

Substituent Effects and the In-Plane Distortion of Aromatic Rings: A Group-Theoretical Approach

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Abstract

The distortions of benzene rings caused by substituents are analysed by application of group-theoretical methods. For each substituent there is a vector whose components represent the distortion of individual angles or bonds. Alternatively these vectors can be represented in terms of the symmetry coordinates of a regular hexagon. On the assumption that substituent effects can be linearly combined, formulae are derived for predicting the distortions of polysubstituted benzene derivatives.

Introduction

In an extensive analysis of the geometry of a large number of selected monosubstituted derivatives of benzene (I) it has been shown (Domenicano, Vaciano & Coulson, 1975*a,b*; Domenicano & Vaciano, 1979) (DVC*a*, DVC*b*, DV respectively) that substituents on the benzene ring can cause significant in-plane distortions of the carbon skeleton from D_{6h} symmetry.* These distortions are most significant experimentally when angles rather than bonds are concerned and the largest effect is usually seen at the atom to which the substituent is attached (*ipso* atom). There is evidence, however, that the angle *para* to the substituent is also affected and, in general, angular distortions are observed at all six C atoms. Similar distortions are also present in bond lengths but experimental errors are large so that they are not as reliably observed. The quantitative aspects of these distortions are investigated by factor analysis and other methods in a following paper (Domenicano, Murray-Rust & Vaciano, 1982) (DMRV). In this paper we consider the representation of distortions by vector methods and the combination of distortions caused by polysubstitution in benzene rings.

* Throughout this paper Schoenflies symbols will be used to describe the symmetries of molecular configurations. Hermann-Mauguin symbols are used for the symmetries of the point groups H related to deformation spaces.

In general a substituent (*e.g.* OMe) may cause different distortions at all six ring angles and all six bonds (Di Rienzo, Domenicano, Portalone & Vaciano, 1976) but many monatomic or highly symmetrical substituents (*e.g.* NO₂, Ph, *etc.*) distort the benzene ring so that it retains C_{2v} symmetry within experimental error (Fig. 1). In this case there cannot be more than four different angles and three different bonds, but since the ring is planar only five can be independent. (One angle is exactly determined by the other three and there is also a ring-closure condition involving lengths and angles.) In this paper we shall restrict ourselves to substituents where the monosubstituted benzene ring retains C_{2v} symmetry. It is fairly straightforward to generalize the approach described here to substituents which cause distortions of lower symmetry.

Combinations of substituent effects

For each symmetrical monosubstituted benzene derivative (I), there is a set of four angular substituent parameters ($\Delta\alpha, \Delta\beta, \Delta\gamma, \Delta\delta$) and three length parameters ($\Delta a, \Delta b, \Delta c$) which are the deviations from a reference unsubstituted benzene molecule with angles of 120° and C–C length r_0 . Elsewhere (Domenicano & Murray-Rust, 1979) (DMR) we have given a table of the angular parameters for 22 common functional groups. Di- and polysubstituted benzene rings normally have lower symmetry (C_s) and can only be described in terms of these parameters if we assume some method of combining substituent effects. The simplest model is a linear combination and here we shall investigate the geometrical basis of the idea that the distortions caused

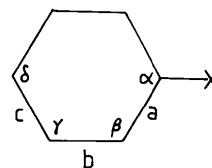
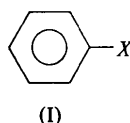


Fig. 1. Parameters used to define the geometry of the carbon skeleton in a phenyl derivative retaining C_{2v} symmetry. H atoms are omitted.

by a number of substituents on a benzene nucleus can be represented as the cumulative effect of all the substituents acting independently. Although there is little theoretical justification for this chemically, we have shown (DMR) that for a large number of *para*-disubstituted benzene derivatives this model gives good agreement with the observed ring angles (bonds were not considered) and gives satisfactory predictions for polysubstituted molecules.* A similar approach has independently been used by Norrestam & Schepper (1981) in analysing the angular distortion of benzene rings polysubstituted with Me, Ph, Cl and OH.



Representation of distortions by symmetry coordinates

The linear combination of distortions of tetrahedra has been fully described both from a group-theoretical aspect and experimentally (Murray-Rust, Bürgi & Dunitz, 1978*a,b*) (MBD*a,b*) and a general procedure, applicable to any point group, has been published (Murray-Rust, Bürgi & Dunitz, 1979) (MBD*c*). Much of the notation and nomenclature used here is taken from these papers. Central to the approach is the representation of a distortion as an n -dimensional vector \mathbf{D} and its decomposition into n orthogonal components D_i . Each component is chosen to transform as an irreducible representation (IR) of the point group of the undistorted molecule (reference point group G). Here we consider a planar irregular hexagon related to the point group D_{6h} . It is shown in many textbooks of applied group theory that there are nine degrees of freedom for an in-plane distortion of a

* Through-conjugation (*i.e.* the cooperative effect of a strong π donor and a strong π acceptor *para* to each other) is clearly a non-linear effect. Although we have shown that it affects the angles in *para*-disubstituted molecules, it probably accounts for less than 1% of the angular variance (DMR).

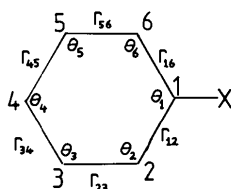


Fig. 2. Internal parameters describing a planar hexagon. All substituted benzene derivatives discussed in the text will have this orientation and numbering regardless of the position of substituents.

regular hexagon and that an arbitrary distortion vector transforms as

$$A_{1g} + B_{2u} + 2E_{2g} + E_{1u} + B_{1u}. \quad (1)$$

The first two relate only to bond-length distortions and the last one only to angle distortions, whereas the degenerate E representations include both bond and angle distortions.

