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Molecular Geometry of Substituted Benzene Derivatives. II.* A Bond Angle *versus* Electronegativity Correlation for the Phenyl Derivatives of Second-Row Elements

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The angular deformations induced in the carbon skeleton of the benzene ring by substitution of a hydrogen atom with a second-row element have been investigated, using the best structural data available in the literature. It is shown that a linear correlation exists between the internal bond angle at the carbon atom at which substitution takes place and Pauling's electronegativity of the substituent. From this correlation, the actual electronegativities of phosphorus and sulphur in several classes of related compounds and individual molecules are evaluated. Similar correlations are shown to exist for the phenyl derivatives of first- and third-row elements.

1. Introduction

Substitution of a H atom in a benzene molecule with a different atom or functional group, X, is known to give rise to small distortions of the C hexagon from perfect D_{6h} ($6/mmm$) symmetry (Domenicano, Vaciago & Coulson, 1975, and references therein). The overall pattern of distortions conforms generally to C_{2v} ($2m$) symmetry, and consists of:

(i) *bond length variations*: the *a* bonds (Fig. 1) are lengthened or shortened with respect to the value of 1·397 (1) Å found in unsubstituted benzene by high-resolution Raman spectroscopy (Stoicheff, 1954; Langseth & Stoicheff, 1956);

(ii) *angular deformations*: the endocyclic bond angles α and β (Fig. 1) deviate from the ideal value of 120°, $\Delta\beta$ being approximately $-\Delta\alpha/2$.

Unlike bond length variations, whose accurate measurement by standard X-ray crystallographic techniques is often prevented by the effects of thermal motion, angular deformations appear to be fairly well measurable. The endocyclic angle α, whose values span a rather wide range (114–125°), is undoubtedly the most suitable parameter for quantitatively assessing the effect of different substituents on the geometry of the ring.

In the first paper of this series (Domenicano, Vaciago & Coulson, 1975) we analysed the ring deformations shown by a number of monosubstituted benzene derivatives, and pointed out their dependence upon (i) the σ-electron-withdrawing or -releasing properties of the substituent, and (ii) the extent of conjugation between the substituent and the ring. This dependence was rationalized (although in a purely qualitative way) in terms of hybridization effects at the C atom bonded to the substituent; or, alternatively, in terms of repulsions between the bonding electron pairs in the valence shell of that atom, according to the VSEPR theory (Gillespie, 1972, and references therein). Geminal intramolecular non-bonded interactions (Bartell, 1968, and references therein) were considered as possible contributors to the ring deformations: it was found, however, that marked in-plane and out-of-plane bending of the C–X bond produced only minor effects, if any, on the ring geometry.

In the light of these results it was anticipated that the values of the endocyclic angle α should correlate with the electronegativity of the substituent, provided (i) the C–X bond was essentially a σ bond, and (ii) the atom X (or, in the case of a polyatomic substituent, the atom in X directly bonded to C) was not allowed to vary outside a row of the periodic table.§

The bond of a phenyl C atom with a second-row element is expected to have – even in favourable cases – a substantially lower amount of π character than a bond with the corresponding first-row element, because of the increase in the covalent radius. Hence the correlation of α with the electronegativity is expected to be better with the phenyl derivatives of

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§ The need for the latter requirement is easily understood in the line of reasoning of the VSEPR theory. If X and Y are two atoms of equal electronegativity, but belonging to different rows of the periodic table and having, therefore, different covalent radii, the spatial requirements of the σ-bonding electron pair will not in general be the same for a C–X and a C–Y bond, thus producing different deformations in the benzene nucleus.

second-row elements. The construction of this correlation, and its application to the measurement of the actual electronegativities of P and S in some classes of related compounds, and even in individual molecules, are the subject of the present paper.

A preliminary communication of this work was given at a joint meeting of the Italian and Yugoslav Crystallographic Associations (Coulson, Domenicano & Vaciago, 1973).

2. Analysis of the structural data

2.1. *Procedure*

The following procedure has been adopted in order to find reliable values of the internal angle α to be attached to the phenyl derivatives of second-row elements.

For each element from Al to Cl we have tabulated and averaged all the best values of α for compounds having one or more phenyl groups bonded to an atom of that element (Tables 1 to 9). The structural data used refer not only to monosubstituted benzene derivatives, but also to *para*-disubstituted derivatives having the element in question as one of the substituents. This is justified, since the angular deformations induced by a substituent in the C hexagon seem to be scarcely affected by *para*-substitution, unless through-conjugation occurs between the substituents (Domenicano, Vaciago & Coulson, 1975). Disubstituted benzene derivatives having a strong π donor *para* to a potential π acceptor were, of course, excluded from the tables. Since the electronegativity of a multivalent element is known to increase with increasing valency (Mulliken, 1934; Haissinsky, 1946), the phenyl derivatives of P, S, and Cl were grouped according to valency.*

A serious criticism of this procedure could be made on the following grounds. The values of α reported in each table refer to different compounds which contain the element, X, in somewhat different bonding environments. It is now firmly established that, even for an element with a fixed valency, the electronegativity is by no means a constant: it depends on the actual hybridization state and partial charge (Walsh, 1947; Iczkowski & Margrave, 1961; Hinze & Jaffé, 1962; Hinze, Whitehead & Jaffé, 1963; Huheey, 1965). No doubt the bonding environment of X has a great influence on both these factors, and hence on the value of α, which we expect to be electronegativity-dependent. Thus the values of α reported in each table do not belong, strictly speaking, to the same population, and the operation of averaging has, in principle, no exact physical meaning.

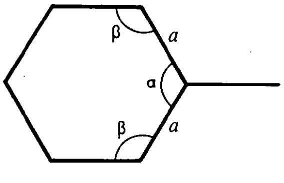


Fig. 1. Lettering of the 'substituent-sensitive' bond lengths and angles of the carbon skeleton in monosubstituted benzene derivatives. C_{2v} (2*m*) symmetry has been assumed.

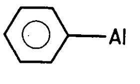
Nevertheless, we feel confident about our mean values. We expect them to give a reasonable indication of the 'average' effects of the various elements on the geometry of the benzene ring. In exactly the same way it is customary – and certainly quite useful – to attach fixed electronegativity values to the various elements, even though fixed electronegativity lacks exact physical meaning, being only an indication of the 'average' tendency of an element in its compounds to attract electrons to itself.

2.2. *Selection of the literature data*

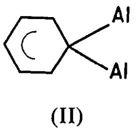
Unless otherwise stated the structural data used in this investigation are the results of X-ray crystal structure analysis studies. They have been gathered from a search of the literature, which has been greatly helped by available compilations (Kennard & Watson, 1970, 1971; Kennard, Watson & Town, 1973, 1974). No relevant molecule for which reliable data were available was intentionally omitted from the tables; the threshold precision required for inclusion was, however, kept as high as possible. Precision was assessed from the value of the estimated standard deviation on the internal angle α, $\sigma(\alpha)$. Additional criteria for rejection were (i) the omission of H atom contributions from the scattering model used in the refinement and (ii) the presence of disorder in the relevant part of the benzene ring.

