_3)_2$	NH_2	BH_2	BCl_2	BF_2	F	CN	NC	NO_2	N^{+}
F[c]	0.03	-0.26	0.15	0.08	0.23	0.19	0.26	0.45	0.51	0.47	0.65	1.58
R[c]	-1.24	-0.55	-0.98	-0.74	0.28	0.34	0.22	-0.39	0.15	0.02	0.13	0.33
r_a[a]	1.4153	1.4394	1.4100	1.4034	1.4099	1.4100	1.4069	1.3830	1.3984	1.3951	1.3912	1.3977
r_b[a]	1.3943	1.3881	1.3918	1.3922	1.3935	1.3914	1.3921	1.3950	1.3920	1.3929	1.3916	1.3875
r_c[a]	1.3990	1.4041	1.3942	1.3958	1.3966	1.3957	1.3950	1.3960	1.3955	1.3955	1.3963	1.4001
α	115.8	114.6	117.6	118.8	117.6	118	118.6	123.2	120.4	120.7	122.5	124.5
β	122.1	122.2	120.9	120.3	121.4	121.1	120.7	118.1	119.7	119.4	118.4	117.1
γ	120.9	121.8	121.2	120.9	119.7	119.9	119.8	120.3	120.0	120.3	120.1	120.1
δ	118.1	117.4	118.3	118.7	120.2	120.2	120.4	120.0	120.2	119.8	120.4	121.2
$\Delta r_a(F)$[e]	0.013	0.022	0.011	0.002	0.010	0.008	0.007	-0.015	-0.002	-0.005	-0.011	-0.015
$\Delta r_a(R)$[f]	0.006	0.021	0.003	0.005	0.004	0.006	0.004	0.001	0.005	0.003	0.006	0.017
Δd[d]	0.0729	0.1026	0.045	0.0258	0.0268	0.0218	0.0107	-0.041	-0.009	-0.01	-0.038	-0.065
ΔA[d]	0.0449	0.0991	0.0165	0.0062	0.0267	0.02	0.0128	-0.037	-0.007	-0.013	-0.024	-0.013
$\Delta\langle r\rangle$[e]	0.0067	0.0143	0.0025	0.0009	0.0038	0.0028	0.0018	-0.005	-0.0009	-0.002	-0.003	-0.001

[a] bond lengths in Å, bond angles in degrees(°)

[b] For benzene, $r_o = r_a = r_b = r_c = 1.3962$ Å, $\alpha = \beta = \gamma = \delta = 120°$ ($\Delta q = q - q^\circ$)

[c] Hammett substituent constant (ref. ?)

[d] $\Delta q = (q - q^\circ) \times 100$

[e] $\Delta r_a(F) = \Delta r_a - \Delta r_a(R)$

[f] $\Delta r_a(R) = 4/3\ (\Delta r_c - \Delta r_b)$

[g] $\Delta\langle r\rangle = (\Delta r_a + \Delta r_b + \Delta r_c / 3) \times 1000$

The relationship between nonbonded distances and angles is explored to get further insight into the distortions of the ring. To that end, the plots, Δd_1 vs. $\Delta(\alpha+\delta)$, Δd_2 vs. $\Delta\alpha$ and Δd_3 vs. $\Delta\delta$ (Figures 3a-c) are shown. These plots show strong correlation of various distance parameters with angular ones. The gradual decrease of the sum of α and δ is accompanied by a simultaneous increase of the axial distance (d_1).

