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Molecular Geometry of Substituted Benzene Derivatives.
I. On the Nature of the Ring Deformations Induced by Substitution

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The small deformations induced by substitution in the skeletal geometry of the benzene ring are analysed in detail in a number of monosubstituted benzene derivatives. It is shown that the available structural data, which come mainly from room-temperature X-ray diffraction experiments, are unsuitable for a detailed investigation of the bond-length distribution within the ring, because of the effects of thermal motion. They are suitable, however, for a study of the internal bond angles. The observed dependence of the ring geometry upon the σ-electron-withdrawing or -releasing properties of the substituent and the extent of its conjugation with the ring is discussed in terms of (i) hybridization effects at the carbon atom at which substitution takes place, (ii) valence-shell electron-pair repulsions, (iii) intramolecular non-bonded interactions, and (iv) coulombic interactions between formally charged atoms. It appears that the experimental evidence is best rationalized in terms of either hybridization changes or valence-shell electron-pair repulsions. An analysis of the structural information available for *para*-disubstituted benzene derivatives has also been carried out. It is shown that the deformations induced by a substituent on the ring geometry are practically unaffected by a second substituent *para* to it, except in the case of through-conjugation.

1. Introduction

It has long been recognized that the regular hexagonal geometry of the carbon skeleton of the benzene ring is slightly modified when an electron-withdrawing functional group is substituted for a hydrogen atom (Bak, Christensen, Dixon, Hansen-Nygaard & Rastrup-Andersen, 1962; Bailey & Prout, 1965; Zvonkova & Khvatkina, 1965; Carter, McPhail & Sim, 1966; Nygaard, Bojesen, Pedersen & Rastrup-Andersen, 1968). The overall deformation is such as to lower the ring symmetry from D_{6h} ($6/mmm$) to C_{2v} ($2m$), and may be described in terms of (i) an increase of a few degrees

from 120° of the endocyclic bond angle, α, opposite to the substituent X (Fig. 1); (ii) a minor decrease of the two adjacent endocyclic angles, β; and (iii) a shortening (by some 0·01–0·02 Å) of the a bonds with respect to the adjacent b bonds. The remaining endocyclic angles, γ and δ, seem to be scarcely, if at all, affected. Opposite deformations are observed with electron-releasing substituents (Zvonkova & Khvatkina, 1965; Carter, McPhail & Sim, 1966; Malone & McDonald, 1967, 1972; Di Vaira & Bianchi Orlandini, 1972).

Thanks to present-day crystal structure analysis techniques, a wealth of accurate information on the molecular geometry of the derivatives of benzene is being accumulated. In this paper we attempt a rationalization of the available data on the ring deformations, particularly for mono- and *para*-di-substituted benzenes.

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2. Ring deformations in monosubstituted benzene derivatives

Some selected examples of ring geometry in monosubstituted benzene derivatives, showing different types and extents of deformation, are collected in Fig. 2. They have been chosen from among the dozens of compounds whose molecular structures are known with sufficient precision, in order to show some important points that deserve comment. The structural data of Fig. 2 have been obtained by either X-ray diffraction analysis [tetraphenylborate anion, hexaphenoxycyclotriphosphazene, 2,2-diphenyl-2-sila-1,3,4-trihydronaphthalene, triphenylphosphine(π-cyclopentadienyl)copper(I), and tetraphenylphosphonium cation] or microwave spectroscopy (cyanobenzene and fluorobenzene).

2.1. Effect of thermal motion on the ring geometry

As clearly indicated by the examples of Fig. 2, monosubstituted benzene derivatives whose molecular structures have been determined by X-ray diffraction analysis show a systematic trend in the distribution of the C–C bond lengths within the ring. The two c bonds, which are farthest from the molecular centre, are almost invariably shorter than the adjacent b bonds by some 0·01–0·02 Å, irrespective of the nature of the substituent. This shortening has been attributed to the effects of rigid (Radonovich, Bloom & Hoard, 1972; Collins, Scheidt & Hoard, 1972; Churchill, Kalra & Veidis, 1973) and non-rigid (Goldstein, Seff & Trueblood, 1968) thermal motion, which are greatest for the peripheral atoms. A contribution from the latter is probably present, since rigid-body thermal motion corrections to the experimental bond lengths usually reduce, but do not eliminate the discrepancy between the c and b bonds of the ring [Robertson, 1961; Hjortås, 1973; see also Fig. 2(e)]. The shortening of the c bonds in the tetraphenylphosphonium cation [Fig. 2(e)], where phosphorus substitution is not accompanied by appreciable variations of the endocyclic bond angles, and its absence in cyanobenzene [Fig. 2(f)] and fluorobenzene [Fig. 2(g)], whose molecular structures have
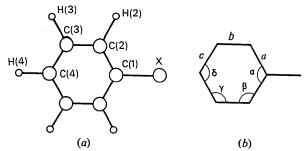
been determined by microwave spectroscopy, strongly favour the above explanation.

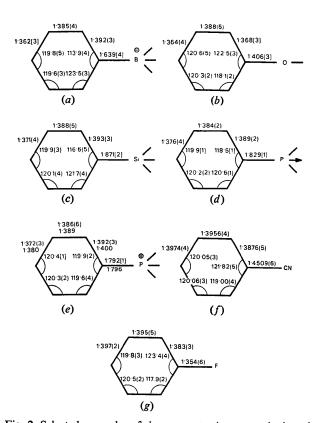Fig. 2 [(a) to (d)] shows how the (apparent) bond shortening due to the effect of thermal motion super-

Fig. 2. Selected examples of ring geometry in monosubstituted benzene derivatives, as obtained by either X-ray diffraction analysis [(a) to (e)] or microwave spectroscopy [(f) and (g)]. Bond lengths are given in Å, angles in degrees; they are followed by their estimated standard deviations, given as units in the last digit. Except for (f) and (g) the bond lengths and angles shown are mean values from several crystallographically independent benzene rings, calculated (as well as their standard deviations) according to Table 1. C_{2v} (2m) symmetry has been assumed throughout. (a) Tetraphenylborate anion in tris-(2-aminoethyl)aminochlorozinc(II) tetraphenylborate (Sime, Dodge, Zalkin & Templeton, 1971). The bond lengths and angles of the four benzene rings have been calculated from the atomic parameters quoted in the original paper. (b) Hexaphenoxycyclotriphosphazene (Marsh & Trotter, 1971). The bond lengths and angles of the six benzene rings have been calculated from the atomic parameters quoted in the original paper. (c) 2,2-Diphenyl-2-sila-1,3,4-trihydronaphthalene (Vidal, Lapasset & Falgueirettes, 1972). (d) Triphenylphosphine-(π-cyclopentadienyl)copper(I) (Cotton & Takats, 1970). (e) Tetraphenylphosphonium cation in tetraphenylphosphonium bis(tetracyanoquinodimethanide) (Goldstein, Seff & Trueblood, 1968). The bond lengths in the lower line are corrected for libration. (f) Cyanobenzene (Casado, Nygaard & Sørensen, 1971). Bond lengths and angles refer to the 'substitution structure'. (g) Fluorobenzene (Nygaard, Bojesen, Pedersen & Rastrup-Andersen, 1968). Bond lengths and angles refer to the 'substitution structure'. The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper.

Fig. 1. Lettering of (a) the C and H atoms and (b) the C–C bonds and C–C–C angles in monosubstituted benzene derivatives. C_{2v} (2m) symmetry has been assumed. A prime is used in the text to denote atoms, bonds or angles related to those shown here by the C(1)–C(4) diad.

imposes on the (real) skeletal deformations arising from substitution. It should be pointed out that the effect of thermal motion is not limited to the outermost bonds of the ring (bonds c), even though these are the most affected.