2.3. *Aluminum*

The bonding of a phenyl group to Al may take place through either a direct σ bond, with a C–Al separation of about 1·96 Å (I), or a three-centred electron-deficient bridge involving two atoms of Al and one of C, with C–Al separations ranging between 2·13 and 2·18 Å (II) (Malone & McDonald, 1967, 1972*a*,*b*). The geometrical deformations experienced by the benzene nucleus are expected to be different in the two cases. Only compounds showing the first type of bonding are, of course, relevant to the purposes of the present paper.



(I)



(II)

As far as we know, the detailed geometry of a phenyl group σ-bonded to an Al atom has been reported only for di-μ-phenylbis(diphenylaluminum) (Malone &

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* It should be pointed out that Pauling's (1960) values for the electronegativities of P, S, and Cl (2·1, 2·5, and 3·0, respectively) were calculated from thermochemical data of compounds containing these elements in their lowest valencies, and apply, therefore, only to these valencies.

Table 1. *Carbon to silicon bond lengths and α angles in phenylsilicon derivatives*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–Si and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}5°$ have been included in this table.

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

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

$$\sigma'_m = \frac{1}{\sqrt{\sum_{i=1}^{N} (1/\sigma_i^2)}}$$

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. 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.

No.	Compound	Ref.	C–Si	α
1	2,2-Diphenyl-2-sila-1,3,4-trihydronaphthalene	*a*	1·871 (3) 1·871 (3)	116·1 (3) 117·1 (3)
2	2,2-Diphenyl-2-sila-Δ^3-3-bromo-1-tetralone	*b*	1·865 (5)	118·1 (4)
3	2,2-Diphenyl-2-silaindane	*c*	1·875 (4) 1·876 (4)	116·9 (4) 118·3 (4)*
4	(+)-*α*-Naphthylphenyl-1-menthoxymethoxysilane	*d*	1·855 (6)	117·9 (5)
5	2,6-*cis*-Diphenylhexamethylcyclotetrasiloxane	*e*	1·861 (3)	116·9 (3)
6	(+)-*α*-(*α*-Naphthylphenylmethylsilyl)benzyl *p*-bromobenzoate	*f*	1·872 (6)	117·2 (5)
7	α-Naphthylphenylmethylsilane	*g*	1·863 (5)	118·5 (5)*
8	Phenyl-(2,2′,2″-nitrilotriethoxy)silane (polymorph *γ*)	*h*	1·894 (5)*	116·6 (5)
9	*p*-Bis(dimethylhydroxysilyl)benzene	*i*	1·865 (4) 1·857 (5) 1·852 (5)*	116·6 (4) 116·6 (4) 115·5 (5)
10	Di-*µ*-diphenylsilyl-bis-(tetracarbonylmanganese)	*j*	1·885 (10)	116·0 (5)
	Mean values		1·8683 (26) [11]	116·98 (22) [11]

(*a*) Vidal, Lapasset & Falgueirettes (1972). (*b*) Vidal, Galigné & Falgueirettes (1972). One of the two phenyls in the molecule shows large, unreasonable distortions, probably due to the high thermal vibration, and has been ignored. (*c*) Vidal & Falgueirettes (1973). (*d*) Kanters & Van Veen (1973). (*e*) Carlström & Falkenberg (1973). The molecule has C_2 (2) crystallographic symmetry. (*f*) Nyburg, Brook, Pascoe & Szymánski (1972). (*g*) Okaya & Ashida (1966). The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (*h*) Párkányi & Simon (1974), and personal communication by L. Párkányi. (*i*) Alexander, Northolt & Engmann (1967). The asymmetric unit contains three crystallographically independent molecules, each having S_2 ($\bar{1}$) crystallographic symmetry. (*j*) Simon & Dahl (1973). One of the two phenyls in the molecule is disordered and has been ignored.

McDonald, 1967, 1972*a*). This molecule has S_2 ($\bar{1}$) crystallographic symmetry in the solid state, and contains, therefore, three crystallographically independent phenyl groups, one bridging and two σ-bonded. The values of the internal angle α for the latter are 116·0 (4)° and 116·7 (4)°, mean 116·4 (4)°.* [It should be noted that the value of α for the bridging phenyl is significantly lower, 113·7 (4)°.] The lengths of the two C–Al σ-bonds are 1·960 (4) and 1·956 (5) Å, mean 1·958 [3] Å.

2.4. *Silicon*

The structural data available for Si derivatives, up to $\sigma(\alpha) = 0{\cdot}5°$, are reported in Table 1. The mean values of the internal angle α and of the C–Si length are 117·0 (2)° and 1·868 (3) Å, respectively. The standard deviations given here, σ_m, are a measure of the 'external' consistency of the data used; they are some two to three times greater than the 'internal' standard deviations, σ'_m, quoted in Table 1.†

This situation, which is found in the majority of the tables in this paper, may reflect the well-known underestimation of the individual standard deviations, as obtained from the inverse least-squares matrix. It may also be indicative, however, of systematic effects in the data averaged. And indeed these data, as pointed out in § 2.1, do not belong, strictly speaking, to the same population, because of the different chemical environment of the central atom in the different molecules.

2.5. *Phosphorus*

The large amount of structural information available for the phenyl derivatives of trivalent P and their coordination compounds has prompted us to restrict our tabulation to molecules whose geometry is known with great precision [$\sigma(\alpha) \leq 0{\cdot}4°$]. These are collected in Table 2, and give a mean value of α of 118·5 (1)°. The associated mean value of the C–P length is 1·828 (1) Å.

Greater values of α are expected to occur in compounds like phenylphosphonium salts and ylids, mainly because of the positive charge necessarily present on a tetracovalent P atom. The structural data available for these two classes of compounds are collected in Tables 3 and 4, respectively. The mean values of α are 119·8 (1)° for phenylphosphonium cations and 119·4 (1)° for phenylphosphonium ylids. As expected, both values are greater than the mean value from Table 2. The corresponding mean values of the C–P lengths are 1·791 (1) and 1·811 (3) Å, respectively.

A comparison of the values of σ_m and σ'_m given in Tables 2, 3, and 4 suggests that – unlike the α angles of the phenyl groups – the C–P lengths in phenylphosphonium ylids are more affected by variations in either chemical environment or thermal motion

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* See Table 1 for calculation of mean values and associated standard deviations.

† A definition of σ_m and σ'_m is given in Table 1.

Table 2. *Carbon to phosphorus bond lengths and α angles in the phenyl derivatives of trivalent phosphorus and their coordination compounds*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–P and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}4°$ have been included in this table.