The in-plane distortion of a planar hexagon from a reference structure of D_{6h} symmetry can be described as a nine-dimensional vector \mathbf{D} . If we define the deviations from regularity in terms of internal coordinates (Fig. 2) as:

$$\Delta r_{12} = r_{12} - r_0, \text{ etc.}, \quad (2)$$

(where r_0 is the reference bond length of an undistorted hexagon) and

$$\Delta \theta_1 = \theta_1 - 120^\circ, \text{ etc.}, \quad (3)$$

the components (D_i) of the distortion vector* can be expressed as linear combinations of r_{jk} and θ_i :

$$D_1(A_{1g}) = 6^{-1/2}(\Delta r_{12} + \Delta r_{23} + \Delta r_{34} + \Delta r_{45} + \Delta r_{56} + \Delta r_{16}), \quad (4)$$

$$D_2(B_{2u}) = 6^{-1/2}(\Delta r_{12} - \Delta r_{23} + \Delta r_{34} - \Delta r_{45} + \Delta r_{56} - \Delta r_{16}), \quad (5)$$

$$D_{3a}(E_{2g}) = 12^{-1/2}(-\Delta r_{12} + 2\Delta r_{23} - \Delta r_{34} - \Delta r_{45} + 2\Delta r_{56} - \Delta r_{16}), \quad (6)$$

$$D_{3b}(E_{2g}) = 4^{-1/2}(-\Delta r_{12} + \Delta r_{34} - \Delta r_{45} + \Delta r_{16}), \quad (7)$$

$$D_{4a}(E_{2g}) = 12^{-1/2}(2\Delta \theta_1 - \Delta \theta_2 - \Delta \theta_3 + 2\Delta \theta_4 - \Delta \theta_5 - \Delta \theta_6), \quad (8)$$

$$D_{4b}(E_{2g}) = 4^{-1/2}(\Delta \theta_2 - \Delta \theta_3 + \Delta \theta_5 - \Delta \theta_6), \quad (9)$$

$$D_{5a}(E_{1u}) = 12^{-1/2}(2\Delta \theta_1 + \Delta \theta_2 - \Delta \theta_3 - 2\Delta \theta_4 - \Delta \theta_5 + \Delta \theta_6), \quad (10)$$

$$D_{5b}(E_{1u}) = 4^{-1/2}(\Delta \theta_2 + \Delta \theta_3 - \Delta \theta_5 - \Delta \theta_6), \quad (11)$$

$$D_6(B_{1u}) = 6^{-1/2}(\Delta \theta_1 - \Delta \theta_2 + \Delta \theta_3 - \Delta \theta_4 + \Delta \theta_5 - \Delta \theta_6). \quad (12)$$

The form of D_1 , D_2 and D_6 is fixed but there is always a choice of how basis vectors for degenerate representations can be chosen (a problem discussed in detail in MBD*a,c*). Here the E_{2g} distortion has been decomposed into two bond and two angle components and D_{3a} and D_{4a} have been chosen so that they correspond to the cokernel symmetry (D_{2h}) of this IR. The

* The numbering of the symmetry coordinates is not the same as in most textbooks, since coordinates involving hydrogen have been omitted.

components D_{3b} and D_{4b} correspond only to the lower kernel symmetry, C_{2h} . The E_{1u} representation contains an inseparable combination of bond and angle components whose relation is essentially the ring-closure condition for hexagons slightly distorted from regularity. Britton (1977) has (without explicitly referring to this IR) derived relationships between bond lengths and angles in planar hexagons. D_{5a} has the cokernel symmetry (C_{2v}), D_{5b} the kernel symmetry C_s . The alternative formulations for the E_{1u} components in terms of bond distortions are:

$$D'_{5a} = 12^{-1/2} (2\Delta r_{23} + \Delta r_{34} - \Delta r_{45} - 2\Delta r_{56} - \Delta r_{16} + \Delta r_{12}), \quad (13)$$

$$D'_{5b} = 4^{-1/2} (-\Delta r_{34} - \Delta r_{45} + \Delta r_{16} + \Delta r_{12}). \quad (14)$$

D'_{5a} is related to D_{5b} and D'_{5b} to D_{5a} by a scale factor derivable from Britton's (1977) equations.

A general nine-dimensional vector \mathbf{D} will contain non-zero components D_1 to D_6 and will correspond to a molecule with no symmetry except the xy mirror plane. Distortions where some of the nine components are zero may, however, correspond to (kernel or cokernel) configurations which retain other symmetry elements of D_{6h} . Thus a distortion whose vector has all components zero except D_2 will result in a molecule with $D_{3h}(x)$ symmetry (the kernel of the B_{2u} representation). For degenerate representations, symmetries higher than the kernel may occur. Thus if all components except D_{3a} and D_{3b} are zero the symmetry of the corresponding molecule will be $C_{2h}(z)$ (the kernel symmetry of E_{2g}) but if only D_{3a} is non-zero the higher cokernel symmetry $D_{2h}(\sigma_{xz}, \sigma_{yz})$ occurs. The same cokernel symmetry (but preserving other σ_x planes) can occur in two other circumstances: when $D_{3a} = \pm 3^{-1/2} D_{3b}$. This situation is concisely expressed in the vector diagram shown in Fig. 3. A bond distortion transforming as E_{2g} is represented by a vector in this (two-dimensional) diagram, the length of the vector expressing the amount of the distortion. The orientation of the vector relates to the symmetry of the distorted molecule. If the vector happens to lie along any of the six special positions OA, OB, OC, OA, OB, OC , the kernel configuration will have the D_{2h} cokernel symmetry. It can be seen that the symmetry of Fig. 2 is $3m$ and that AOC represents the asymmetric unit. The diagram is non-centrosymmetric so that OA and OA represent different distortions. For example, a vector along OA corresponds to a lengthening of the *ortho/meta* bonds (r_{23} and r_{56}) whilst OA corresponds to a compression (a quinonoid structure). OA and OB represent isometric distortions identical except for the labelling of the atoms or, alternatively, the orientation of the molecule. For each IR there is a kernel symmetry and for degenerate ones there are also one or more cokernel symmetries (MBDc) and these, along with the sym-

