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Structural Chemistry of Substituted Benzene Derivatives

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Structural data for substituted benzene derivatives (bond lengths and angles) are summarised. A structural scheme of the deformation of σ bonds in the benzene ring under the influence of electron-donating and electron-accepting substituents is based on X-ray diffraction results. The general rule is revealed that the valence angle of a substituted carbon atom in the benzene ring increases with the nuclear potential of the substituents. A correlation is established between such angles and the Taft inductive constants. The structural characteristics of substituted benzenes are compared with those of metal complexes. A list of 258 references is included.

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I. INTRODUCTION

The present Review is based on X-ray diffraction data for crystals of substituted benzene derivatives, and is confined to a discussion of the nature of the intramolecular interaction between atoms. Questions of the packing of molecules in a crystal and the interaction of non-bonded atoms are not considered. Special monographs[1] and reviews have been devoted to the latter problem.

The modern theory of organic chemistry interprets the properties of molecules in terms of the displacement of valency electrons by inductive and conjugative mechanisms[2,3]. The electronic nature of chemical substituents was first characterised quantitatively by Hammett's σ_p and σ_m constants[4]. These constants were subsequently separated by Taft and Lewis[5] into components representing inductive σ_I and conjugative σ_R effects. Dewar and Grisdale[6] have since suggested that five mechanisms should be distinguished--the field σ-induction, π-induction, mesomeric, and electromeric effects--but Hammett[4] considers that there is no need to introduce more than two structural variables.

It is of great importance to place the qualitative electronic theory of organic chemistry on a quantitative basis by establishing correlations[7] between the structure and the physicochemical properties of a molecule. The chemical shifts δ_H and $\delta_{^{19}F}$ of the nuclear magnetic resonance spectra are adopted as sensitive measures of the effects of substituents on the distribution of electron density in the benzene ring. A correlation has been found between the chemical shifts and the Hammett constants.

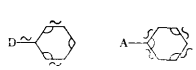
X-Ray structural investigations of the nature of the donor–acceptor interaction in organic molecules provide the most direct information for establishing a correlation between structure and physicochemical properties.

II. STRUCTURAL SCHEME OF SUBSTITUTED BENZENES

The benzene molecule is a regular hexagon in which the angles between the bonds are 120° and the carbon–carbon bond lengths are 1.392(4) and 1.398 Å according to X-ray[8] and neutron[9] diffraction respectively. The mean carbon–carbon bond lengths in aromatic compounds are 1.398(5)–1.395(3) Å.[10,11]

The influence of an acceptor substituent A on the geometry of a substituted benzene molecule was first established for nitro-derivatives by Trotter[12], Bailey and Prout[13], Carter, McPhail, and Sim[14], and many later investigators. The valence angle of the substituted carbon atom C(NO_2) in the ring has increased to a value that is independent of the angle of deflection of the nitro-group from the plane of the benzene ring, while the (NO_2)C–C bond length is shorter than in unsubstituted benzene. In a paper at the Ninth International Congress of Crystallography Hamilton[15] pointed out that donor substituents D—nitrogen, phosphorus, and antimony—diminish the C(D) bond angles and increase the (D)C–C bond lengths in the benzene ring. Papers both at the First All-Union Conference on Organic Crystal Chemistry[16] and at the Tenth International Congress of Crystallography[17] reported that the C(D,A) angles increase with the electronegativity of the elements along a period on passing from σ donors to σ acceptors, and also that they correlate with the Taft σ_I inductive constants.

A scheme of deformation of σ bonds in the benzene ring under the influence of electron-donating and electron-accepting substituents D and A was based[18] on X-ray diffraction data. According to the scheme the structure of such substituted benzenes can be represented as



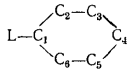
where a tilde represents a shortened carbon-carbon bond length, and an arc an increased valence angle at a carbon atom, in the ring. A consequence of the rehybridisation of σ bonds is an increased proportion of the p state of the hybrid sp^2 orbital of the carbon atom in an exocyclic A–C bond, with a resultant increase in the proportion of the s state in the adjacent (A)C–C bonds forming an angle exceeding 120° in the benzene ring. The increased proportion of the s state of the carbon atom leads to contraction of the bond. In an exocyclic D–C bond the proportion of the s state of the hybrid orbital of the carbon atom is increased, and also the proportion of the p state in the (D)C–C cyclic bonds, so that the angle they form is $< 120°$, while the (D)C–C bond becomes longer.