Since the great majority of the available structural data on substituted benzene derivatives has been obtained from the results of room-temperature X-ray diffraction experiments, it is clear that a systematic investigation of the effects of different substituents on the C–C bond lengths of the benzene nucleus is irremediably hampered for the time being, and must be deferred until very good, low-temperature X-ray diffraction data become available. Fortunately, bond angles appear to be less severely affected than bond distances by the effects of thermal motion, and an analysis of their variations has proved possible.
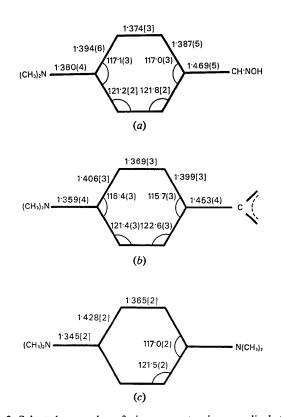

Fig. 3. Selected examples of ring geometry in *para*-disubstituted benzene derivatives showing extensive conjugation between the substituents and the ring. Bond lengths are given in Å, angles in degrees; they are followed by their estimated standard deviations, given as units in the last digit. Whenever necessary, mean values and their standard deviations have been calculated according to Table 1. $C_{2v}(2m)$ symmetry has been assumed in examples (*a*) and (*b*), $D_{2h}(mmm)$ symmetry in example (*c*). (*a*) *syn-p*-Dimethylaminobenzaldoxime (Bachechi & Zambonelli, 1972). (*b*) 2-(*p*-Dimethylanilino)-4-phenyl-6a-thiathiophthene (Hordvik & Sæthre, 1972). (*c*) *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine radical cation in its salt with the perchlorate anion, low-temperature phase (De Boer & Vos, 1972).

2.2. *The* C···C *contacts within the ring*

The lengths of all the C···C contacts within the ring for the seven monosubstituted benzene derivatives of Fig. 2 and for benzene itself are reported in Table 1. They show several systematic variations that will be discussed briefly.

The shortening of C(2)···C(3′) and C(3)···C(3′) with respect to unsubstituted benzene in all five compounds whose molecular geometries have been determined by X-ray diffraction analysis is probably an artifact, resulting from the effect of thermal motion on the outermost portion of the ring. This is not the case for cyanobenzene and fluorobenzene, whose molecular geometries have been determined by microwave spectroscopy, and indeed both compounds show the expected lengths for these contacts.

On the other hand C(1)···C(4) and C(2)···C(2′), though shortened to different extents by thermal motion in the first five compounds of Table 1, appear to be strongly dependent upon the nature of the substituent, as are the values of the endocyclic angles α and β quoted in Fig. 2. It appears that the deformations of the ring induced by substitution may be described as arising mainly from C(1) being pushed inwards or pulled outwards along the C(1)···C(4) line, with a simultaneous increase or decrease, respectively, of C(2)···C(2′).

2.3. *In- and out-of-plane bending of the* C(1)–X *bonds*

Table 2 shows important details of the individual ring geometries in a selection of monosubstituted benzene derivatives whose molecular structures are known with great precision. The details given include the C(2)···X distances, the C(2)–C(1)–X angles, and the distances of X from the least-squares planes of the rings. Inspection of Table 2 shows that the C(1)–X bonds of the given compounds often undergo large in-plane and out-of-plane bending, probably to minimize intramolecular non-bonded interactions. As a result the two C(2)···X distances for a substituted ring may differ by more than 0·10 Å from one another. This result is not confined to the examples of Table 2, but is widespread among substituted benzene derivatives, particularly when the substituent is lacking axial symmetry or when more than one ring is linked to the same atom. Quite interestingly, the asymmetries in the C(2)···X distances seem to have only little effect on the skeletal geometry of the ring, which, even in these extreme cases, shows almost no deviation from the C_{2v} (2m) symmetry assumed throughout this paper.

3. Interpretation of the ring deformations

3.1. *Hybridization effects*

The skeletal deformations of the benzene ring induced by substitution have been given a qualitative explanation, within the framework of the hybridization theory, by Carter, McPhail & Sim (1966) and by Nygaard, Bojesen, Pedersen & Rastrup-Andersen (1968).

Both groups of authors have associated the observed deformations of the ring with changes in the hybridization state of C(1), induced by the electron-withdrawing or -releasing properties of the substituent.

In his comprehensive survey of the effects of hybridization and electronegative substituents on a number of molecular properties, Bent (1961a,b) has stressed the importance of the rule – originally formulated by Walsh (1947) – that the p character of an atom tends to concentrate in the hybrid orbitals directed towards electronegative substituents. This follows from the fact that p electrons in an atom are held more loosely than s electrons, since they penetrate the inner core of electrons less than s electrons do, thus experiencing a smaller effective nuclear charge. When applied to benzene derivatives, Walsh's rule may be expressed by saying that a shift of electron density from the ring to an electron-withdrawing functional group can most effectively be accomplished through an increase in the p character of the carbon σ-bonding orbital pointing towards that group (Carter, McPhail & Sim, 1966; Nygaard, Bojesen, Pedersen & Rastrup-Andersen,

1968). This implies a decrease in the p character of the other two hybrid orbitals of carbon, and leads, therefore, to (i) a greater value for the endocyclic angle, α, and (ii) smaller values for the lengths of the adjacent C-C bonds, a. The opposite is true for an electron-releasing substituent. The deformations of the endocyclic angles, β, follow as a necessary requirement to preserve the planarity of the ring.

A criticism of this explanation may arise from the fact that it ignores any distinction between conjugated and unconjugated substituents. We think that such a distinction is needed, and that the above explanation only holds for σ-bonded, unconjugated functional groups.

Conjugation between the substituent, X, and the ring may occur whenever the former has filled or unfilled orbitals of suitable size and symmetry available for mixing with the π-orbitals of the ring. In both cases, i.e. with either π-electron donors or acceptors, a certain amount of π-bonding in the C(1)–X bond gives rise to a shortening of the C(1)–X distance, the actual extent of the shortening being dependent upon the extent of

Table 1. *Lengths of the carbon–carbon contacts within the ring for the seven monosubstituted benzene derivatives of Fig. 2 and for benzene itself*

All entries have been calculated from the atomic parameters quoted in the original papers. Entries for cyanobenzene and fluorobenzene refer to individual rings; all others are mean values from several crystallographically independent rings. C_{2v} (2m) symmetry has been assumed throughout.

Here and throughout this paper mean values and their standard errors have been calculated from individual values with the formulae:

$$x_m = \frac{\sum_{i=1}^{N} (x_i/\sigma_i^2)}{\sum_{i=1}^{N} (1/\sigma_i^2)} \; ; \; \sigma_m = \sqrt{\frac{\sum_{i=1}^{N} \{(x_i - x_m)^2/\sigma_i^2\}}{(N-1)\sum_{i=1}^{N} (1/\sigma_i^2)}} \; ; \; \sigma_m' = \frac{1}{\sqrt{\sum_{i=1}^{N} (1/\sigma_i^2)}}$$

where σ_i is the estimated standard deviation of the quantity x_i. Values of σ_m are given in parentheses; values of σ_m' in square brackets. Only the larger of the two is usually shown. It should be pointed out that whilst σ_m is a measure of the 'external' consistency of the data averaged, σ_m' is a measure of their 'internal' consistency.

All values are in Å. Standard deviations are given in parentheses (or square brackets, see above) as units in the last digit.