No.	Compound	Ref.	C–P	α
1	*p*-Dimethylaminophenyl-diphenylphosphine	*a*	1·835 (3)	118·5 (2)
			1·824 (3)	117·7 (3)
2	Dimenthylphenylphosphine	*b*	1·845 (3)*	117·7 (3)
3	Bis(diphenylphosphino)acetylene	*c*	1·834 (3)	118·5 (4)
			1·827 (3)	118·7 (4)
			1·830 (3)	119·6 (4)
			1·837 (3)*	118·5 (4)
4	1,1,3,3,5,5-Hexaphenylcyclotriborataphosphoniane	*d,e*	1·836 (4)	119·3 (3)
			1·822 (4)	118·8 (3)
			1·816 (5)	119·4 (4)
			1·830 (4)	118·4 (4)
			1·807 (4)*	118·8 (3)
5	Pentacarbonyltriphenylphosphine-chromium(0)	*f*	1·828 (4)	117·4 (3)*
			1·834 (4)	117·7 (3)
			1·821 (3)	117·6 (3)
6	Tricarbonyl-2-(1′,2′-dimethyloxopropenyl)-phenyldiphenylphosphinomanganese	*g*	1·823 (3)	119·4 (3)
			1·823 (3)	118·6 (3)
7	Dicarbonylnitrosyltriphenylphosphine-cobalt(0)	*h*	1·824 (4)	118·2 (4)
			1·821 (4)	118·4 (4)
			1·816 (4)	117·5 (4)
8	Bis-(9-phenyl-9-phosphabicyclo[3,3,1]nonane)nickel(II) chloride	*i,j*	1·807 (3)*	118·4 (3)
9	*trans*-Bis(methyldiphenylphosphine)bis-(σ-pentafluorophenyl)-nickel(II)	*k,j*	1·817 (3)*	118·6 (3)
			1·828 (3)	118·3 (3)
10	Dicarbonylbis(triphenylphosphine)-nickel(0)	*l,e,m*	1·837 (3)*	118·3 (3)
			1·835 (3)	119·1 (3)
			1·829 (4)	118·8 (3)
11	Borohydridobis(triphenylphosphine)-copper(I)	*n,e,m*	1·814 (5)	118·2 (4)
			1·829 (4)	118·1 (4)
			1·817 (4)	119·2 (4)
12	Triphenylphosphine-(π-cyclopentadienyl)-copper(I)	*o*	1·828 (2)	118·5 (2)
			1·829 (2)	118·6 (2)
			1·829 (2)	118·5 (2)
13	*cis*-Dihydridotetrakis-(diethyl-phenylphosphonite)iron(II)	*p*	1·837 (4)	118·7 (4)
			1·839 (5)	118·1 (4)
			1·839 (6)	119·5 (4)
			1·836 (5)	119·1 (4)
	Mean values	*q*	1·8276 (14) [5]	118·50 (9) [5]

(*a*) Dreissig & Plieth (1972*a*). One of the three benzene rings in this molecule has a strong π-electron-releasing functional group *para* to phosphorus and has been ignored. (*b*) Krüger & Roberts (1974). (*c*) Bart (1969*a*). (*d*) Bullen & Mallinson (1973). One of the six phenyl groups in the molecule is disordered and has been ignored. (*e*) Bond lengths and angles have been calculated from the atomic parameters quoted in the paper. (*f*) Plastas, Stewart & Grim (1973). (*g*) Robertson & Whimp (1973). (*h*) Ward, Caughlan, Voecks & Jennings (1972). (*i*) Smith (1972). (*j*) The molecule has S_2 ($\bar{1}$) crystallographic symmetry. (*k*) Churchill & Veidis (1972). (*l*) Krüger & Tsay (1974). (*m*) The molecule has C_2 (2) crystallographic symmetry. (*n*) Lippard & Melmed (1967). (*o*) Cotton & Takats (1970). (*p*) Guggenberger, Titus, Flood, Marsh, Orio & Gray (1972). (*q*) See Table 1 for calculation of mean values.

Table 3. *Carbon to phosphorus bond lengths and α angles in phenylphosphonium cations*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–P and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}4°$ have been included in this table.

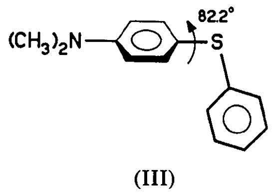
No.	Compound	Ref.	C–P	α
1	Tetraphenylphosphonium bis(tetracyanoquinodimethanide)	*a,b*	1·792 (3)	119·7 (2)
			1·791 (3)	120·1 (2)
2	Methyltriphenylphosphonium bis(tetracyanoquinodimethanide)	*c*	1·792 (3)	120·0 (3)
			1·794 (3)	119·9 (3)
			1·790 (3)	120·8 (3)*
3	Methyltriphenylphosphonium 1,1,1-tricarbonyl-4,6-dicarba-1-mangana-*closo*-nonaborate(1−)	*d,b*	1·796 (3)	118·9 (3)
			1·797 (3)	119·0 (4)
			1·788 (3)	118·4 (4)*
4	Benzyltriphenylphosphonium chloride	*e*	1·788 (3)	119·8 (3)
			1·785 (3)	119·7 (3)
			1·796 (3)	119·8 (3)
5	(3,7-Dimethyl-2,6-octadienyl)triphenylphosphonium bromide	*f*	1·790 (4)	119·2 (4)
			1·794 (4)	119·7 (4)
			1·790 (4)	119·1 (4)
6	2,4,4,6-Tetraphenyl-4-phosphoniapyran perchlorate	*g*	1·786 (3)	120·1 (3)
			1·784 (3)	120·4 (3)
	Mean values	*h*	1·7908 (10) [8]	119·78 (14) [7]

(*a*) Goldstein, Seff & Trueblood (1968). The molecule has C_2 (2) crystallographic symmetry. (*b*) Bond angles have been calculated from the atomic parameters quoted in the paper. (*c*) McPhail, Semeniuk & Chesnut (1971). (*d*) Hollander, Templeton & Zalkin (1973). (*e*) Skapski & Stephens (1974). (*f*) Hjortås (1973). (*g*) Guilhem (1974). (*h*) See Table 1 for calculation of mean values.

effects than the corresponding lengths in phenylphosphines and phenylphosphonium cations.

2.6. *Sulphur*

Table 5 gives the structural data for the phenyl derivatives of bivalent S, up to $\sigma(\alpha) = 0{\cdot}5°$. The mean value of α is 119·7 (3)°, and that of the C–S length 1·781 (3) Å. Inspection of Table 5 shows that the values of α for compounds No. 3 and 4 deviate by 5 and 3σ, respectively, from the mean value. In view of the limited number of entries in this table, we shall discuss these deviations in some detail.



(III)

In the case of compound No. 3, *p*-dimethylaminophenyl phenyl sulphide (III), the somewhat low values of α observed with both rings [117·8 (4)° for the unsubstituted phenyl, 118·4 (4)° for the *para*-substituted one] may be attributed to some degree of π bonding with S. The orientation of the two benzene rings in this molecule with respect to the C–S–C plane is indeed such as to favour the interaction of the filled $3p_z$ orbital of S with the π system of the unsubstituted ring, and of the empty $3d_{xy}$ orbital of S with the π system of the other ring, which has a strong π donor in the *para* position. It should be said, however, that the results of CNDO calculations by Bandoli, Clemente, Tondello & Dondoni (1974) suggest that the 3*d* orbitals of S are not involved in conjugative interactions with the two adjacent π systems.