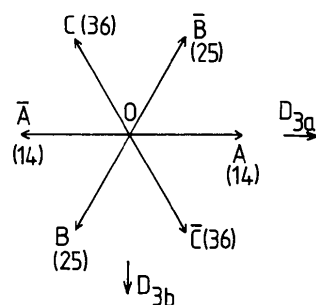


Fig. 3. Representation of bond-length distortions transforming solely as E_{2g} . The components of a general distortion vector are measured on the orthogonal axes D_{3a} and D_{3b} . A general vector corresponds to a molecular configuration with the kernel symmetry $C_{2h}(z)$ but when a vector lies along any of OA, OC, OB, OA, OC, OB the molecular configuration has D_{2h} cokernel symmetry. The numbers in parentheses indicate which of the mirror planes along the z axis is preserved (see Fig. 2). Since distortions OA and OA are not equivalent the diagram has $3m$ symmetry.

Table 1. Kernel and cokernel symmetries for irreducible representations of D_{6h} where the kernel retains the xy mirror plane (Murray-Rust, Bürgi & Dunitz, 1979)

Symmetry of deformation space relates to the symmetry of diagrams such as Fig. 3 and Hermann-Mauguin symbols are used (the H groups of MBDc).

IR	Kernel	Cokernel(s)	H (symmetry of deformation space)
A_{1g}	D_{6h}	—	1
B_{2u}	$D_{3h}(x)$	—	1
E_{2g}	$C_{2h}(z)$	D_{2h}	$3m$
E_{1u}	$C_s(z)$	$C_{2v}(x), C_{2v}(y)$	$3m$
B_{1u}	$D_{3h}(y)$	—	1

metries of the corresponding deformation spaces H, are given in Table 1.

Substituent parameters for irreducible representations

It will be convenient to consider the distortion caused by a substituent as a nine-dimensional vector having components which transform as individual IR's. Thus a distortion retaining C_{2v} symmetry (appropriate to a monosubstituted benzene) may have five components $D_1, D_{3a}, D_{4a}, D_{5a}, D_6$ (see Table 2). No combination of these components can give a non-zero D_2 component and hence no combination of symmetrical substituents can produce a molecule with $D_{3h}(x)$ symmetry if our model of linear combination holds.

We shall take the case of a single IR to illustrate the representation of distortion. Assume that at position 1 substituent X causes a bond length distortion (X_3) whose D_{3a} component is X_3 and whose D_{3b} component is zero. Assume secondly that all other distortion

Table 2. Subgroups of D_{6h} which retain the xy mirror plane

For each subgroup are given the distortion coordinates corresponding to IR's with kernel or cokernel symmetries which are supergroups of the group in each row. The combinations marked with an asterisk require the a and b components of a distortion vector to be present in the ratio $1: \pm\sqrt{3}$.

$C_3(z)$	D_1	D_2	D_{3a}	D_{3b}	D_{4a}	D_{4b}	D_{5a}	D_{5b}	D_6
$C_{2v}(y)$	D_1		D_{3a}		D_{4a}		D_{5a}	D_{5b}	D_6
$C_{2v}(x)$	D_1	D_2					$(D_{5a} + D_{5b})^*$		
$C_{2h}(z)$	D_1		D_{3a}	D_{3b}	D_{4a}	D_{4b}			
$D_{2h}(xz, yz)$	D_1		D_{3a}		D_{4a}				
$D_{3h}(y)$	D_1								D_6
$D_{3h}(x)$	D_1	D_2							

components happen to be zero. Assume also that a different ligand Y at position 1 *independently* causes a distortion (Y_3) whose D_{3a} component is Y_3 . In general for any symmetrical substituent we assume a scalar substituent parameter for the E_{2g} (bond) distortion.* Vector diagrams such as Fig. 4 show how substituent effects can be described. The distortion due to each substituent is represented by a vector lying along one of the three axes: OA for substitution at 1 or 4; OB for substitution at 2 or 5; and OC for substitution at 3 or 6. The magnitude of the vector is the D_3 substituent effect for each ligand. The case for a monosubstituted benzene ring is shown in Fig. 4(a). The distortion due to X must be combined with the distortions due to the five H atoms and can be seen to result in a final vector along OA of magnitude $X_3 - H_3$. It turns out that for all IR's the resultant is always a *difference* between substituent effects and we shall arbitrarily set all distortion parameters for hydrogen to zero. With this new terminology the hydrogen substituents need not be explicitly considered further.

The X, Y *para*-disubstitution of benzene is represented in Fig. 5(b). The resultant D_3 vector is simply the

* For an unsymmetrical substituent, e.g. OMe, a two-dimensional substituent vector will be required, but this case will not be further considered.