Compound	Ref.	Technique[a]	C(1)···C(4)	C(2)···C(2')[b]	C(2)···C(3')[b]	C(3)···C(3')[b]
Tetraphenylborate anion in tris-(2-aminoethyl)aminochlorozinc(II) tetraphenylborate	c	X	2·825 (7)	2·333 [4]	2·723 (5)	2·355 [5]
Hexaphenoxycyclotriphosphazene	d	X	2·720 (6)	2·398 (5)	2·757 (4)	2·367 [4]
2,2-Diphenyl-2-sila-1,3,4-trihydronaphthalene	e	X	2·807 (4)	2·370 [3]	2·744 (8)	2·371 (4)
Triphenylphosphine(π-cyclopentadienyl)copper(I)	f	X	2·782 (2)	2·389 (4)	2·757 (3)	2·383 (4)
Tetraphenylphosphonium cation in tetraphenylphosphonium bis-(tetracyanoquinodimethanide)	g	X	2·766 [2]	2·409 (2)	2·767 (7)	2·383 (8)
Cyanobenzene	h,i	M	2·768 (1)	2·425 (1)	2·796 (1)	2·421 (1)
Fluorobenzene	j,i	M	2·752 (3)	2·434 (5)	2·798 (4)	2·416 (5)
Unsubstituted benzene	k		2·794	2·420	2·794	2·420

(a) X and M denote X-ray diffraction analysis and microwave spectroscopy, respectively. (b) Primed atoms are related to unprimed atoms by the C(1)···C(4) diad. (c) Sime, Dodge, Zalkin & Templeton (1971). (d) Marsh & Trotter (1971). (e) Vidal, Lapasset & Falgueirettes (1972). (f) Cotton & Takats (1970). (g) Goldstein, Seff & Trueblood (1968). (h) Casado, Nygaard & Sørensen (1971). (i) The values given here refer to the 'substitution structure'. (j) Nygaard, Bojesen, Pedersen & Rastrup-Andersen (1968). (k) Considered to be a regular hexagon with a side of 1·397 Å.

conjugation. Since the covalent radius of carbon is known to decrease as the s character of the bonding orbital increases, it is reasonable to associate the shortening of the C(1)–X distance caused by conjuga-tion with an increase in the s character of the hybrid orbital of C(1) used in the σ bond with X. This is necessarily accompanied by an increase in the p character of the other two hybrid orbitals of C(1). As

Table 2. *Details of the individual ring geometries in several monosubstituted benzene derivatives showing in- and out-of-plane bending of the exocyclic C(1)–X bonds*

Distances are in Å, angles in degrees. Estimated standard deviations are given in parentheses as units in the last digit. No assumptions have been made about the symmetry of the ring.

Compound	Ref.	C(2)–C(1)–X C(2')–C(1)–X	d_x[b,c]	C(2)···X C(2')···X[c]	a a'	a–a'	β β'	β–β'
B,B-Diphenylboroxazolidine	d	120·0 (2) 124·1 (2)	0·150 (2)	2·605 (4) 2·656 (4)	1·395 (3) 1·393 (3)	0·002	122·9 (2) 121·8 (2)	1·1
α-2-Ethyl-5-methyl-3,3-diphenyltetrahydrofuran	e	118·9 (2) 123·3 (3)	0·011 (3)	2·516 (3) 2·560 (3)	1·395 (4) 1·382 (4)	0·013	121·1 (3) 120·7 (3)	0·4
		119·3 (2) 123·4 (2)	0·039 (3)	2·536 (5) 2·578 (4)	1·397 (4) 1·387 (4)	0·010	121·5 (3) 120·9 (3)	0·6
trans-3-Phenyl-3-methoxy-carbonyl-4-p-methoxy-phenyl-1-pyrazoline	f	117·2 (2) 123·5 (2)	0·016 (2)	2·499 (2) 2·572 (2)	1·386 (3) 1·379 (3)	0·007	119·9 (2) 119·9 (2)	0·0
α-Cyanocinnamonitrile	g,h	116·1 (2) 125·3 (2)	0·005 (2)	2·424 (3) 2·527 (3)	1·407 (3) 1·396 (3)	0·011	120·6 (2) 120·0 (2)	0·6
3-Methyl-4-benzylidene-isoxazolin-5-one	i	114·7 (2) 126·2 (2)	0·000 (2)	2·415 (4) 2·543 (4)	1·404 (3) 1·387 (3)	0·017	120·4 (2) 120·2 (2)	0·2
Hippuric acid	j	117·3 (3) 123·2 (3)	0·054 (3)	2·466 (4) 2·544 (4)	1·392 (4) 1·397 (4)	−0·005	119·9 (3) 119·7 (3)	0·2
Phenylazotribenzoylmethane	k,h	116·1 (2) 124·5 (2)	0·049 (2)	2·444 (4) 2·548 (4)	1·392 (4) 1·391 (4)	0·001	120·5 (3) 119·8 (3)	0·7
		116·8 (2) 122·9 (2)	0·043 (2)	2·454 (3) 2·531 (4)	1·390 (4) 1·391 (4)	−0·001	119·9 (3) 119·2 (3)	0·7
		117·7 (3) 123·7 (3)	0·013 (3)	2·470 (5) 2·536 (4)	1·393 (4) 1·382 (4)	0·011	120·6 (3) 120·8 (3)	−0·2
		115·9 (3) 123·3 (3)	0·011 (3)	2·389 (5) 2·487 (5)	1·376 (4) 1·383 (5)	−0·007	120·0 (4) 118·3 (4)	1·7
p-Phenylazoazobenzene	l,h	113·6 (3) 125·7 (3)	0·026 (3)	2·380 (4) 2·537 (4)	1·381 (4) 1·388 (5)	−0·007	119·5 (3) 119·4 (3)	0·1
Acetanilide	m	116·6 (2) 123·8 (2)	0·049 (2)	2·392 (3) 2·474 (3)	1·397 (3) 1·391 (3)	0·006	120·2 (2) 119·1 (2)	1·1
5-Anilino-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazolo[3,4-d]thiazole	n	116·0 (2) 124·3 (2)	0·040 (2)	2·372 (2) 2·472 (2)	1·385 (3) 1·385 (3)	0·000	120·1 (2) 119·3 (2)	0·8
Tetraphenylphosphonium cation in tetraphenylphosphonium bis(tetracyanoquinodimethanide)	o	118·1 (1) 122·2 (1)	0·066 (1)	2·742 (2) 2·790 (2)	1·396 (3) 1·387 (3)	0·009	120·4 (2) 118·7 (2)	1·7
		117·9 (1) 121·9 (1)	0·122 (1)	2·740 (2) 2·783 (2)	1·398 (3) 1·385 (3)	0·013	119·8 (2) 119·3 (2)	0·5
Triphenylphosphine(π-cyclopentadienyl)copper(I)	p	117·7 (2) 123·8 (2)	0·037 (1)	2·768 (3) 2·846 (2)	1·396 (3) 1·390 (3)	0·006	120·8 (2) 120·3 (2)	0·5
		118·1 (2) 123·3 (2)	0·035 (1)	2·771 (2) 2·836 (2)	1·392 (3) 1·383 (3)	0·009	120·3 (3) 121·0 (2)	−0·7
		117·3 (2) 124·2 (2)	0·089 (1)	2·753 (3) 2·851 (3)	1·384 (3) 1·389 (4)	−0·005	120·9 (2) 120·3 (2)	0·6
Orthothiocarbonic acid tetraphenylester	q,h	112·8 (2) 127·7 (3)	0·086 (1)	2·633 (3) 2·827 (3)	1·380 (5) 1·373 (5)	0·007	120·6 (3) 119·4 (4)	1·2
		119·7 (2) 120·4 (2)	0·109 (1)	2·739 (3) 2·748 (4)	1·374 (5) 1·373 (5)	0·001	118·8 (4) 120·7 (4)	−1·9
		118·2 (2) 122·7 (2)	0·095 (1)	2·728 (4) 2·769 (3)	1·393 (4) 1·369 (4)	0·024	120·0 (4) 120·5 (3)	−0·5
		119·9 (3) 120·5 (3)	0·210 (1)	2·738 (4) 2·749 (4)	1·381 (5) 1·384 (4)	−0·003	120·5 (3) 120·2 (2)	0·3