In the case of compound No. 4, pentacarbonyl-[methyl(phenylthio)carbene]chromium (IV), the somewhat high value of α [120·6 (3)°] may be attributed to the increased electronegativity of S, which is carrying a partial positive charge resulting from substantial π donation to the carbene C atom. And indeed the S–C(carbene) bond is markedly shorter than the S–C(phenyl) bond, although both involve formally sp^2-hybridized C atoms (Hoare & Mills, 1972).

Table 4. *Carbon to phosphorus bond lengths and* α *angles in phenylphosphonium ylids*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–P and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}5°$ have been included in this table.

No.	Compound	Ref.	C–P	α
1	Methylenetriphenylphosphorane	*a,b*	1·821 (5)	119·0 (5)
			1·839 (5)*	120·2 (5)
			1·811 (5)	119·0 (5)
			1·833 (5)*	119·6 (5)
			1·824 (5)	119·8 (5)
			1·812 (5)	117·8 (5)*
2	Cyclopentadienylidenetriphenylphosphorane	*c*	1·808 (2)	119·5 (2)
			1·802 (2)*	119·3 (2)
			1·807 (2)	120·1 (2)*
3	2,2,3,3,4,4-Hexafluorocyclobutylidenetriphenylphosphorane	*d,e*	1·802 (3)	119·5 (3)
			1·796 (3)*	118·2 (4)
			1·796 (3)*	119·9 (3)
4	2,2-Diethoxyvinylidenetriphenylphosphorane	*f*	1·828 (5)*	119·7 (5)
			1·837 (6)*	119·4 (5)
			1·830 (5)*	118·8 (5)
5	Dicyanomethylenephenyldi-n-propylphosphorane	*g*	1·799 (2)*	120·1 (2)*
6	3,3-Dimethylallylidenetriphenylphosphorane	*h,b,e*	1·819 (4)	118·3 (4)
			1·809 (3)	119·5 (3)
			1·832 (3)*	118·4 (3)*
			1·798 (4)*	118·3 (4)
			1·829 (3)*	118·2 (4)
			1·833 (3)*	118·7 (3)
	Mean values	*i*	1·8110 (28) [7]	119·35 (14) [7]

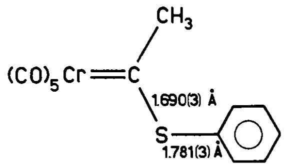
(*a*) Bart (1969*b*). (*b*) The asymmetric unit contains two crystallographically independent molecules. (*c*) Ammon, Wheeler & Watts (1973). (*d*) Howells, Howells, Baenziger & Burton (1973). (*e*) Bond lengths and angles have been calculated from the atomic parameters quoted in the paper. (*f*) Burzlaff, Voll & Bestmann (1974). The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (*g*) Dreissig, Hecht & Plieth (1973). (*h*) Barnett & Krüger (1973). (*i*) See Table 1 for calculation of mean values.

Table 5. *Carbon to sulphur bond lengths and* α *angles in the phenyl derivatives of bivalent sulphur*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–S and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}5°$ have been included in this table.

No.	Compound	Ref.	C–S	α
1	Orthothiocarbonic acid tetraphenylester	*a*	1·770 (3)*	119·3 (3)
			1·778 (3)	119·0 (3)
			1·773 (3)	119·2 (3)
			1·784 (3)	119·7 (3)
2	Diphenyl disulphide	*b*	1·789 (3)	120·1 (2)
			1·788 (2)*	120·2 (2)
3	*p*-Dimethylaminophenyl phenyl sulphide	*c*	1·769 (4)	117·8 (4)*
4	Pentacarbonyl[methyl(phenylthio)carbene]-chromium	*d*	1·781 (3)	120·6 (3)
	Mean values	*e,f*	1·7808 (27) [10]	119·73 (26) [9]

(*a*) Kato (1972). (*b*) Sacerdoti, Gilli & Domiano (1975). (*c*) Bandoli, Clemente, Tondello & Dondoni (1974). One of the two benzene rings in this molecule has a strong π-electron-releasing functional group *para* to sulphur and has been ignored. (*d*) Hoare & Mills (1972). (*e*) See Table 1 for calculation of mean values. (*f*) The mean value of α is 119·75 (21) [10]° when compounds No. 3 and 4 are excluded from the calculation.



(IV)

In the light of these findings, it might be safer to exclude compounds No. 3 and 4 from the calculation of the mean value of α in Table 5. This, however, has practically no effect on the result.

Higher values of α are expected for the phenyl derivatives of tetra- and hexavalent S, especially if the S atom is bonded to strongly electronegative atoms. We were unable to find in the literature precise [$\sigma(\alpha) \leq 0{\cdot}5°$] structural data for the phenyl derivatives of tetravalent S, with the sole exception of methyl *p*-tolyl sulphoxide, for which α is reported to be 120·3 (3)° (De la Camp & Hope, 1970). On the contrary, a wealth of structural information is available on three different classes of molecules containing a phenyl group bonded to hexavalent S, namely (i) phenylsulphonate anions, (ii) phenylsulphonic esters and amides, and (iii) phenylsulphones. Relevant data are reported in Tables 6, 7 and 8, respectively. The mean values of α are 120·6 (2)° for phenylsulphonate anions, 120·4 (2)° for phenylsulphonic esters and amides, 121·2 (1)° for phenylsulphones. Although the last value is slightly higher than the other two (a point that will be discussed in § 3.1), they are all greater, as expected, than that obtained for the phenyl derivatives of bivalent S. The corresponding mean values of the C–S lengths are 1·770 (8), 1·755 (1), and 1·753 (1) Å, respectively. The remarkably large spectrum of values of the C–S length in phenylsulphonate anions should be noticed.

2.7. *Chlorine*

The structural data available in the literature for *p*-chloro-substituted benzene derivatives, up to $\sigma(\alpha)=$ 0·5°, are reported in Table 9. The mean value of α is 121·4 (1)°, with no individual value differing from it by more than 3σ. It should be noted that the values of $\sigma_m(\alpha)$ and $\sigma'_m(\alpha)$ reported in Table 9 are almost equal, which indicates that (i) the standard deviations of the individual values are not underestimated and (ii) the data averaged really belong to the same population. This result is in agreement with chemical expectation, since – apart from long-range interactions – the chemical environment of Cl is the same in all the molecules of Table 9.

Table 9 also provides a mean value for the length of the C–Cl bond in *p*-chloro-substituted benzene derivatives, 1·740 (1) Å.

Higher values of α are expected to occur with molecules having a phenyl group linked to an atom of tri-, penta-, or heptavalent Cl. These unusual compounds have received very little attention by X-ray crystallographers: the only structural report we could find refers to *m*-nitroperchlorylbenzene (Palenik, Donohue & Trueblood, 1968), where a value of α as high as 126·0 (6)° is associated with the strongly σ-electron-withdrawing perchloryl moiety.