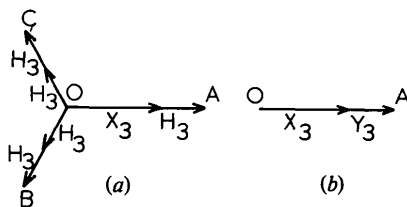


Fig. 4. Vector addition of substituent effects in (a) c1ccccc1X and

(b) c1ccc(cc1X)Y for the E_{2g} representation (see Fig. 3). Note

that in (b) the substituent effect from hydrogen has been set to zero.

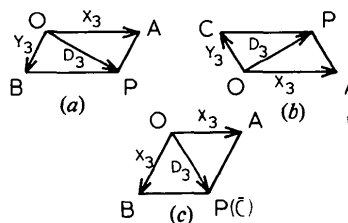
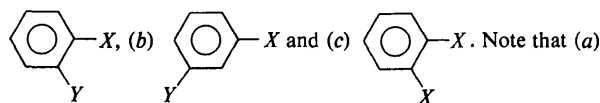


Fig. 5. Resultant D_3 distortion vectors (see Fig. 3) for (a)



and (b) are related by a mirror plane and that in (c) the resultant D_3 is of equal magnitude to X_3 and lies along OC , corresponding to D_{2h} (36) cokernel symmetry.

sum of the individual X_3 and Y_3 scalars (either of which may, of course, be negative). *Ortho* and *meta* substitution is more involved since the resultant molecule no longer has D_{2h} cokernel symmetry (Fig. 5a). It is seen that the resultant vector OP makes an arbitrary angle with OA . The corresponding situation for *meta* substitution is shown in Fig. 5(b). The D_3 vectors for *ortho* and *meta* substitution are identical in magnitude and related by a mirror plane. (This means that if all substituent parameters except X_3 and Y_3 happened to be zero, the *ortho*- and *meta*-substituted molecules would have the same geometry. Put another way, we expect the E_{2g} kernel configuration for *ortho*- and *meta*- C_6H_4XY to be identical.) Where substituents are identical, distortion vectors may lie in special positions of the deformation space (Fig. 5c). Patterns of polysubstitution are easily worked out in a similar manner.

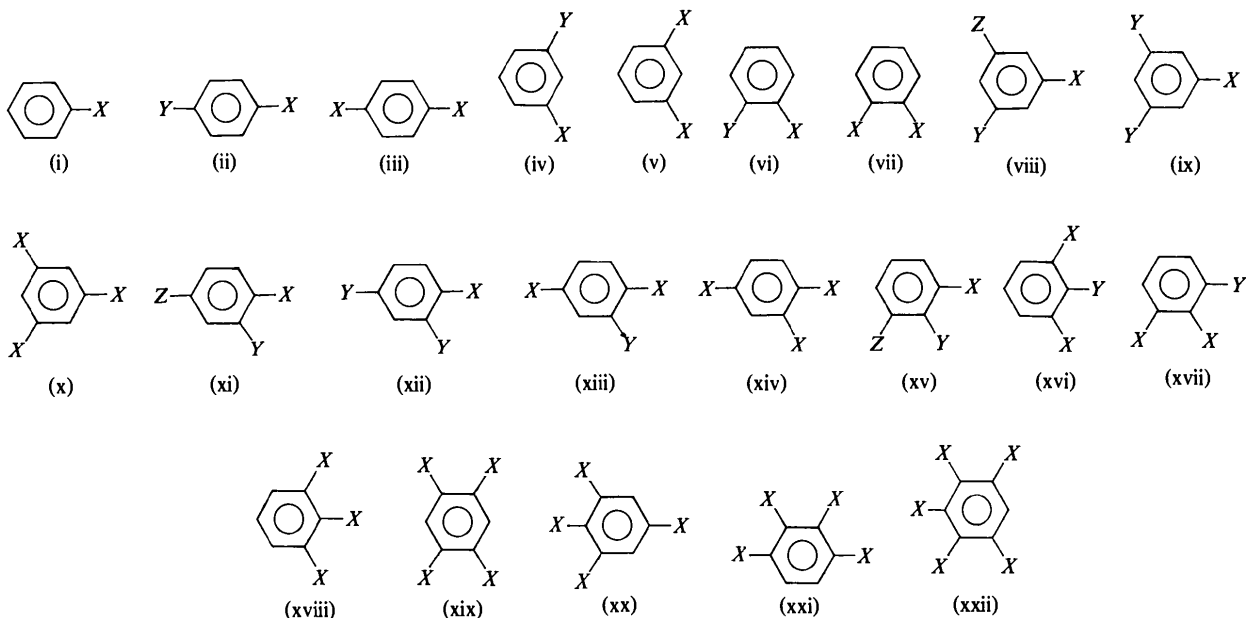
The E_{2g} (bond) distortion (D_3) has been used as an example but similar combinations of substituent effects are possible for all the other IR's. We have five scalar distortion parameters for a (symmetrical) substituent X : X_1 (bonds), X_3 (bonds), X_4 (angles), X_5 (angles/bonds) and X_6 (angles). For the A_{1g} component the resultant is simply the sum of the substitution parameters regardless of the pattern of ligands:

$$D_2 = X_1 + Y_1 + Z_1 \dots \text{etc.} \quad (15)$$

For E_{2g} , E_{1u} and B_{1u} components, the addition depends on the substitution pattern and this is given in Table 3 for all combinations of up to three ligands and for some special cases of higher substitution. Several points may be noted. Because symmetrical substituents cannot combine to give a non-zero D_2 component, the total distortion predicted by this model is given by an *eight*-dimensional vector (whose components are D_1 , D_{3a} , D_{3b} , D_{4a} , D_{4b} , D_{5a} , D_{5b} , D_6). Certain patterns of substitution for certain IR's give a kernel configuration with cokernel symmetry (marked by an asterisk in Table 2). Some types of substitution bear an inverse

