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SUBSTITUENT EFFECTS IN THE BENZENE SERIES: A STRUCTURAL APPROACH[1]

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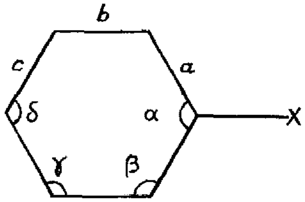
Substitution of a hydrogen atom in the benzene molecule by a functional group, X, has measurable effects on the ring geometry.[3] Significant deviations from perfect D_{6h} symmetry occur in the carbon hexagon, mainly as a result of variations in the lengths of the a bonds and in the α and β angles. A recent analysis of the structural information available for substituted benzene derivatives has shown that the ring deformations depend markedly upon the electronic properties of the substituent.[4,5] This has been rationalised in terms of either hybridisation effects or valence-shell electron-pair repulsions.



The α angle, the values of which span a rather wide range (114–125°), is undoubtedly the most suitable parameter for assessing the effect of different substituents on the geometry of the ring. Within a row of the periodic table it increases regularly with the σ-electronegativity (*i.e.* the σ-electron-withdrawing character) of the substituent.[5] For a substituent capable of sharing π-electrons with the ring it decreases with increasing conjugation.[4,6] Provided suitable crystals are available, α may be measured with great precision $[\sigma(\alpha) = 0.1°]$ by standard X-ray crystallographic techniques. The systematic effect of thermal motions on molecular parameters being less severe on bond angles than on bond distances, accurate measurements of α are possible even from room-temperature X-ray diffraction data, at least with compounds having a reasonably high melting point.[7]

The large mass of structural information that is available on *para*-disubstituted benzene derivatives strongly suggests the approximate rule that the value of α associated with a given substituent is not affected by *para*-substitution.[4] Within the limits of validity of this rule[8] α may therefore be regarded as a substituent constant.[9]

A study of the endocyclic bond angles in the derivatives of benzene may conceivably be expected to provide informations on the electronic effects of the substituents. Whilst accurate experimental work is in progress[10] to increase the body of knowledge on the angular deformations induced by substitution, and to check the validity of the approximate rule given above, we here report α values for a number of functional groups (Table 1). Since only few structural studies of simple monosubstituted benzene derivatives have been carried out with sufficiently high accuracy, the majority of the values given here have been obtained by averaging a large number of accurate data from para-disubstituted derivatives.

The data shown indicate that the σ-electron-withdrawing or -releasing character of the substituent is more effective than its ability to share π-electrons with the ring in determining the value of α. It may be noted that the first entry of Table 1 is the $-B(C_6H_5)_3^-$ group (α = 114.1°), in which the inherently low electronegativity of boron is further lowered by the negative charge, while the last entry is $-\overset{+}{N}\equiv N$ (α = 124.9°), which is the most powerful σ-electron-withdrawing functional group known. The effect of mesomeric interactions on the value of α is apparent, however, in the strongest π-donor of Table 1, $-N(CH_3)_2$ (α = 117.2°).

The values of α for the $-C_6H_5$, $-CH=CH_2$, and $-CH_3$ groups (117.6, 118.0, and 118.1°, respectively) indicate that the origin of the α scale for 'first-row' substituents (i.e. the value of α associated with a functional group having exactly the same electronegativity as the ring) should be set at about 117.5-118.0°, not at 120°.[11] It appears that substitution of hydrogen by carbon gives rise per se to a decrease of α by some 2.0-2.5°, probably as a result of different spatial requirements for the C-C vs C-H σ-bonding electron pairs in the valence shell of the ipso carbon.

TABLE 1

Mean values of the angle α for functional groups[a,b]

$-B(C_6H_5)_3^-$	114.1°	$-CONH_2$	119.8	$-NH_3^+$	121.6
$-N(CH_3)_2$	117.2	$-COOH$	119.8[c]	$-CN$	121.8[e]
$-C_6H_5$	117.6[c]	$-OCH_3$	119.9	$-NO_2$	122.1[c]
$-CH=CH_2$	118.0	$-H$	120.0	$-F$	123.4
$-CH_3$	118.1[c]	$-N=N-C_6H_5$	120.0	$-\overset{+}{N}\equiv N$	124.9
$-NH_2$	118.4	$-OH$	120.2		
$-COCH_3$	118.8	$-Cl$	121.4[d]		

(a) Full details on the data averaged will be given elsewhere. (b) Standard deviations are typically 0.1-0.2°. (c) Ref. 4. (d) Ref. 5. (e) From a structural study of cyanobenzene by microwave spectroscopy (ref. 12).