Table 6. *Carbon to sulphur bond lengths and α angles in phenylsulphonate anions*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–S and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha)\leq 0\cdot5°$ have been included in this table.

No.	Compound	Ref.	C–S	α
1	Oxonium toluene-*p*-sulphonate (X-ray diffraction)	*a*	1·753 (2)*	120·3 (2)
2	Oxonium toluene-*p*-sulphonate (neutron diffraction)	*b*	1·738 (5)*	120·8 (2)
3	Deuterated oxonium toluene-*p*-sulphonate (neutron diffraction)	*c*	1·761 (4)	121·1 (2)
4	1,5-*endo*-Methylenequinolizidinium toluene-*p*-sulphonate	*d*	1·780 (4)	118·8 (4)*[e]
5	Sodium *p*-dimethylaminoazobenzene-*p*′-sulphonate monohydrate monoethanolate	*f*	1·780 (2)*	119·9 (2)*
6	Benzenediazonium-*p*-sulphonate	*g*	1·798 (3)*	121·0 (3)
	Mean values	*h*	1·770 (8) [1]	120·57 (23) [9]

(*a*) Arora & Sundaralingam (1971). (*b*) Lundgren & Williams (1973). (*c*) Finholt & Williams (1973). Bond lengths and angles have been calculated from the atomic parameters quoted in the paper. (*d*) Huber (1969). Bond lengths and angles are corrected for thermal motion. (*e*) Value excluded from the calculation of the mean. (*f*) Hanson (1973). The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (*g*) Rømming (1972). (*h*) See Table 1 for calculation of mean values.

3. Results

3.1. *Bond angle versus electronegativity correlation*

If the mean values of α obtained in § 2 for the phenyl derivatives of Al, Si, trivalent P, bivalent S, and univalent Cl are plotted against Pauling's (1960) electro-

Table 7. *Carbon to sulphur bond lengths and α angles in phenylsulphonic esters and amides*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–S and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha)\leq 0\cdot4°$ have been included in this table.

No.	Compound	Ref.	C–S	α
1	2-*exo*-Norbornyl toluene-*p*-sulphonate	*a*	1·758 (2)	120·9 (2)
2	*cis*-4-t-Butylcyclohexyl toluene-*p*-sulphonate (polymorph *A*)	*b*	1·754 (3)	120·2 (3)
3	*cis*-4-t-Butylcyclohexyl toluene-*p*-sulphonate (polymorph *B*)	*c*	1·756 (2)	120·6 (2)
4	*trans*-4-t-Butylcyclohexyl toluene-*p*-sulphonate	*d*	1·754 (2)	120·7 (3)
5	*trans*-3-t-Butylcyclohexyl toluene-*p*-sulphonate	*e*	1·751 (3)	119·1 (3)*
6	*cis,trans*-2,5-Di-t-butylcyclohexyl toluene-*p*-sulphonate	*f*	1·756 (3)	119·6 (3)
7	3-Oxo-5α-androstan-17β-ol toluene-*p*-sulphonate	*g*	1·762 (5)	120·3 (4)
8	Poly-[1,2-bis(toluene-*p*-sulphonyloxymethylene)-1-butene-3-inylene]	*h*	1·752 (3)	120·4 (3)
9	*p*-Aminobenzenesulphonamide (sulphanilamide)	*i*	1·750 (2)	120·5 (2)
10	2-(*p*-Aminobenzenesulphonamido)thiazole (sulphathiazole)	*j*	1·759 (3)	119·8 (3)
11	1-(Toluene-*p*-sulphonyl)-1,2-diazepine	*k*	1·759 (3)	120·9 (3)
12	*N*-(Toluene-*p*-sulphonyl)-2,12-ethano-2-ethyl-8-methoxy-1,4-methylene-1,2,3,4,5,6,12,13-octahydrophenanthridin-3-one	*l*	1·760 (4)	120·3 (4)
13	*N*-(Toluene-*p*-sulphonyl)-iminotriphenylphosphorane	*m*	1·778 (4)*[n]	119·7 (4)
	Mean values	*o*	1·7551 (10) [8]	120·35 (15) [8]

(*a*) Altona & Sundaralingam (1972). (*b*) Johnson, Schaefer, James & McConnell (1972). (*c*) James & Grainger (1972). (*d*) Johnson, Cheer, Schaefer, James & Moore (1972). (*e*) James (1973). (*f*) Faber & Altona (1974). The C–S bond length is corrected for thermal motion. (*g*) De Graaf & Romers (1974). (*h*) Kobelt & Paulus (1974). (*i*) O'Connell & Maslen (1967). (*j*) Kruger & Gafner (1971). (*k*) Allmann, Frankowski & Streith (1972). (*l*) Cameron, Freer, Doyle & Wright (1974). (*m*) Cameron, Hair & Morris (1974). (*n*) Value excluded from the calculation of the mean. (*o*) See Table 1 for calculation of mean values.

negativities of these elements, χ, a linear correlation is obtained (Fig. 2). The equation of the weighted least-squares line is:

$$\alpha = 3{\cdot}33\chi + 111{\cdot}4\,. \tag{1}$$

Equation (1) may be used to calculate the electronegativity of a second-row element in a class of related compounds, *if it is assumed that the electronegativity of the substituent is the only factor affecting* α. We suggest that by this technique the actual electronegativities of second-row elements may be evaluated even in individual molecules, provided structural data of outstanding quality are at hand, and preferably for molecules containing two or more crystallographically independent but chemically equivalent phenyl groups, so as to allow an internal check of the precision. This is gratifying, since in principle the electronegativity of an element has different values in different molecules. A few chemically relevant examples are discussed here.

When substituted in equation (1), the mean value of α obtained in Table 3 yields 2·5 for the electronegativity of P in phenylphosphonium cations, where the formal positive charge on the central atom is expected to cause a substantial increase in its electronegativity. In phenylphosphonium ylids, whose structure is best described as intermediate between the canonical forms (V) and (VI), we expect the electronegativity of P to be somewhat lower than 2·5, but still greater than Pauling's value of 2·1; and indeed the mean value of α obtained in Table 4 yields $\chi = 2{\cdot}4$. [This result must, of course, be considered just as a broad indication,

Table 8. *Carbon to sulphur bond lengths and* α *angles in phenyl sulphones*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–S and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}5°$ have been included in this table.