Table 3. *Linear combination of substituent effects*

Substituent effects are expressed as X_3 (E_{2g}), X_4 (E_{2g}), X_5 (E_{1u}) and X_6 (B_{1u}) for a substituent X at position 1. The treatment of X_4 uses the same equations as X_3 and is omitted. Additional substituents Y and Z are given similar parameters. The ring is numbered in the same way for all substitution patterns regardless of the position of substituents. Thus C(1) is always at the right-hand end of the molecule (Fig. 2). By orienting some of the molecules in an unusual manner the relationships are made particularly simple. Entries with asterisks correspond to cokernel configurations for the hexagon (for that particular IR only).



IR	E_{2g}	E_{1u}	B_{1u}		
Coordinate	S_{3a} (S_{4a})	S_{3b} (S_{4b})	S_{5a} S_{5b}	S_6	
Molecule					
Monosubstituted benzenes					
(i) 1- X - C_6H_5	X_3^*	0	X_5^*	0	X_6
Disubstituted benzenes					
(ii) 1- X -4- Y - C_6H_4	$X_3 + Y_3^*$	0	$X_5 - Y_5^*$	0	$X_6 - Y_6$
(iii) 1- X -4- X - C_6H_4	$2X_3^*$	0	0	0	0
(iv) 2- X -6- Y - C_6H_4	$(X_3 + Y_3)/2$	$\sqrt{3}(X_3 - Y_3)/2$	$(X_5 + Y_5)/2$	$\sqrt{3}(X_5 + Y_5)/2$	$-(X_6 + Y_6)$
(v) 2- X -6- X - C_6H_4	X_3^*	0	X_5^*	0	$-2X_6$
(vi) 2- X -3- Y - C_6H_4	$-(X_3 + Y_3)/2$	$\sqrt{3}(X_3 - Y_3)/2$	$(X_5 - Y_5)/2$	$\sqrt{3}(X_5 + Y_5)/2$	$-X_6 + Y_6$
(vii) 2- X -3- X - C_6H_4	$-X_3^*$	0	0	$\sqrt{3}X_5^*$	0
Trisubstituted benzenes					
(viii) 1- X -3- Y -5- Z - C_6H_3	$X_3 - (Y_3 + Z_3)/2$	$\sqrt{3}(X_3 - Y_3)/2$	$X_5 - (Y_5 + Z_5)/2$	$\sqrt{3}(Y_5 - Z_5)/2$	$X_6 + Y_6 + Z_6$
(ix) 1- X -3- Y -5- Y - C_6H_3	$X_3 - Y_3^*$	0	$X_5 - Y_5^*$	0	$X_6 + 2Y_6$
(x) 1- X -3- X -5- X - C_6H_3	0	0	0	0	$3X_6$
(xi) 1- X -2- Y -4- Z - C_6H_3	$X_3 - Y_3/2 + Z_3$	$\sqrt{3}Y_3/2$	$X_5 + Y_5/2 - Z_5$	$\sqrt{3}Y_5/2$	$X_6 - Y_6 - Z_6$
(xii) 1- X -2- Y -4- Y - C_6H_3	$X_3 + Y_3/2$	$\sqrt{3}Y_3/2$	$X_5 - Y_5/2$	$\sqrt{3}Y_5/2$	$X_6 - 2Y_6$
(xiii) 1- X -2- Y -4- X - C_6H_3	$2X_3 - Y_3/2$	$\sqrt{3}Y_3/2$	$Y_5/2^*$	$\sqrt{3}Y_5/2^*$	$-Y_6$
(xiv) 1- X -2- X -4- X - C_6H_3	$3X_3/2$	$\sqrt{3}X_3/2$	$X_5/2^*$	$\sqrt{3}X_5/2^*$	$-X_6$
(xv) 1- X -2- Y -3- Z - C_6H_3	$X_3 - (Y_3 + Z_3)/2$	$\sqrt{3}(Y_3 - Z_3)/2$	$X_5 + (Y_5 - Z_5)/2$	$\sqrt{3}(Y_5 + Z_5)/2$	$X_6 - Y_6 + Z_6$
(xvi) 1- Y -2- X -6- X - C_6H_3	$-X_3 + Y_3$	0	$X_5 + Y_5$	0	$-2X_6 + Y_6$
(xvii) 1- Y -2- X -3- X - C_6H_3	$-X_3 + Y_3$	0	Y_5	$\sqrt{3}X_5$	Y_6
(xviii) 1- X -2- X -6- X - C_6H_3	0	0	$2X_5^*$	0	$-X_6$
Symmetrical tetrasubstitution					
(xix) 2- X -3- X -5- X -6- X - C_6H_2	$-2X_3^*$	0	0	0	0
(xx) 1- X -3- X -4- X -5- X - C_6H_2	$-X_3^*$	0	$-X_5^*$	0	$2X_6$
(xxi) 1- X -4- X -5- X -6- X - C_6H_2	X_3^*	0	0	$\sqrt{3}X_5^*$	0
Symmetrical pentasubstitution					
(xxii) 2- X -3- X -4- X -5- X -6- X - C_6H	$-X_3^*$	0	$-X_5^*$	0	$-X_6$