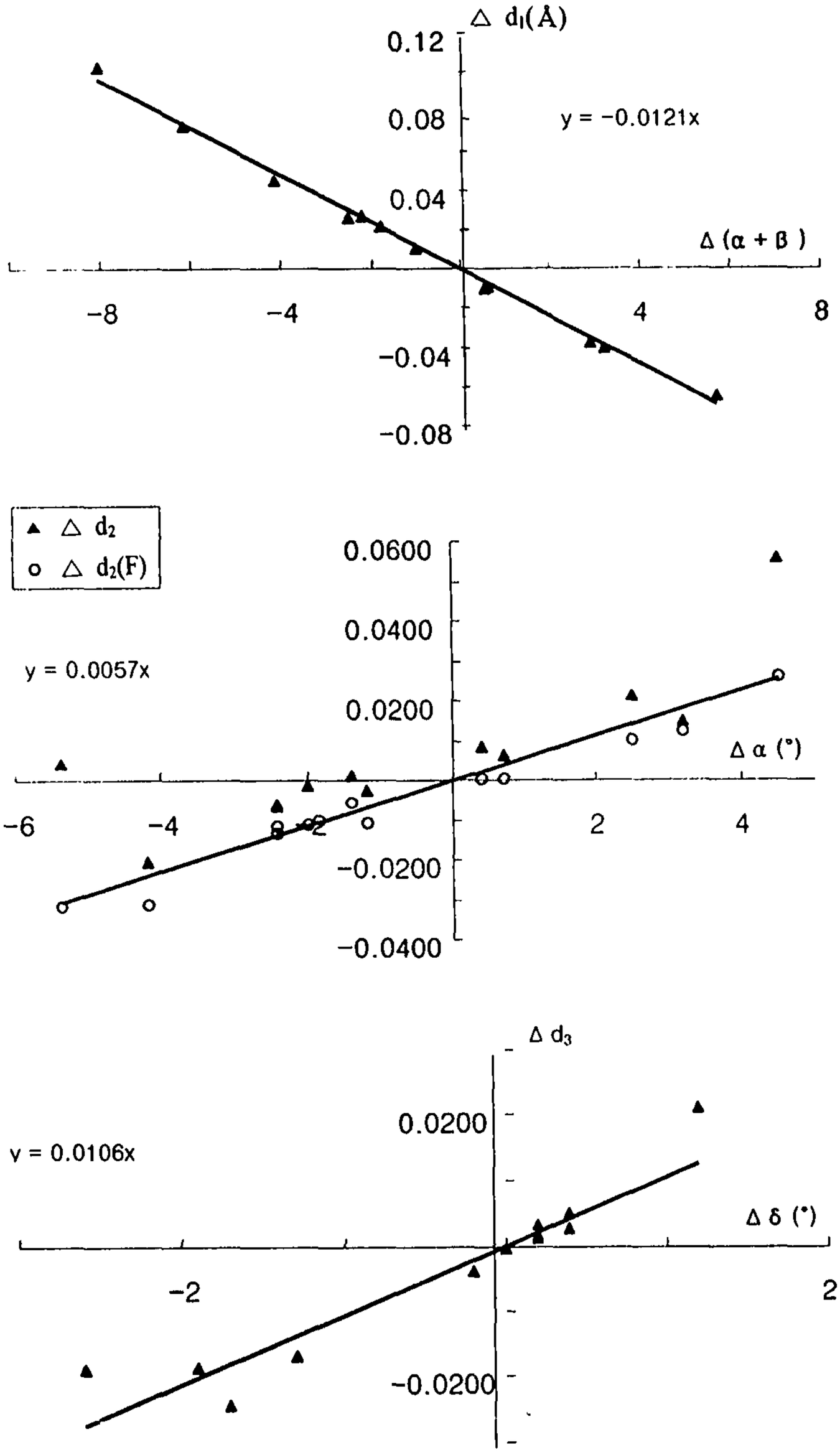


Figure 3. Plot of the nonbonded distances against the angular parameters.

The correlation between these two geometrical parameters is indeed extremely good and quite perfect with R^2= 0.997. Domenicano et al. showed that α is correlated well with d_1,[13] in the

present study we find with a wide variety of substituents having appreciable resonance effects, the change in the sum of the angles α and δ is correlated with the variation in d_1. This linear relationship has some significance: the nonbonded distance (d_1) is not an independent parameter for the ring geometry, and the ring distortion due to a substituent group takes place along the principal axis or dipole axis of these systems. As stated earlier, the ring distortions depend mainly upon the electronic properties of the substituent. The angles α and δ are mainly controlled by the field and the resonance effects respectively. Thus, with the same electronegativity of the substituents, the π-electron donor—substituted systems has longer d_1 distance than the ones with π-electron acceptors. Our results show that the magnitude and direction of ring distortion along the principal axis is determined by the electronic properties of the substituent. Furthermore, it is observed in Figure 3 (b) that covariation of Δd_2 with $\Delta \alpha$ is very small. As the extent of conjugation has increased, the r_a and d_2 length has also increased simultaneously. But, as the electronegativity increases, r_a has decreased (Figure 2) and d_2 length has increased (Figure 3(b)). Δd_2 (F) has a good correlation with $\Delta \alpha$ which is a substituent field effect parameter. A quite good correlation of d_3 with the angle δ is observed in Figure 3(c). Depending upon the π-electron donating or accepting property of the substituents, the d_3 distance has become shorter or longer than that of the benzene molecule.

Our simple model based on valence bond approach predicts that the average bond length determines the area of ring, and the sum of α and δ angles determines the axial distance (d_1). The deformations of the ring induced by σ-electron donating or accepting substitution can be described as arising from ipso atom being pushed inwards (electronegative substituents) or pulled outwards (electropositive substituents) along the principal axis with a simultaneous increase of r_a and d_1 and decrease of d_2, or vice versa. The ring distortion induced by π-electron donating or accepting substituents shows different behavior. In this case, r_a and d_2 increase simultaneously. The structure of ring site opposite to the substituent is mainly determined by the resonance effect. The d_3 distance and the angle δ bear a good correlation. The π-electron donating substituents decrease the d_3 distance and the angle δ, while the π-electron accepting substituents increase those parameters.

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