(b) Distance of X from the least-squares plane of the six carbon atoms of the ring. (c) All entries in this column have been calculated from the atomic parameters quoted in the original papers. (d) Rettig & Trotter (1973). Only one of the two phenyl rings in the asymmetric unit has been included in this table. (e) Singh & Ahmed (1969). (f) Rousseaux, Meunier-Piret, Putzeys, Germain & Van Meerssche (1972). (g) Auvray & Genet (1971). (h) The molecular geometry has been calculated from the atomic parameters quoted in the original paper. (i) Meunier-Piret, Piret, Germain, Putzeys & Van Meerssche (1972). (j) Harrison, Rettig & Trotter (1972). (k) Pendergrass, Curtin & Paul (1972). (l) Gilardi & Karle (1972). (m) Brown (1966). (n) Smith (1969). (o) Goldstein, Seff & Trueblood (1968). The molecule has C_2 (2) crystallographic symmetry. (p) Cotton & Takats (1970). (q) Kato (1972b).

a result the endocyclic angle, α, is closed up, whilst the lengths of the a bonds are increased, *irrespective of whether the substituent is a π donor or a π acceptor.*

Three selected examples of ring geometry in *para*-disubstituted benzene derivatives showing extensive conjugation between the substituents and the ring are reported in Fig. 3.* The compounds chosen [namely, *syn-p*-dimethylaminobenzaldoxime, 2-(*p*-dimethylanilino)-4-phenyl-6a-thiathiophthene, and the N,N,N',N'-

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* A fuller account of the ring deformations occurring in *para*-disubstituted benzene derivatives is given in § 5.1.

Table 3. *Exocyclic carbon–carbon bond lengths, endocyclic bond angles, and dihedral angles in several aryl substituted benzenes*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Only compounds with $\sigma(\alpha) \leq 0.5°$ have been included in this table.

Compound	Ref.	C(1)–X	α	β	τ^a
Biphenyl	b,c	1·497 (3)	117·4 (2)	121·2 (2)	0·0
				121·2 (2)	
p-Terphenyl	d,c	1·496 (4)	117·9 (3)	120·9 (3)	0·4
				121·3 (3)	
p-Nitrobiphenyl	e	1·479 (4)	118·1 (3)	120·9 (3)	33·0
				120·7 (3)	
2,6-Dimethyl-4-phenylphos-phorin	f	1·493 (7)	118·0 (5)	120·1 (5)	38·8
				120·7 (5)	
1,1-Dimethyl-2,4,6-tri-phenylphosphorin	g	1·492 (7)	117·7 (5)	121·0 (6)	63·8
				120·7 (7)	
		1·483 (7)	118·0 (5)	119·3 (6)	50·0
				121·5 (5)	
		1·489 (7)	116·5 (5)	121·3 (5)	25·3
				121·8 (5)	
1,1-Bis(dimethylamino)-2,4,6-triphenylphosphorin	h	1·498 (5)	117·5 (4)	121·2 (4)	45·9
				120·6 (4)	
		1·486 (5)	118·2 (4)	119·5 (5)	47·4
				122·2 (5)	
		1·480 (5)	117·0 (4)	120·9 (5)	32·5
				122·3 (4)	
2-Phenyl-4-acetylphenoxy-2,6-dimethylphenylimino-methanesulphenic acid	i	1·491 (3)	117·6 (2)	120·9 (3)	43·2
				121·4 (2)	
Mean values	j	1·491 (2)	117·6 (1)	121·1 (1)	

(a) Dihedral angle between the least-squares planes of the two rings. (b) Robertson (1961). Bond lengths and angles are corrected for libration. (c) The molecule has S_2 ($\bar{1}$) crystallographic symmetry. (d) Rietveld, Maslen & Clews (1970). The C(1)–X length is corrected for libration. (e) Casalone, Gavezzotti & Simonetta (1973). (f) Bart & Daly (1970). (g) Daly (1970). (h) Thewalt & Bugg (1972a). (i) Kato (1972a). The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (j) See Table 1 for calculation of mean values.

Table 4. *Bending of the ortho carbon–fluorine bonds in pentafluorophenyl derivatives*

Distances are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Only compounds with $\sigma(C–C–F) \leq 0.5°$ have been included in this table.

Compound	Ref.	C(2)–F(2)	C(1)–C(2)–F(2)	C(3)–C(2)–F(2)	$x_{F(2)}{}^a$
Pentafluorobenzoic acid	b	1·332 (2)	121·3 (1)	117·1 (1)	0·013 (1)
		1·335 (2)	121·3 (1)	116·9 (1)	0·024 (1)
Tetrakis(pentafluorophenyl)-cyclotetraphosphane	c	1·342 (4)	118·5 (3)	119·2 (4)	0·004 (2)^d
		1·341 (4)	119·9 (3)	116·8 (3)	0·080 (2)^d
		1·330 (4)	119·8 (3)	117·8 (3)	0·004 (2)^d
		1·342 (4)	119·9 (3)	117·0 (3)	−0·090 (2)^d
Tetrakis(pentafluorophenyl)-germanium	e	1·344 (5)	120·4 (4)	117·4 (4)	0·005 (3)^d
		1·360 (6)	119·0 (4)	117·9 (4)	−0·015 (3)^d
trans-Bis(methyldiphenyl-phosphine)bis(σ-pentafluoro-phenyl)nickel(II)	f	1·360 (4)	119·6 (3)	117·0 (3)	0·018 (2)
		1·353 (4)	119·5 (3)	116·2 (3)	0·049 (2)
trans-Bromobis(methyldiphen-ylphosphine) (σ-pentafluoro-phenyl)nickel(II)	g	1·368 (5)	119·0 (4)	115·8 (4)	0·009 (3)^d
		1·363 (5)	119·3 (4)	117·6 (4)	−0·002 (3)^d

(a) Distance of F(2) from the least-squares plane of the six carbon atoms of the ring. (b) Benghiat & Leiserowitz (1972). (c) Sanz & Daly (1971). The molecule has C_2 (2) crystallographic symmetry. (d) This value has been calculated from the atomic parameters quoted in the original paper. (e) Karipides & Thomas (1973). The molecule has S_4 ($\bar{4}$) crystallographic symmetry. (f) Churchill & Veidis (1972). The molecule has S_2 ($\bar{1}$) crystallographic symmetry. (g) Churchill, Kalra & Veidis (1973).

tetramethyl-*p*-phenylenediamine radical cation] exemplify the effect of both π-donor and π-acceptor functional groups on the ring geometry.

3.2. *Valence-shell electron-pair repulsions*

An alternative approach to the general problem of understanding and predicting molecular geometry has been developed by Gillespie & Nyholm (1957) and Gillespie (1963a, 1967, 1970, 1972), and is known as the Valence-Shell Electron-Pair Repulsion (VSEPR) theory. It emphasizes the importance of the repulsive interactions between the electron pairs in the valence shell of a central atom in determining its stereochemistry. When applied to substituted benzene derivatives the VSEPR theory provides a pictorial, but effective rationalization of the bond-angle deformations observed in these compounds.