No.	Compound	Ref.	C–S	α
1	3-Methyl-4-phenylsulphonylfuroxan	*a*	1·757 (4)	122·0 (4)
2	1-Chloro-1-phenylsulphonyl-2,3-dimethylcyclopropane	*b*	1·758 (3)	121·9 (3)
3	Propenyl *p*-tolyl sulphone	*c*	1·766 (3)*	120·7 (3)
4	*cis*-Mesityl(phenylsulphonyl)sulphine	*d*	1·757 (3)	121·4 (3)
5	Ethyl *N*-methyl-*N*-(*p*-tolylsulphonylmethyl)-carbamate	*e*	1·751 (1)	121·1 (1)
6	*p,p'*-Dichlorodiphenyl sulphone	*f*	1·765 (6)	121·1 (5)
7	2,4-Dinitrobenzyl *p*-tolyl sulphone	*g*	1·753 (4)	119·4 (3)*[h]
8	Diphenyl disulphone	*i*	1·753 (1)	122·5 (1)*[h]
	Mean values	*j*	1·7534 (14) [6]	121·19 (14) [8]

(*a*) Chiari, Viterbo, Gaetani-Manfredotti & Guastini (1973). (*b*) Saenger & Schwalbe (1971). (*c*) Klazinga & Vos (1973). (*d*) Hummelink (1974). (*e*) Tickle & Engberts (1973). (*f*) Sime & Abrahams (1960). The molecule has C_2 (2) crystallographic symmetry. (*g*) Harlow, Simonsen, Pfluger & Sames (1974). (*h*) Value excluded from the calculation of the mean. (*i*) Kiers & Vos (1972). (*j*) See Table 1 for calculation of mean values.

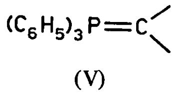
Table 9. *Carbon to chlorine bond lengths and* α *angles in para-substituted chlorobenzenes*

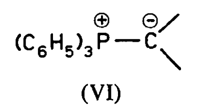
Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Values of C–Cl and α differing from the respective mean values by more than 3σ are marked with an asterisk. Only compounds with $\sigma(\alpha) \leq 0{\cdot}5°$ have been included in this table.

No.	Compound	Ref.	C–Cl	α
1	*syn-p*-Chlorobenzaldoxime	*a*	1·728 (6)	121·6 (5)
2	*anti-p*-Chlorobenzaldoxime	*b*	1·736 (6)	121·4 (5)
3	Potassium *p*-chlorophenyldinitromethanide	*c*	1·745 (5)	122·2 (5)
4	1-(*p*-Chlorobenzoyl)-5-methoxy-2-methylindole-3-acetic acid	*d,e*	1·735 (2)	121·0 (2)
5	*p*-Chlorobenzoic acid	*f*	1·744 (5)	122·1 (5)
6	*p*-Chlorocinnamide	*g*	1·745 (3)	121·8 (3)
7	α-(*p*-Chlorophenyl)-α-methyl-α'-cyanosuccinimide	*h*	1·743 (3)	121·4 (3)
8	1-(*o*-Chlorophenyl)-1-(*p*-chlorophenyl)-2,2,2-trichloroethane	*i,j*	1·737 (5) 1·750 (5)	121·5 (4) 121·1 (4)
9	*trans-p,p'*-Dichloroazobenzene	*k,l,e*	1·737 (3)	121·7 (3)
10	*N*-(*p*-Chlorobenzylidene)-*p*-chloroaniline	*m,l*	1·741 (3)	121·3 (3)
11	*N*-(*p*-Chlorophenyl)-α-isopropyl-β-phenyl-β-lactam	*n*	1·741 (3)	121·2 (3)
12	*p*-Chlorophenol	*o,j*	1·741 (5) 1·739 (4)	121·0 (4) 121·0 (4)
13	*p*-Chlorophenyldiphenylphosphine oxide	*p*	1·739 (3)	122·0 (3)
14	*p*-Chlorophenyldiphenylphosphine sulphide	*q*	1·728 (5)	122·2 (4)
15	*p,p'*-Dichlorodiphenyl sulphone	*r*	1·736 (7)	121·8 (5)
16	1-(*p*-Chlorophenyl)-5-isopropylbiguanide hydrochloride	*s,e*	1·734 (5)	120·7 (5)
17	(+)-*S*-1-(*p*-Chlorophenyl)-1-(2-pyridyl)-3-*N,N*-dimethylpropylamine maleate	*t*	1·748 (5)	120·6 (4)
18	*cis*-1-(*p*-Chlorophenyl)-3-methyl-2-methylisoindoline	*u,e*	1·746 (2)	121·2 (2)
	Mean values	*v*	1·7404 (11) [8]	121·37 (9) [7]

(*a*) Folting, Lipscomb & Jerslev (1964). (*b*) Gram Jensen (1970). (*c*) Klewe & Ramsøy (1972). (*d*) Kistenmacher & Marsh (1972). (*e*) The standard deviations given here have been calculated from the standard deviations of the atomic parameters quoted in the paper. (*f*) Miller, Paul & Curtin (1974). (*g*) Rabinovich (1969). (*h*) Baudour & Messager (1971). (*i*) DeLacy & Kennard (1972). (*j*) The asymmetric unit contains two crystallographically independent molecules. (*k*) Hope & Victor (1969). (*l*) The molecule has S_2 ($\bar{1}$) crystallographic symmetry. (*m*) Bernstein & Schmidt (1972). (*n*) Parthasarathy (1970). (*o*) Shiono & Wu (1972), and personal communication by R. Shiono. (*p*) Dreissig & Plieth (1971). (*q*) Dreissig & Plieth (1972*b*). (*r*) Sime & Abrahams (1960). The molecule has C_2 (2) crystallographic symmetry. (*s*) Brown (1967). (*t*) James & Williams (1974). (*u*) Brisse & Sygusch (1974). (*v*) See Table 1 for calculation of mean values.

since the relative contributions of the canonical forms (V) and (VI) may differ widely in the different molecules of Table 4.]


(V)


(VI)

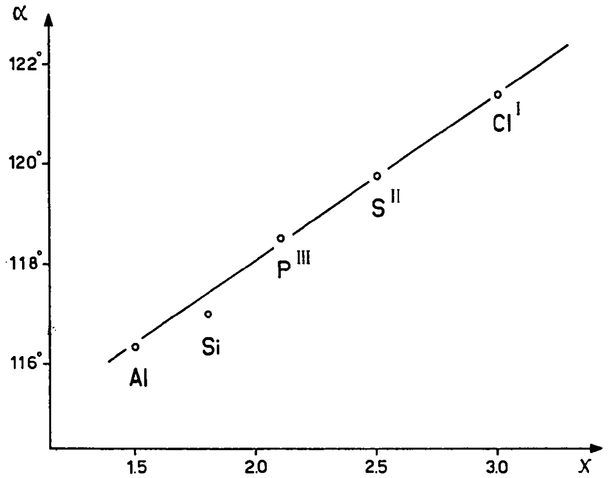


Fig. 2. Plot of the internal angle α *versus* Pauling's electronegativity, χ, for the phenyl derivatives of second-row elements.