relationship: thus symmetrical *para*-disubstitution ($C_6H_4X_2$) should show an exactly opposite distortion (for all IR's and hence for the total distortion vector) to 1,2,4,5-tetrasubstitution ($C_6H_2X_4$). Similar complementarity can be found between other $C_6X_nY_{6-n}$ and $C_6X_{6-n}Y_n$ substitution patterns where X and Y are interchanged. More importantly, given the experimental geometry of a molecule we can calculate the components of the distortion and, if some (but not all) of the substituent effects are known, we can calculate other substituent effects by vectorial subtraction. An example of this is given in the Appendix.

Distortions represented as combinations of internal parameters

We have used symmetry-distortion coordinates to represent distortions because of their geometrical orthogonality, but internal coordinates can also be used. Considering angles alone, the distortion of a monosubstituted benzene (C_6H_5X) can be described by three components X_4 , X_5 and X_6 . For a combination of substituents (X, Y, \dots) the angular distortion of a benzene ring is described in general by D_{4a} , D_{4b} , D_{5a} , D_{5b} and D_6 . These can be retransformed into angles with (8)–(12) and the requirement that the sum of $\Delta\theta_1$ to $\Delta\theta_6$ is zero. Since all these transformations are linear, a linear combination of substituent effects implies a linear combination of individual angle distortions. In many cases this is more useful than the use of symmetry coordinates and elsewhere (DMR) we have shown that angles in *para*-disubstituted benzene rings are very well represented by linear combinations of the distortions in the appropriate monosubstituted rings.

As an example consider the geometry of (V) as a linear combination of substituent effects. The geometry of the monosubstituted molecules is shown in Fig. 6. The distortions of (II) from regularity can be represented by $\Delta\alpha_X$, $\Delta\beta_X$, $\Delta\gamma_X$ and $\Delta\delta_X$. Similarly, we use $\Delta\alpha_Y$,

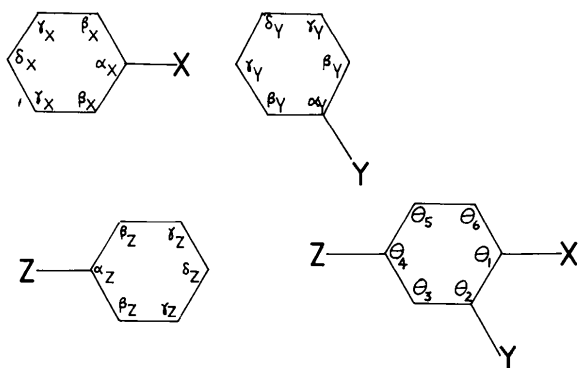


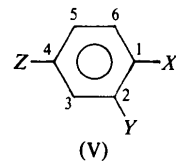
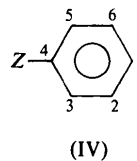
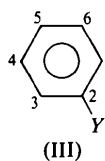
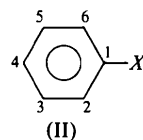
Fig. 6. Individual angles in monosubstituted benzene rings, defining substituent effects, and in a trisubstituted ring.

etc. for (III) and $\Delta\alpha_Z$, *etc.* for (IV). The D_{4a} distortion components for (II), (III) and (IV) (related to the numbering in Fig. 6) are:

$$D_{4a}(\text{II}) = 12^{-1/2}(2\Delta\alpha_X - 2\Delta\beta_X - 2\Delta\gamma_X + 2\Delta\delta_X), \quad (16)$$

$$\begin{aligned} D_{4a}(\text{III}) &= 12^{-1/2}(2\Delta\beta_Y - \Delta\gamma_Y - \Delta\delta_Y + 2\Delta\gamma_Y - \Delta\beta_Y \\ &\quad - \Delta\alpha_Y) \\ &= 12^{-1/2}(\Delta\beta_Y + \Delta\gamma_Y - \Delta\alpha_Y - \Delta\delta_Y), \quad (17) \end{aligned}$$

$$D_{4a}(\text{IV}) = 12^{-1/2}(2\Delta\alpha_Z - 2\Delta\beta_Z - 2\Delta\gamma_Z + 2\Delta\delta_Z). \quad (18)$$



The linear combination of these distortions results in a D_{4a} component:

$$\begin{aligned} D_{4a}(\text{II}+\text{III}+\text{IV}) &= D_{4a}(\text{II}) + D_{4a}(\text{III}) + D_{4a}(\text{IV}) \\ &= 12^{-1/2}(2\Delta\alpha_X - 2\Delta\beta_X - 2\Delta\gamma_X + 2\Delta\delta_X \\ &\quad - \Delta\alpha_Y + \Delta\beta_Y + \Delta\gamma_Y - \Delta\delta_Y + 2\Delta\alpha_Z \\ &\quad - 2\Delta\beta_Z - 2\Delta\gamma_Z + 2\Delta\delta_Z). \quad (19) \end{aligned}$$