If the bond between the substituent, X, and the ring is mainly a σ bond the VSEPR theory predicts a correlation between the endocyclic angle α and the electronegativity of the substituent. A σ-electron-withdrawing substituent polarizes the localized C(1)–X σ-bonding molecular orbital, so that the bonding electron pair takes up a decreasing amount of space in the valence shell of carbon and interacts less strongly with the two neighbouring C(1)–C(2) σ-bonding pairs [Fig. 4(a)]. This causes an increase in the actual value of the internal angle α with respect to the value, α_0, expected for a substituent having the same electronegativity as
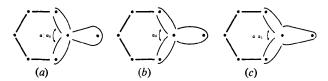

Fig. 4. The effect of valence-shell electron-pair repulsions on the endocyclic bond angle, α, of a monosubstituted benzene derivative. The bond between the substituent, X, and the ring is assumed to be a σ bond. (a) A σ-electron-withdrawing substituent. (b) A substituent having the same electronegativity as the ring. (c) A σ-electron-releasing substituent.
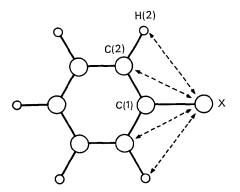

Fig. 5. Diagram of the most important intramolecular non-bonded interactions in monosubstituted benzene derivatives. C_{2v} (2m) symmetry has been assumed.

the ring [Fig. 4(b)]. (It should be noted that α_0 may differ from 120°, since the spatial distribution of the σ-bonding electron pair is not necessarily the same for a C–X and a C–H bond.) The reversed pattern of effects is expected with a σ-electron-releasing substituent [Fig. 4(c)].

If the substituent is conjugated with the ring the distribution of the bonding electrons in the region of the C(1)–X bond undergoes the following changes: (i) a building-up of π-electron density alongside the σ bond, both above and below the molecular plane, and (ii) an increase of electron density within the σ-bonding molecular orbital, due to the shortening of the internuclear separation. Both effects act so as to increase the repulsive interactions between the electron clouds of the C(1)–X and C(1)–C(2) bonds, so that the endocyclic angle α is squeezed below the value, α_0, expected for the same substituent in the absence of conjugation. (It should again be noted that α_0 will, in general, be different from 120°.) The difference between α and α_0 is expected to increase with increasing conjugation.

3.3. *Intramolecular non-bonded interactions*

Bartell (1960, 1962, 1968) has observed that the packing of non-bonded atoms often seems to exert a governing influence on molecular geometry. He has shown that even a simple hard-sphere model is able to reproduce bond angles in a number of ethylene and ethylene-like derivatives.

In the case of monosubstituted benzenes the most important intramolecular interactions that may affect the geometry of the ring are those between the *ortho* hydrogens and carbons [H(2) and C(2), respectively] and the first atom of the substituent group, X (Fig. 5). Interactions may also occur between C(2) [or H(2)] and some other atom of the substituent, provided this is a polyatomic functional group. It is unlikely, however, that these are of great importance in determining the skeletal geometry of the ring, since they are usually minimized through either a bending of the C(1)–X bond, as in the examples of Table 2, or a rotation of the ring along the C(1)$\cdots$C(4) axis. In the aryl substituted benzenes of Table 3 the values of the endocyclic angles, α and β, are uncorrelated with the dihedral angle, τ, between the planes of the rings: this rules out the possibility, supported by Miller & Murrell (1967), that H$\cdots$H repulsions between *ortho* hydrogens are responsible for the ring deformations observed in crystalline biphenyl (Robertson, 1961).

3.3.1. H(2)$\cdots$X *interactions*. The H(2)$\cdots$X interactions are expected to be released through small in-plane bendings of the C(2)–H(2) bonds, and eventually through small out-of-plane bendings (Coulson & Haigh, 1963), without any major alteration of the internal geometry of the ring. The structural information available for substituted benzene derivatives comes mainly from X-ray diffraction studies, and is unsuitable

for a detailed investigation of this point, since the positional parameters of the hydrogen atoms cannot be determined with great accuracy. Accurate information is available, however, for several monosubstituted perfluorobenzene derivatives, which do show the expected small bendings (2–3°) of the C(2)–F(2) bonds (Table 4).

Even smaller bendings are expected for C–H bonds, owing to the peculiar 'softness' of hydrogen;* and indeed no appreciable bending of the C(2)–H(2) bonds is observed in cyanobenzene (Casado, Nygaard & Sørensen, 1971) and in the toluene-p-sulphonate anion (Lundgren & Williams, 1973), whose molecular structures (including hydrogen atom positions) have been determined with great accuracy by microwave spectroscopy and neutron diffraction analysis, respectively.

It should be pointed out that the H(2)···X interactions may be attractive in character. A relevant example is given by fluorobenzene, where the H(2)–C(2)–C(1) and H(2)–C(2)–C(3) angles, as obtained by microwave spectroscopy (Nygaard, Bojesen, Pedersen & Rastrup-Andersen, 1968), are 120·0 (4)° and 122·1 (3)°, respectively.

3.3.2. C(2)···X interactions.

The C(2)···X interactions affect directly the carbon skeleton of the ring, and it is reasonable to expect that they may be of importance in determining its geometry. [Interactions of this type have been called 'geminal' (Bartell, 1968) since they occur between atoms linked to the same atom.] Though intrinsically different from the electron pair repulsions of the VSEPR model (Gillespie, 1963b; Bartell, 1968) the geminal non-bonded interactions often have similar effects, and it may be exceedingly difficult to assess their relative importance in determining molecular geometry.†

This is indeed the case of monosubstituted benzene derivatives. If the bond between the substituent and the ring is mainly a σ bond, and if the first atom of the substituent, X, is moved to the right within a row of the periodic table, we expect the C(2)···X interactions to vary regularly, since the higher effective nuclear charge and the increased number of lone pairs are contracting steadily the non-bonded radius of X. (The simultaneous decrease of the covalent radius of X

must, however, be taken into account.) Thus the skeletal deformations of the ring which may result from C(2)···X interactions are expected to correlate with the atomic number of X, and hence with its electronegativity. Such correlations are expected to hold only within single rows of the periodic table, because of the large variations in the bonded and non-bonded radii of the elements (and, therefore, in geminal non-bonded interactions) which occur when jumping from one row to another.

If the substituent is conjugated with the ring the shortening of the C(1)–X distance gives rise to a shortening of the C(2)···X distances, and this increases the geminal non-bonded repulsions. This is in keeping with the observed lengthening of the a bonds and squeezing of the α angle.

3.4. Bonded versus non-bonded interactions

Although geminal non-bonded interactions cannot be ignored, we think that the ring deformations induced by substitution are more easily described in terms of either hybridization effects or valence-shell electron-pair repulsions. There are at least two reasons for this, which will be discussed below.

As exemplified in § 2.3 the C(1)–X bonds often show marked in-plane bending, generally due to non-geminal non-bonded interactions between the ring and the (polyatomic) substituent, which give rise to large differences in the two C(2)···X distances, but appear to have only minor effects on the ring geometry (see Table 2). Should the C(2)···X interactions be the main factor responsible for the ring deformations, it would be hard to explain why their large variations with the bending of the C(1)–X bond are not accompanied by correspondingly large variations in the ring geometry. It may be added that the fact that large differences in the values of the two C(2)–C(1)–X angles for a given monosubstituted benzene ring are associated with only exceedingly small differences in the lengths of the two a bonds (see Table 2) is hard to reconcile even with a description of the ring deformations in terms of changes in the hybridization state of C(1), unless the possibility is considered that the C(1)–X internuclear line is not collinear with the axis of the hybrid orbital of C(1) used in the C(1)–X bond. The VSEPR model appears to be superior in this case, since the valence-shell electron-pair repulsions, which act in the immediate neighbourhood of C(1), are presumably less affected than geminal non-bonded interactions by a bending of the C(1)–X bond.

Another point is the increase of the mean endocyclic angle, α, from 117·6 (1)° in aryl substituted benzenes (Table 3) to 119·8 (2)° in para-substituted benzoic acids (Table 5). This variation (which is not an effect of para-substitution, see § 5.1) is not accompanied by a change in the mean lengths of the exocyclic C(1)–X bonds [1·491 (2) and 1·490 (4) Å, respectively], and is hard to explain in terms of changes in geminal non-bonded interactions, unless these are considered to be strongly

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* In a recent paper on the molecular structure of adamantylideneadamantane (Swen-Walstra & Visser, 1971) it has been observed that even a H···H contact distance as short as 1·90 Å [where a separation of 2·4 Å should be expected on the basis of Pauling's (1960a) van der Waals radius for hydrogen] is not associated with any appreciable distortion of the C–C–H angles.