A close inspection of the most precise among the data shown in Table 2 strongly suggests that the internal angle α in coordinated phenylphosphines is sensitive to variations in the electronegativity of P resulting from the balance between its σ-donor and π-acceptor properties. It should be noted that the mean value of α in compound No. 4, 1,1,3,3,5,5-hexaphenylcyclotriborataphosphoniane (VII), is 119·0 (2)°, higher than in any other compound in Table 2 (with the sole exception of compound No. 6, which has exactly the same mean value of α). This is in agreement with chemical expectation, since the lack of suitable filled orbitals on B prevents back-donation to P in this molecule.* On the other hand a significantly lower mean value of α, 117·6 [2]°, is observed with compound No. 5, pentacarbonyltriphenylphosphinechromium(0), where the metal is supposed to be a weak σ acceptor and a good π donor. There is little doubt that the small difference, 1·4°, between the mean values of α in these two molecules is *real*, and indicative of a substantially lower electronegativity of P in the Cr complex, resulting from the different nature of the P–B and P–Cr

Table 10. C–X *bond lengths and* α *angles in some representative compounds having a phenyl group bonded to a first-row element*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit.

Compound	Ref.	Element	Electro-negativity	C–X	α
Tetraphenylborate anion in tris-(2-aminoethyl)aminochlorozinc(II) tetraphenylborate	*a*	B⁻	<2·0	1·645 (8) 1·630 (8) 1·640 (8) 1·640 (7)	115·0 (5) 113·4 (5) 113·4 (5) 113·9 (4)
Triphenylboron	*b,c*	B	2·0	1·589 (5) 1·571 (3)	116·3 (4) 117·1 (4)
α-2-Ethyl-5-methyl-3,3-diphenyltetrahydrofuran	*d*	C	2·5	1·525 (4) 1·541 (4)	117·9 (3) 117·2 (3)
Biphenyl	*e*			1·497 (3)	117·4 (2)
cis-Azobenzene	*f,c*	N	3·0	1·443 (3)	119·8 (3)
trans-Azobenzene	*g*			1·433 (3)	120·3 (2)
N,N-Diphenylacetamide	*h*			1·441 (3) 1·433 (3)	120·6 (2) 119·7 (2)
Pentacarbonyl(triphenylphosphite)-chromium(0)	*i*	O	3·5	1·409 (6) 1·397 (6) 1·392 (4)	121·9 (5) 121·1 (5) 121·8 (4)
Phenylphosphorodiamidate	*j*			1·398 (3)	122·2 (3)
Fluorobenzene (by microwave spectroscopy)	*k*	F	4·0	1·354 (6)	123·4 (4)

(*a*) Sime, Dodge, Zalkin & Templeton (1971). Bond lengths and angles have been calculated from the atomic parameters quoted in the paper. (*b*) Zettler, Hausen & Hess (1974). (*c*) The molecule has C_2 (2) crystallographic symmetry. (*d*) Singh & Ahmed (1969). (*e*) Robertson (1961). The molecule has S_2 ($\bar{1}$) crystallographic symmetry. Bond lengths and angles are corrected for libration. (*f*) Mostad & Rømming (1971). (*g*) Brown (1966). The asymmetric unit contains two crystallographically independent molecules, each having S_2 ($\bar{1}$) crystallographic symmetry. One of the two molecules, however, is disordered and has been ignored. (*h*) Krigbaum, Roe & Woods (1968). (*i*) Plastas, Stewart & Grim (1973). (*j*) Bullen & Dann (1973). (*k*) 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.

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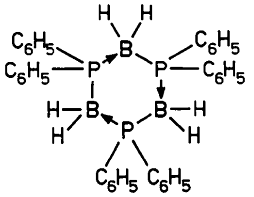
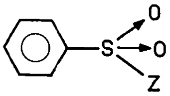
* A kind of hyperconjugative interaction where the B–H bonding orbitals overlap the empty *d* orbitals of P has been invoked by Burg & Wagner (1953) to explain the exceptional inertness of cycloborataphosphonianes towards protonic reagents. No evidence for this interaction is provided, however, by the geometry of the heterocyclic six-membered ring in (VII) (Bullen & Mallinson, 1973).

interactions. From equation (1), the electronegativity of P is estimated to be 2·3 in the cycloborataphosphoniane, and 1·9 in the Cr complex.



(VII)

The same procedure may be adopted to estimate the electronegativity of S in compounds where its valency is greater than two. From the mean values of α obtained in Tables 6, 7, and 8 the electronegativity of this element is estimated to be 2·7–2·8 in phenylsulphonate anions, phenylsulphonic esters and phenylsulphonamides, and 2·9–3·0 in phenylsulphones.



(VIII)

The different values of χ obtained here deserve some comment. The structures of these molecules undoubtedly contain a contribution from the canonical form (VIII), which in principle should imply a substantial increase of χ relative to bivalent S. In phenylsulphonate anions ($Z=O^-$), however, a large increase of χ is prevented by the presence of the negative charge (which is, of course, delocalized over the three O atoms). A large increase of χ is also prevented in phenylsulphonic esters (Z=OR) and amides (Z=NRR′), where a large fraction of negative charge is shifted from Z to S through a $(p\rightarrow d)\pi$ mechanism, involving a lone-pair orbital of O (or N) and an empty *d* orbital of S. (This shift accounts, *inter alia*, for a number of chemical properties of these compounds, including the greater resistance to hydrolysis of both phenylsulphonic esters and amides relative to the corresponding carboxylic derivatives, and the slight acidity of phenylsulphonamides having $Z=NH_2$ or NHR.)

A different situation occurs with phenylsulphones (Z=CRR′R″), where a shift of negative charge from Z to S may only take place *via* a less effective σ mechanism. This accounts for the higher values of α normally observed with these compounds (Table 8). An extreme case is that of diphenyl disulphone (C_6H_5–SO_2–SO_2–C_6H_5, compound No. 8 in Table 8): here two S atoms, each carrying a partial positive charge, are directly linked to each other, which prevents *any* shift of negative charge. The electronegativity of S in this molecule is expected to be particularly high: and indeed α is 122·5 (1)°, which, supposing equation (1) to be still valid, yields $\chi=3\cdot3$.

Since the electronegativity of a given element in a given hybridization state is a function of partial charge, for which explicit analytical expressions have

Table 11. C–X *bond lengths and* α *angles in compounds having a phenyl group bonded to a third-row element*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Entries for positively charged arsenic and for bromine have been chosen from among the best data of the literature. For the other elements all the available data are reported, up to σ(α)=0·6°.