Similar combinations lead to:

$$\begin{aligned} D_{4b}(\text{II}+\text{III}+\text{IV}) &= 4^{-1/2}(-\Delta\alpha_Y + \Delta\beta_Y \\ &\quad + \Delta\gamma_Y - \Delta\delta_Y). \quad (20) \end{aligned}$$

$$\begin{aligned} D_{5a}(\text{II}+\text{III}+\text{IV}) &= 12^{-1/2}(2\Delta\alpha_X + 2\Delta\beta_X - 2\Delta\gamma_X - 2\Delta\delta_X \\ &\quad - \Delta\alpha_Y - \Delta\beta_Y + \Delta\gamma_Y + \Delta\delta_Y \\ &\quad - 2\Delta\alpha_Z - 2\Delta\beta_Z + 2\Delta\gamma_Z + 2\Delta\delta_Z), \quad (21) \end{aligned}$$

$$\begin{aligned} D_{5b}(\text{II}+\text{III}+\text{IV}) &= 4^{-1/2}(-\Delta\alpha_Y - \Delta\beta_Y \\ &\quad + \Delta\gamma_Y + \Delta\delta_Y), \quad (22) \end{aligned}$$

$$\begin{aligned} D_6(\text{II}+\text{III}+\text{IV}) &= 6^{-1/2}(\Delta\alpha_X - 2\Delta\beta_X + 2\Delta\gamma_X - \Delta\delta_X \\ &\quad - \Delta\alpha_Y + 2\Delta\beta_Y - 2\Delta\gamma_Y + \Delta\delta_Y \\ &\quad - \Delta\alpha_Z + 2\Delta\beta_Z - 2\Delta\gamma_Z + \Delta\delta_Z). \quad (23) \end{aligned}$$

If the angles in (V) are denoted by θ_1 to θ_6 (Fig. 6) the distortion components will be found to be:

$$D_{4a}(\text{V}) = 12^{-1/2}(2\theta_1 - \theta_2 - \theta_3 + 2\theta_4 - \theta_5 - \theta_6), \quad (24)$$

$$D_{4b}(\text{V}) = 4^{-1/2}(\theta_2 - \theta_3 + \theta_5 - \theta_6), \quad (25)$$

$$D_{5a}(\text{V}) = 12^{-1/2}(2\theta_1 + \theta_2 - \theta_3 - 2\theta_4 - \theta_5 + \theta_6), \quad (26)$$

$$D_{5b}(\mathbf{V}) = 4^{-1/2}(\theta_2 + \theta_3 - \theta_5 - \theta_6), \quad (27)$$

$$D_6(\mathbf{V}) = 6^{-1/2}(\theta_1 - \theta_2 + \theta_3 - \theta_4 + \theta_5 - \theta_6). \quad (28)$$

If substituent effects combine linearly we have:

$$D_{4a}(\mathbf{V}) = D_{4a}(\text{II} + \text{III} + \text{IV}), \text{ etc.}, \quad (29)$$

and combining (19)–(29), we can calculate the angles in (I) as:

$$\theta_1 = 120 + \Delta\alpha_X + \Delta\beta_Y + \Delta\delta_Z, \quad (30)$$

$$\theta_2 = 120 + \Delta\beta_X + \Delta\alpha_Y + \Delta\gamma_Z, \quad (31)$$

$$\theta_3 = 120 + \Delta\gamma_X + \Delta\beta_Y + \Delta\beta_Z, \quad (32)$$

$$\theta_4 = 120 + \Delta\delta_X + \Delta\gamma_Y + \Delta\alpha_Z, \quad (33)$$

$$\theta_5 = 120 + \Delta\gamma_X + \Delta\delta_Y + \Delta\beta_Z, \quad (34)$$

$$\theta_6 = 120 + \Delta\beta_X + \Delta\gamma_Y + \Delta\gamma_Z. \quad (35)$$

Thus the distortions of θ_1 to θ_6 from regularity are simply the combination of the respective distortions in (II), (III) and (IV). The quantities $\Delta\alpha_X$, $\Delta\beta_X$, $\Delta\gamma_X$ and $\Delta\delta_X$ can be regarded as the *angular substituent parameters* for X but it must be remembered that only three of them can be *geometrically* independent since $\Delta\alpha_X + 2\Delta\beta_X + 2\Delta\gamma_X + \Delta\delta_X = 0$.

The combination of angle distortions turned out to be particularly simple because the reference angles were fixed by symmetry. The combination of bond-length distortions is not so simple since we have to include the reference bond length, r_0 , explicitly. Following a similar procedure to that for angles we can derive the expressions for the bond lengths in the trisubstituted molecule (V) from a linear combination of the geometries of (II), (III) and (IV):

$$r_{12} = a_X + b_Y + c_Z - 2r_0 \quad (36)$$

$$r_{23} = b_X + c_Y + b_Z - 2r_0 \quad (37)$$

$$r_{34} = c_X + c_Y + a_Z - 2r_0, \quad (38)$$

$$r_{45} = c_X + b_Y + a_Z - 2r_0, \quad (39)$$

$$r_{56} = b_X + a_Y + b_Z - 2r_0, \quad (40)$$

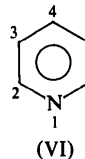
$$r_{16} = a_X + a_Y + c_Z - 2r_0. \quad (41)$$

Thus, unlike angles, bond-length distortions cannot be combined without a knowledge of the reference bond length, r_0 . This is because the bond lengths transform as a combination of IR's which include the totally symmetric IR. Errors in the experimental determination of r_0 will be transmitted in double amount to the estimates of r_{12} , etc., from (36)–(41). Since there is an apparent bond shortening in many molecules observed by room-temperature X-ray diffraction, symmetry-distortion coordinates may often be more useful.