† It should be pointed out that geminal non-bonded interactions are probably not so strongly repulsive as could appear from a straightforward comparison of the non-bonded contact distance with the sum of van der Waals radii. Pauling (1960b) has suggested that 'the non-bonded radius of an atom in directions close to a bond direction (within 35°) is about 0·5 Å less than the van der Waals radius;' so that 'a unicovalent atom can be considered as a sphere that is whittled down on the side of the bond.'

dependent upon the chemical environment of the interacting atoms. [Such a dependence is indeed quite reasonable, but it rules out the simple hard-sphere model of Bartell (1960, 1962)]. On the other hand the difference between the mean values of α for the two classes of substituted benzene derivatives considered above is easily accounted for by both the hybridization theory and the VSEPR model, as a consequence of the increased electronegativity of carbon when bonded to two strongly electronegative oxygen atoms.

Table 5. *Exocyclic carbon–carbon bond lengths and endocyclic bond angles in para-substituted benzoic acids*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Only compounds with $\sigma(\alpha) \leq 0.6°$ have been included in this table. p-Aminobenzoic acid (Lai & Marsh, 1967) and p-hydroxybenzoic acid monohydrate (Fukuyama, Ohkura, Kashino & Haisa, 1973) have not been included since they show deformations in the benzene ring due to the effect of through-conjugation (see § 5.1).

Compound	Ref.	C(1)–X	α	β
p-Nitrobenzoic acid	a	1·487 (6)	119·8 (4)	120·9 (4)
				119·7 (4)
Terephthalic acid	b,c	1·483 (3)	120·4 (3)	119·4 (3)
				120·2 (3)
Ammonium hydrogen terephthalate	d,c	1·493 (3)	119·6 (2)	120·2 (2)
				120·2 (2)
Potassium hydrogen di-p-hydroxybenzoate monohydrate	e	1·504 (6)	119·6 (4)	120·7 (4)
				120·5 (4)
p-Methoxybenzoic acid	f	1·502 (9)	119·7 (6)	121·2 (6)
				119·9 (6)
Mean values	g	1·490 (4)	119·8 (2)	120·2 (1)

(a) Tavale & Pant (1971). (b) Bailey & Brown (1967). (c) The molecule has S_2 ($\bar{1}$) crystallographic symmetry. (d) Cobbledick & Small (1972). The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (e) Manojlović (1968). (f) Bryan (1967). (g) See Table 1 for calculation of mean values.

3.5. *Coulombic interactions between formally charged atoms*

When a substituent is attached to a benzene ring, it often induces changes in the electron-density distribution which are best described in terms of the building-up of effective charge densities on the carbon atoms of the ring as well as on the substituent.

A typical case is that of a substituent acting as a π donor. The resulting π-charge distribution, as obtained by *ab initio* molecular orbital calculations (Hehre, Radom & Pople, 1972), is characterized by the presence of small amounts of negative charge on the *ortho* and *para* carbons, and of positive charge on the *meta* carbons as well as on the substituent; a charge of either sign may be present on the *ipso* carbon. The calculated π charges are quite small, only seldom exceeding one tenth of an electron.

Should the deformations of the ring be determined by the combined influence of (i) the repulsive interactions between the homonymous charges on the *ortho*

carbons and (ii) the attractive interactions between the heteronymous charges on the substituent and on the *ortho* carbons, the value of the internal angle α should be greater than the value, α_0, observed with the same substituent in the absence of conjugation, which is against experimental evidence.

It may be concluded, therefore, that coulombic interactions between formally charged atoms are not as important as the other factors discussed in the preceding sections of this paper in determining the skeletal geometry of the ring.

4. Bond angles – electronegativity correlations

From the discussion in § 3 it follows that a correlation should exist between the value of the endocyclic angle, α, opposite to the substituent in a monosubstituted benzene derivative, and the electronegativity of the substituent itself, provided (i) conjugative effects are absent and (ii) the element directly linked to carbon is constrained to vary within a row of the periodic table. We have found that a very good correlation does in fact exist for the phenyl derivatives of second-row elements, for which a wealth of accurate structural data is available (Coulson, Domenicano & Vaciago, 1973). These results will be presented in detail in the following paper of this series.

5. Ring deformations in di- and poly-substituted benzene derivatives

5.1. *Para-disubstituted benzene derivatives*

We have seen that in monosubstituted benzenes the skeletal deformations induced by substitution do not practically extend beyond the half of the ring nearest to the substituent. The introduction of a second substituent *para* to the first is expected, therefore, to have no appreciable effect on the geometry of the opposite part of the ring, unless a change occurs in the nature of the bond between the first substituent and the ring. The experimental evidence available strongly suggests the rule that *the angular deformations induced by a substituent are usually unaffected by a second substituent para to it*. This is exemplified by the data reported in Tables 6 and 7, which give the values of the endocyclic angles, α and β, for a number of *para*-substituted nitro- and methyl benzenes, respectively, both with a wide variety of functional groups as *para*-substituents. The two tables have been prepared from an extensive search of the literature, with no deliberate omission of any relevant molecule for which reliable data are available.

Exceptions to this rule are expected to occur whenever the nature of the bond between the first substituent and the ring is modified by the introduction of the second substituent. This is indeed the case of through-conjugated benzene derivatives, having a strong π donor *para* to a π acceptor. The effect of through-conjugation on the internal bond angles of the ring may be

seen from the examples of Fig. 6. The effect on bond lengths is well known (the expected lengthening of the *a* and *c* bonds is accompanied by a 'quinoidal' shortening of the *b* bonds) and has not been shown in these examples.

5.2. Ortho- and meta-disubstituted benzene derivatives

When the second substituent is not *para* to the first a more complex pattern of ring deformations is expected, since the deformations caused by a substituent partly overlap with those from the other. We have not investigated *ortho* and *meta* disubstitution in detail, but

it appears from several examples in the literature that the angular deformations observed are in keeping with a superimposition of separate effects from the two substituents (Palenik, Donohue & Trueblood, 1968; Arcovito, Bonamico, Domenicano & Vaciago, 1969; Irngartinger, Leiserowitz & Schmidt, 1970; Bois, 1973; Hughes, 1973).

5.3. Highly substituted benzene derivatives

When several (and eventually all) of the five hydrogen atoms in a monosubstituted benzene derivative C_6H_5–X are replaced by other substituents, large
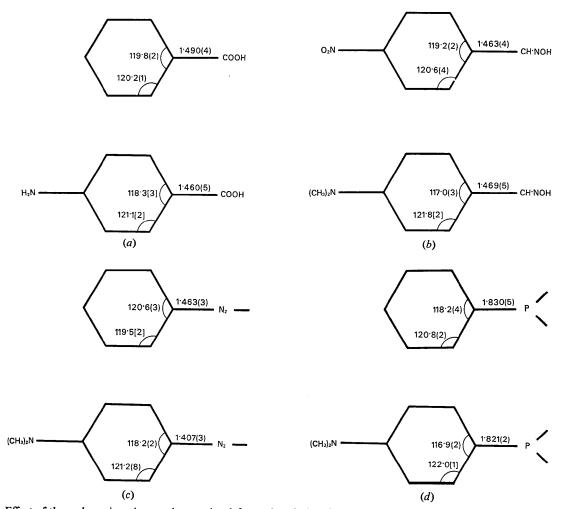