Compound	Ref.	Element	Electro-negativity	C–X	α
cis-Diphenylbis-(2,2′-bipyridyl)chromium(III) iodide	*a,b*	Cr	1·6	2·087 (4)	115·2 (4)
Bis[phenyl(acetylacetonato)zinc(II)]-bis(acetylacetonato)zinc(II)	*c*	Zn	1·6	1·950 (7)	115·8 (6)
				1·951 (6)	115·9 (6)
Triphenylgallium	*d,b*	Ga	1·6	1·946 (7)	116·2 (6)
				1·968 (5)	117·5 (4)
Tetraphenylgermanium (two independent analyses)	*e,f*	Ge	1·8	1·957 (4)	118·4 (4)
	g,f			1·956 (5)	118·1 (5)
Dicarbonylbis(diphenylarsino)methanechromium	*h*	As	2·0	1·950 (3)	119·2 (3)
				1·941 (3)	118·5 (3)
				1·959 (4)	118·4 (4)
Tetraphenylarsonium cation in tetraphenylarsonium tris-(*cis*-1,2-dicyano-1,2-ethylenedithiolato)iron(IV)	*i*	As^+	>2·0	1·902 (3)	119·6 (3)
				1·897 (3)	120·6 (3)
				1·907 (4)	120·4 (4)
				1·898 (4)	120·9 (4)
1-(*p*-Bromophenyl)azetidin-2-one	*j*	Br	2·8	1·914 (3)	121·7 (3)
N-(*p*-Bromobenzoyl)-*exo*-2,3-aziridinobicyclo[2,2,1]heptane	*k*			1·890 (4)	121·2 (4)
4-Methyl-3-(*p*-bromophenyl)-1,2,5-oxadiazole-2-oxide	*l*			1·899 (4)	121·0 (5)
4-Methyl-3-(*p*-bromophenyl)-1,2,5-oxadiazole-5-oxide	*m*			1·908 (5)	122·0 (5)

(*a*) Daly, Sanz, Sneeden & Zeiss (1973). (*b*) The molecule has C_2 (2) crystallographic symmetry. (*c*) Spek (1973). (*d*) Malone & McDonald (1970). (*e*) Karipides & Haller (1972). (*f*) The molecule has S_4 ($\bar{4}$) crystallographic symmetry. (*g*) Chieh (1971). Bond lengths and angles have been calculated from the atomic parameters quoted in the paper. (*h*) Robertson & Whimp (1974). One of the four phenyl groups in the molecule is involved in a π interaction with the metal and has been ignored. (*i*) Sequeira & Bernal (1973). (*j*) Kartha & Ambady (1973). (*k*) Gopalakrishna (1972). (*l*) Calleri, Ferraris & Viterbo (1969*a*). (*m*) Calleri, Ferraris & Viterbo (1969*b*).

been proposed (Iczkowski & Margrave, 1961; Huheey, 1965), it should be possible in principle to evaluate partial charges from the values of α. This possibility is currently being investigated in the particularly favourable case of compounds containing the Ph_3P moiety (Colapietro, Domenicano & Vaciago, 1975).

3.2. *Bond angle versus bond length correlation*

It is well known that the covalent radii of the elements decrease steadily on moving to the right within a row of the periodic table. Thus the internal angle α in the phenyl derivatives of second-row elements is expected to decrease regularly as the length of the exocyclic C–X bond is increased.

In Fig. 3 the mean values of α obtained in § 2 are plotted against the corresponding mean values of the C–X lengths. The correlation is good, and seems to be linear in the region between Si and Cl. It should be noted, however, that the remarkable increase of α observed in going from phenylsulphonic esters and amides to phenyl sulphones and eventually to diphenyl disulphone is not paralleled by a substantial decrease of the C–S length, which is practically constant throughout Tables 7 and 8. A similar situation has been found to occur with aryl- and carboxy-substituted benzene derivatives, where a variation of α by approximately 2° is not associated with any appreciable change of the C–X length (Domenicano, Vaciago & Coulson, 1975). It appears that the internal angle α is a much more reliable probe for the electronegativity of the substituent than the length of the C–X bond.

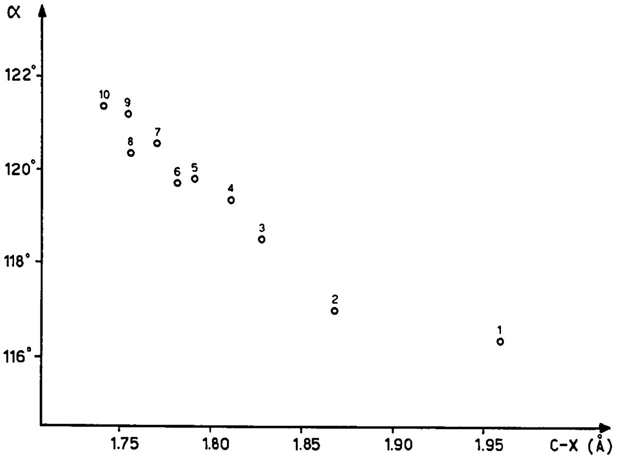


Fig. 3. Plot of the internal angle α *versus* the carbon to substituent bond length for the phenyl derivatives of second-row elements. The experimental points refer to the following classes of compounds: (1) phenylaluminum derivatives; (2) phenylsilicon derivatives; (3) phenyl derivatives of trivalent phosphorus; (4) phenylphosphonium ylids; (5) phenylphosphonium cations; (6) phenyl derivatives of bivalent sulphur; (7) phenylsulphonate anions; (8) phenylsulphonic esters and amides; (9) phenyl sulphones; (10) *para*-substituted chlorobenzenes.

4. Extension to other rows of the periodic table

4.1. *First-row elements*

Bond angle *versus* electronegativity correlations similar to that discussed in § 3.1 are expected to hold with the phenyl derivatives of elements belonging to other rows of the periodic table. With first-row elements, however, the pattern of deformations induced by substitution in the benzene nucleus is often complicated by the effect of conjugative interactions between the ring and the substituent. These cause the internal angle α to decrease, irrespective of whether the substituent is acting as a π donor or as a π acceptor (Domenicano, Vaciago & Coulson, 1975). Moreover, the electronegativities of first-row elements are much more sensitive to changes in both hybridization state and partial charge than those of second-row elements, as shown by the values of orbital electronegativities and charge coefficients tabulated by Huheey (1965).

In the light of these facts, it is not surprising that values of α as widely different as 117·1 (3)° and 122·7 (2)° have been reported for two 'N-substituted' benzene derivatives, namely *syn-p*-dimethylaminobenzaldoxime (Bachechi & Zambonelli, 1972) and *syn-p*-nitrobenzaldoxime (Bachechi & Zambonelli, 1973). The choice of a value of α typical of 'N-substitution' is clearly not obvious, and a similar difficulty is experienced with O.

Nevertheless, the existence of a correlation between the values of α and the electronegativities of first-row elements is indicated beyond doubt by the selected structural data of Table 10, all of which refer to compounds where conjugative interactions are presumed to give only a minor contribution, if any, to the C–X bond.

An alternative approach to the study of ring deformations in substituted benzene derivatives with first-row substituents is that of investigating the effect of the various functional groups on the ring geometry. Work is in progress along this line, with the aim of obtaining a set of reliable values of α for the most common functional groups, and studying their correlations with suitable physical parameters, such as group electronegativities and substituent constants (Domenicano, Mazzeo & Vaciago, 1975).

4.2. *Third-row elements*

The structural information available on the phenyl derivatives of elements heavier than Cl is much more scanty and less reliable than that analysed in the present paper, mainly because of the inherent difficulty of the X-ray diffraction technique in providing accurate positional parameters for the light atoms when heavier atoms are present. There is little doubt, however, that the trend observed with the phenyl derivatives of first- and second-row elements is maintained in the third row. A selection of reliable data is shown in Table 11: these data give a clear indication that the angle α is a regularly increasing function of the electronegativity of the substituent.

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