The prevalence of σ-effects over π-effects in determining the values of α is consistent with the existence of reasonable correlations of α with (i) Taft's inductive parameter, σ_I,[13] (Fig. 1) and (ii) Huheey's group electronegativity, χ_H[14] (Fig. 2). The appreciable scatter of the experimental points in both plots is far from unexpected. It may arise from several causes, including (i) the neglect of resonance effects, (ii) the overestimation of group electronegativities for the most polar functional groups,[14] (iii) the neglect of Huheey's charge coefficients, and (iv) the inherent difference between σ_I, a reaction parameter measuring the effect of a functional group on a remote reaction centre, and α, a ground-state structural parameter measuring the effect of the substituent on the neighbouring part of the ring.

The values of α given in Table 1 should be taken into account when constructing geometrical models of the benzene ring to be used for MO calculations of charge distributions and dipole moments. (The models used so far have assumed perfect $\underline{D_{6h}}$ symmetry for the carbon hexagon[15]). They might also be of interest for the rationalisation of some, as yet unexplained, deviations of NMR parameters from the values expected.[16]

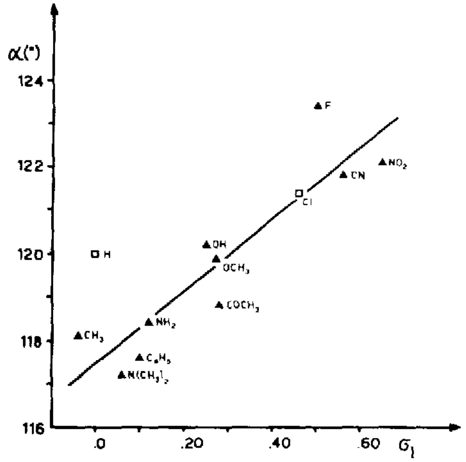


Fig. 1 - Plot of the angle α vs Taft's inductive parameter for first-row functional groups. The correlation coefficient is 0.90 on 10 data sets.

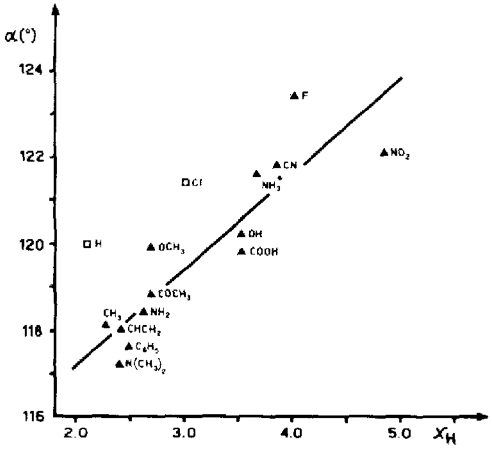


Fig. 2 - Plot of the angle α vs Huheey's group electronegativity for first-row functional groups. The correlation coefficient is 0.89 on 13 data sets.

References and Notes

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7. Very accurate measurements of α may be carried out by microwave spectroscopy in the gaseous state, but this requires the preparation of several isotopic modifications of the molecule.
8. Exceptions have been found to occur whenever one of the two substituents is a strong π-donor and the other a potential π-acceptor. This leads to a marked decrease (up to 3° in extreme cases) in the value of α for the π-acceptor, with no appreciable variation for that of the π-donor. This effect has been attributed[4] to through-conjugation, which is undoubtedly responsible for part of the decrease. More recent results, however, indicate that π-donor functional groups do *per se* produce a small decrease of the endocyclic angle at the *para* carbon, δ.[6]
9. The much less extensive body of structural information on *meta*-disubstituted benzene derivatives is consistent with this result.
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11. The corresponding figure for 'second-row' substituents is 119.7°, as obtained from the α *vs* electronegativity correlation of ref. 5, by interpolation at $\chi = 2.5$.
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