Fig. 6. Effect of through-conjugation on the angular deformations induced by a substituent in the carbon skeleton of the benzene ring. Each example shows how the introduction of a strong π donor *para* to a potential π acceptor modifies the endocyclic bond angles, α and β, nearest to the latter. Bond lengths are given in Å, angles in degrees; they are followed by their estimated standard deviations, given as units in the last digit. Whenever necessary, mean values and their standard deviations have been calculated according to Table 1. C_{2v} $(2m)$ symmetry has been assumed throughout. (*a*) Benzoic acid (estimated molecular geometry, from the *para*-substituted benzoic acids of Table 5) and *p*-aminobenzoic acid (Lai & Marsh, 1967; the bond lengths and angles given here are mean values from the two crystallographically independent molecules in the asymmetric unit). (*b*) *syn-p*-Nitrobenzaldoxime (Bachechi & Zambonelli, 1973) and *syn-p*-dimethylaminobenzaldoxime (Bachechi & Zambonelli, 1972). (*c*) *p*-Phenylazoazobenzene (Gilardi & Karle, 1972) and sodium *p*-dimethylaminoazobenzene-*p'*-sulphonate monohydrate monoethanolate (Hanson, 1973; the standard deviations of the individual bond lengths and angles have been calculated from the standard deviations of the atomic parameters quoted in the paper). (*d*) *p*-Dimethylanilinodiphenylphosphine (Dreissig & Plieth, 1972): comparison of the mean geometry of the two unsubstituted phenyls with that of the *para*-substituted one.

changes may result in the electron-withdrawing or -releasing properties of the ring, and, therefore, in the polar character of the C(1)–X bond. According to both

Table 6. *Carbon to nitrogen bond lengths and endocyclic bond angles in para-substituted nitrobenzenes*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of α and β differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0.5°$ have been included in this table.

Compound	Ref.	C(1)–N	α	β
p-Nitrobenzoic acid	a	1·479 (6)	122·6 (4)	117·9 (4)
				119·1 (4)
p-Nitrophenol (polymorph α)	b	1·442 (6)	122·3 (4)	118·9 (4)
				118·6 (4)
p-Nitrophenol (polymorph β)	c	1·446 (3)	121·9 (2)	118·8 (2)
				118·8 (2)
p-Nitroaniline	d	1·454 (7)	121·2 (4)	119·2 (4)
				119·8 (4)
p-Nitrotoluene	e	1·477 (7)	122·7 (5)	116·7 (4)*
				119·1 (5)
p-Nitroacetophenone	f	1·466 (4)	121·7 (3)	118·8 (3)
				118·5 (3)
syn-p-Nitrobenz- aldoxime	g	1·472 (3)	122·7 (2)	118·3 (2)
				118·5 (2)
p-Nitrophenyl acetate	h	1·453 (6)	120·7 (4)*	120·1 (5)
				119·1 (4)
		1·465 (6)	122·3 (4)	119·5 (4)
				117·8 (4)
p-Nitrobiphenyl	i	1·465 (4)	122·2 (3)	118·5 (3)
				118·8 (3)
1,1-Bis-(p-nitrophenyl)- ethylene	j	1·466 (6)	122·1 (4)	118·1 (4)
				119·1 (4)
		1·465 (6)	122·2 (4)	118·4 (4)
				118·5 (4)
cis-2-Isopropyl-3-(p- nitrophenyl)- oxaziridine	k	1·460 (4)	122·3 (3)	118·8 (3)
				118·3 (3)
Bis-(p-nitrophenyl)- carbodi-imide	l	1·458 (7)	122·6 (5)	118·9 (5)
				118·5 (5)
		1·453 (8)	121·5 (5)	119·6 (6)
				119·2 (6)
1-p-Nitrophenyl-3- methylperhydro-2,9- pyridoxazine	m	1·468 (4)	122·1 (3)	118·7 (3)
				118·4 (3)
Bis-(p-nitrophenyl) phosphate anion in p-carbethoxyani- linium bis-(p-nitro- phenyl)phosphate	n	1·458 (5)	122·3 (4)	118·3 (4)
				119·6 (4)
		1·481 (5)	121·6 (4)	119·6 (4)
				118·9 (3)
Bis-(p-nitrophenyl) phosphate anion in procaine bis-(p-ni- trophenyl)phosphate	o	1·475 (5)	122·1 (4)	119·3 (4)
				119·3 (5)
		1·471 (9)	122·2 (5)	118·3 (4)
				119·0 (4)
Mean values	p	1·463 (2)	122·1 (1)	118·7 (1)

(a) Tavale & Pant (1971). (b) Coppens & Schmidt (1965a). (c) Coppens & Schmidt (1965b). (d) Trueblood, Goldish & Donohue (1961). (e) Barve & Pant (1971). (f) Kim, Boyko & Carpenter (1973). (g) Bachechi & Zambonelli (1973). (h) Guttormson & Robertson (1972). The asymmetric unit contains two crystallographically independent molecules. The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (i) Casalone, Gavezzotti & Simonetta (1973). (j) Casalone & Simonetta (1971). (k) Cannon, Daly, Silverton, Boyd & Jerina (1972). (l) Vincent & Wheatley (1972b). (m) Huber (1972). (n) Pletcher, Sax & Yoo (1972). (o) Sax, Pletcher & Gustaffson (1970). (p) See Table 1 for calculation of mean values.

Table 7. *Exocyclic carbon–carbon bond lengths and endocyclic bond angles in para-substituted methylbenzenes*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of α and β differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0.5°$ have been included in this table.

Compound	Ref.	C(1)–X	α	β
p,p'-Bitolyl	a,b	1·517 (9)	117·9 (5)	121·3 (5)
				121·0 (5)
		1·521 (9)	117·1 (5)	121·3 (4)
				122·5 (4)
		1·537 (9)	119·2 (5)	120·0 (6)
				121·2 (6)
		1·503 (9)	117·0 (5)	121·8 (5)
				121·3 (5)
1,1-Di-p-tolylethylene	c	1·509 (5)	118·0 (3)	120·7 (3)
				121·3 (3)
		1·503 (5)	117·9 (3)	121·0 (3)
				121·3 (3)
p-Methylbenzylidene- p-nitroaniline	d,b	1·512 (9)	118·3 (5)	121·1 (5)
				121·1 (6)
ω-(p-Toluoyl)- acetophenone enol	e	1·507 (4)	118·1 (3)	120·5 (3)
				121·7 (3)
p-Toluate anion in piperidinium p- toluate	f	1·505 (9)	117·5 (5)	120·6 (5)
				122·5 (5)
p-Toluoyl chloride in its 1:1 adduct with aluminum trichlor- ide	g	1·507 (4)	119·2 (2)*	120·9 (2)
				121·0 (2)
2-p-Toluidinyl-6- naphthalenesulphon- ate anion in the potassium salt	h	1·514 (3)	117·4 (2)*	121·9 (2)
				121·4 (2)
Di-p-tolylcarbodi- imide	i	1·520 (6)	117·6 (4)	122·1 (3)
				121·5 (3)
		1·507 (5)	117·8 (3)	120·7 (3)
				122·1 (3)
p-Toluidinium cation in p-toluidinium hexafluorosilicate monohydrate	j	1·503 (7)	118·6 (4)	121·6 (4)
				120·9 (4)
p-Nitrotoluene	k	1·502 (9)	117·5 (5)	122·8 (5)
				121·3 (5)
(+)-Methyl-p- tolyl sulphoxide	l,b	1·515 (6)	118·2 (3)	121·9 (3)
				121·0 (4)
Propenyl-p-tolyl sulphone	m	1·524 (5)	118·6 (3)	121·4 (3)
				121·2 (3)
1-Toluene-p-sulphon- yl-1,2-diazepine	n	1·507 (5)	118·9 (3)	121·3 (3)
				120·8 (3)
trans-4-t-Butyl-1- (N-ethyl-N-toluene- p-sulphonylamino)- 1-thioniacyclohexane tetrafluoroborate	o	1·503 (8)	118·1 (5)	122·3 (5)
				122·3 (5)
Toluene-p-sulphonate anion in oxonium toluene-p-sulphonate (X-ray diffraction)	p	1·510 (3)	118·1 (2)	121·5 (2)
				121·8 (2)
Toluene-p-sulphonate anion in oxonium toluene-p-sulphonate (neutron diffraction)	q	1·507 (4)	118·8 (2)*	120·9 (2)
				121·0 (2)
Toluene-p-sulphonate anion in 1,5- endo-methylene- quinolizidinium toluene-p-sulphonate	r	1·511 (7)	117·9 (4)	120·9 (4)
				121·0 (4)

Table 7 (cont.)