Extension to other systems

There is evidence that a similar linear combination of substituent effects holds for other less symmetrical

molecules, such as pyridine (VI). Monosubstitution at the 2, 3, or 4 positions causes distortions but there is no symmetry requirement for them to be equal. Thus for 2-substitution all six angles may change by different amounts (although there are only five independent angular substituent parameters). The extension to polysubstituted systems is then analogous to (30)–(41). An important difference, however, is that the angles in the reference structure (VI) must now be known since they are not fixed by symmetry.



APPENDIX

We take as an example the trisubstituted molecule in Fig. 7 (Chiaroni, 1971). Considering angles alone (all numbers are in degrees) we can compute:

$$D_{4a} = (2 \times 117.3 - 119.6 - 121.7 - 124.1 - 122.9 + 2 \times 114.3) / \sqrt{12} = -7.24^\circ,$$

$$D_{4b} = (119.6 - 124.1 + 122.9 - 121.7) / 2 = -1.65,$$

$$D_{5a} = (2 \times 117.3 + 119.6 - 124.1 - 114.3 - 2 \times 122.9 + 121.7) / \sqrt{12} = 0.72,$$

$$D_{5b} = (119.6 + 124.1 - 122.9 - 121.7) / 2 = -0.45,$$

$$D_6 = (117.3 - 119.6 + 124.1 - 114.3 + 122.9 - 121.7) / \sqrt{6} = 3.55.$$

From Table 3 we find that D_{4b} and D_{5b} contain only terms related to Y (in this case NO_2). On the basis of a linear combination of substituent effects we can derive

$$D_4(\text{NO}_2) = \frac{2D_{4b}}{3} = -1.90^\circ$$

$$D_5(\text{NO}_2) = \frac{2D_{5b}}{3} = -0.52$$

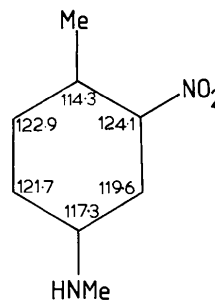


Fig. 7. The ring angles ($^\circ$) in 3-nitro-4-methyl-*N*-methylaniline (see Appendix).

without having to know the effects of the Me— and MeNH— substituents. (The linear combination is likely to hold well here as there is no mechanism for through-conjugation.) Let us suppose that substituent parameters are known for two of the three parameters. We have published (DMR) values for 22 substituents, among them NO₂ and Me, but no values are available for NHMe. They have been estimated as follows on the basis of the linear hypothesis. From DMR we have:

$$\begin{aligned}\Delta\alpha(\text{NO}_2) &= 2.9^\circ & \Delta\alpha(\text{Me}) &= -1.9^\circ \\ \Delta\beta(\text{NO}_2) &= -1.9 & \Delta\beta(\text{Me}) &= 1.0 \\ \Delta\gamma(\text{NO}_2) &= 0.3 & \Delta\gamma(\text{Me}) &= 0.4 \\ \Delta\delta(\text{NO}_2) &= 0.4 & \Delta\delta(\text{Me}) &= -0.7.\end{aligned}$$

From (30)–(35) we have

$$\begin{aligned}\Delta\alpha(\text{NHMe}) + 0.3 - 0.7 + 120 &= 117.3^\circ \\ \Delta\beta(\text{NHMe}) - 1.9 + 0.4 + 120 &= 119.6 \\ \Delta\gamma(\text{NHMe}) + 2.9 + 1.0 + 120 &= 124.1 \\ \Delta\delta(\text{NHMe}) - 1.9 - 1.9 + 120 &= 114.3 \\ \Delta\gamma(\text{NHMe}) + 0.3 + 1.0 + 120 &= 122.9 \\ \Delta\beta(\text{NHMe}) + 0.4 + 0.4 + 120 &= 121.7.\end{aligned}$$

Hence

$$\begin{aligned}\Delta\alpha(\text{NHMe}) &= -2.3^\circ \\ \Delta\beta(\text{NHMe}) &= 1.0 \\ \Delta\gamma(\text{NHMe}) &= 0.9 \\ \Delta\delta(\text{NHMe}) &= -1.9.\end{aligned}$$

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Structural Studies of Benzene Derivatives.

XI.* The Structure of *p*-Toluidine Hydrochloride

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Abstract

Crystals of the title compound, C₇H₁₀N⁺.Cl⁻, are monoclinic, space group *P*2₁/*c*, with *a* = 9.116 (1), *b* =

* Part X: Colapietro & Domenicano (1982).

0567-7408/82/112825-05\$01.00

It is gratifying to note that these values are close to those for —NH₂ and —NMe₂ (DMR):

$$\begin{aligned}\Delta\alpha(\text{NH}_2) &= -1.3^\circ & \Delta\alpha(\text{NMe}_2) &= -2.4^\circ \\ \Delta\beta(\text{NH}_2) &= 0.3 & \Delta\beta(\text{NMe}_2) &= 0.7 \\ \Delta\gamma(\text{NH}_2) &= 1.0 & \Delta\gamma(\text{NMe}_2) &= 1.4 \\ \Delta\delta(\text{NH}_2) &= -1.3 & \Delta\delta(\text{NMe}_2) &= -1.7.\end{aligned}$$

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9.357 (1), *c* = 9.913 (2) Å, β = 108.56 (2)°, *Z* = 4. The structure, originally determined by Von Eller [*Bull. Soc. Fr. Minéral. Cristallogr.* (1955), **78**, 275–300], has been redetermined from 1615 counter intensities and refined to a final *R* value of 0.0330. The benzene

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