2-exo-Norbornyl toluene-p-sulphonate	s	1·508 (4)	117·8 (2)	121·8 (2) 121·6 (2)
trans-4-t-Butylcyclo-hexyl toluene-p-sulphonate	t	1·504 (4)	117·9 (3)	121·0 (3) 122·3 (3)
cis-4-t-Butylcyclo-hexyl toluene-p-sulphonate (poly-morph A)	u	1·496 (6)	118·2 (4)	121·3 (3) 121·4 (4)
cis-4-t-Butylcyclo-hexyl toluene-p-sulphonate (poly-morph B)	v	1·487 (3)	117·7 (2)	121·3 (2) 121·9 (2)
trans-3-t-Butylcyclo-hexyl toluene-p-sulphonate	w	1·478 (6)	117·5 (3)	122·2 (3) 120·9 (3)
Mean values	x	1·506 (2)	118·1 (1)	121·4 (1)

(a) Casalone, Mariani, Mugnoli & Simonetta (1969). The asymmetric unit contains two crystallographically independent molecules. (b) The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (c) Casalone, Gavezzotti, Mariani, Mugnoli & Simonetta (1970). (d) Bürgi & Dunitz (1970). (e) Kato (1971). (f) Kashino (1973). (g) Chevrier, Le Carpentier & Weiss (1972). (h) Camerman & Jensen (1970). (i) Vincent & Wheatley (1972a). (j) Denne, Mathieson & Mackay (1971). (k) Barve & Pant (1971). (l) De la Camp & Hope (1970). (m) Klazinga & Vos (1973). (n) Allmann, Frankowski & Streith (1972). (o) Cook, Glick, Rigau & Johnson (1971). (p) Arora & Sundaralingam (1971). (q) Lundgren & Williams (1973). (r) Huber (1969). (s) Altona & Sundaralingam (1972). (t) Johnson, Cheer, Schaefer, James & Moore (1972). (u) Johnson, Schaefer, James & McConnell (1972). (v) James & Grainger (1972). (w) James (1973). (x) See Table 1 for calculation of mean values.

the hybridization theory and the VSEPR model this should modify the deformations induced by X in the skeletal geometry of the ring.

The effect of replacing the five hydrogens of a phenyl group with fluorines on the internal bond angles of the ring may be seen from the examples of Fig. 7. The observed decrease of α (about 3° in all the examples shown) is in keeping with the strong increase in the σ-electron-withdrawing properties of the ring induced by perfluoro substitution.

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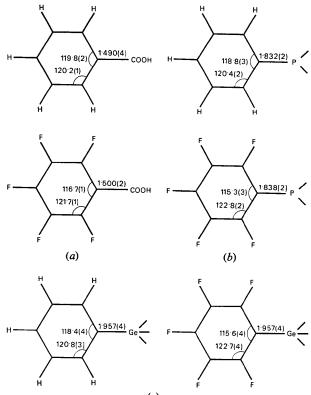Fig. 7. Effect of perfluoro substitution on the internal bond angles, α and β, of a phenyl group: some selected examples. Bond lengths are given in Å, angles in degrees; they are followed by their estimated standard deviations, given as units in the last digit. Whenever necessary, mean values and their standard deviations have been calculated according to Table 1. C_{2v} (2m) symmetry has been assumed throughout. (a) Benzoic acid (estimated molecular geometry, from the para-substituted benzoic acids of Table 5) and pentafluoro-benzoic acid (Benghiat & Leiserowitz, 1972). (b) Bis(di-phenylphosphino)acetylene (Bart, 1969; the bond lengths and angles given here are mean values from four crystallographically independent phenyl groups) and tetrakis-(pentafluorophenyl)cyclotetraphosphane (Sanz & Daly, 1971; the bond lengths and angles given here are mean values from two crystallographically independent phenyl groups). (c) Tetraphenylgermanium (Karipides & Haller, 1972) and tetrakis(pentafluorophenyl)germanium (Karipides & Thomas, 1973). Both molecules have S_4 ($\overline{4}$) crystallographic symmetry.

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The Crystal Structure of Ferroelastic Antimony(III) Oxide Iodide α-Sb₅O₇I

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Ferroelastic antimony(III) oxide iodide α-Sb₅O₇I is monoclinic, space group $P2_1/c$, with $a = 6.772$ (3), $b = 12.726$ (4), $c = 13.392$ (5) Å, $\beta = 120.1$ (1)°, $Z = 4$. The structure was solved from 1401 reflexions and refined to $R = 3.7\%$. It consists of pseudohexagonal sheets of $Sb_2[Sb_3O_7]_\infty^+$ connected by intermediate iodine; the latter occupies the centre of a slightly distorted cubo-octahedron of antimony. The atomic displacements from plausible positions of space group $P6_3/m$ of the high-temperature parent phase β-Sb₅O₇I which are considered responsible for the observed ferroelasticity are of the order of 0·2 Å.

Introduction

Recently we reported the synthesis and crystal growth of a series of new antimony(III) oxide iodides of the compositions Sb₃O₄I, Sb₈O₁₁I₂, and Sb₅O₇I (Krämer, Schuhmacher & Nitsche, 1973). In the course of further investigations it was found that Sb₅O₇I exists in (*a*) a low-temperature monoclinic (pseudohexagonal) phase, α-Sb₅O₇I, and (*b*) the hexagonal high-temperature phase, β-Sb₅O₇I.

The phase transition is reversible and takes place at a temperature of 208°C. Crystals of α-Sb₅O₇I show pure ferroelastic behaviour. They can exist in three different orientation states of mechanical strain which can be converted into each other by external stresses (Krämer, Nitsche & Schuhmacher, 1974).

Since the Sb₅O₇I phases represent a new structure type and in order to elucidate the ferroelastic behaviour, a crystal structure determination was performed.

Experimental

X-ray powder data were obtained with a Philips diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å) with As₂O₃ (cubic, $a = 11.0810$ Å) as a standard. Cell parameters were refined by least-squares calculations. A vapour-grown single-domain crystal was selected for Weissenberg and precession photographs. Intensites from the same crystal were measured on a computer-controlled automatic X-ray diffractometer (Enraf–Nonius CAD-4) by the ω–2θ scan method. A Mo tube

Table 1. *Crystal data*

Formula	Sb₅O₇I
Formula weight	847·65
Habit	Flat pseudohexagonal prism
Colour	Transparent, colourless
Lattice parameters	$a = 6.772$ (3) Å
	$b = 12.726$ (4)
	$c = 13.392$ (5)
	$\beta = 120.1$ (1)°
	$V = 998.3$ Å³
	$Z = 4$
Density	$D_{meas} = 5.55$ g cm⁻¹
	$D_{calc} = 5.64$
Reflexion conditions	$h0l$: $l = 2n$; $0k0$: $k = 2n$
Space group	$P2_1/c$
Radiation	Mo $K\alpha$, $\lambda = 0.71069$ Å
Linear absorption coefficient:	$\mu_{Mo} = 162.2$ cm⁻¹
Crystal size:	$370 \times 70 \times 330$ μm