Such a view of the nature of atomic interaction in substituted benzenes reflects the general character of the structure of molecular compounds and is consistent with several published communications. As Bent showed[19], the *s* component of a hybrid orbital has a tendency to concentrate in those orbitals that are directed towards electropositive atoms. This conclusion is based on the results of a microwave spectral analysis of molecules of general formula HCO.R (where R = H, CH_3, OH, OCH_3, F), in which increase in the electronegativity of the substituent R is accompanied by contraction of the C–H and C=O bonds and increase in the H–C=O angle. A similar conclusion can be reached by quantum-chemical calculation[20]: formation of a D–A σ bond leads to decrease in the proportions of the *s* state of the electropositive atom D and of the *p* state of the electronegative atom A in comparison with the D–D and A–A σ bonds. Hence the populations of σ bonds can be written D(*p*)–(*s*)C and A(*s*)–(*p*)C. Since *p* electrons are more weakly bound to the atomic nucleus than are *s* electrons, an acceptor A acquires a *p* electron preferentially from the carbon atom, but a donor D donates a *p* electron preferentially to the carbon atom.

III. STRUCTURAL CHARACTERISTICS (BOND LENGTHS AND ANGLES)

In the most exact modern X-ray structural work the accuracy of the determination of interatomic distances and bond angles is respectively ±0.001–0.003 Å and ±0.1–0.3 deg. More detailed information on the accuracy of individual data can be found in the references cited. Systematic information on the crystal structures of organic molecules is given in works of reference[21-24]. The above structural scheme of the deformation of σ bonds in the benzene ring enables conclusions on the σ donor–acceptor character of a substituent L in any structure to be reached directly from the angle at the substituted carbon atom C(L) in the benzene ring.

1. Monosubstituted Benzene Derivatives



Experimental values are averages for the chemically equivalent valence angles at $C_{(2)}$ ($C_{(6)}$) and $C_{(3)}$ ($C_{(5)}$) and bond lengths $C_{(1)}$–$C_{(2)}$ ($C_{(1)}$–$C_{(6)}$), $C_{(2)}$–$C_{(3)}$ ($C_{(5)}$–$C_{(6)}$), and $C_{(3)}$–$C_{(4)}$ ($C_{(4)}$–$C_{(5)}$). It is difficult to judge from experimental results the extent to which the alternation of bond lengths and angles is transmitted to all atoms in the benzene ring. One difficulty is the thermal oscillation of the atoms, which becomes stronger on passing from the centre of gravity of the molecule to the terminal atoms, producing a tendency for their bonds to contract. In any case, changes in bond angles and lengths are more clearly defined for the three carbon atoms nearest the substituent. The changes in the angle at the substituted atom C(L) provide a considerably more sensitive criterion for regarding the substituent L as a donor D or an acceptor A than do the changes in bond lengths.

Alkyl substituents produce a sharp decrease below 120° in the cyclic angle at the carbon atom, and are thus strong σ donors. In tetraphenylmethane[25], triphenylmethane[26], diphenylaminotriphenylmethane[27], *N*-1′-phenylcyclohexylpiperidinium chloride[28], 3-diphenylacetoxy-1-ethylpiperidinium chloride[29], (+)-benzylmethyl-1-methyl-2-*N*′-phenylpropionamidoethylammonium bromide[30], and tribenzylamine[31] this angle is respectively 117.5°, 117.8°, 117.9°, 117.6°, 117.4°, 116.8°, and 117.4°.

Although hyperconjugation of methyl groups has been discussed in the literature, structurally the need for this hypothesis does not arise. In several cases it is advisable to use instead a mechanism of σ rehybridisation, since with donor substituents D the two mechanisms—σ rehybridisation and π conjugation—have the same effect on the structural characteristics of the benzene ring: the D–$C_{(1)}$ and $C_{(2)}$–$C_{(3)}$ bonds contract, the (D)$C_{(1)}$–$C_{(2)}$ bond becomes longer, and the cyclic $C_{(1)}$(D) angle becomes smaller.

Substituents containing multiple bonds C=C and C≡C also have a well defined σ-donor character. In structures possessing a substituent vinyl group—tetraphenylethylene[27], 1,2-diphenylcyclopentene[32], tetraphenylcyclopenta-1,3-diene[33], *trans*-stilbene[34], 2,3-diphenylindole[35], 2,5-distyrylpyrazine[36], *cis*-1,*cis*-3-distyrylazulene[37], anthr-9-yl styryl ketone[38], β-*p*-tolylthio-*trans*-cinnamic acid[39], chalcone[40], 1,6-diphenylocta-1,2,4,5-tetraene[41], and dicinnamyl disulphide[42]—the C(C : C) angles are respectively 118.7°, 117.6°, 118.3°, 118.1°, 118.9°, 117.7°, 118.2°, 118.5°, 118.6°, 118.2°, 117.5°, and 118.4°. The substituted carbon atoms in biphenyl[43], terphenyl[44], and quaterphenyl[45] have bond angles of 117.9°. In 1,8-bisphenylethynylnaphthalene[46] C(C : C) angle is 119.2°. Thus the vinyl group is a stronger σ donor than the ethynyl group, a result that is consistent with the chemical properties of these molecules.

The σ-acceptor power increases on passing from the vinyl to the carbonyl group. The C(C : O) angle in benzamide[47], acetyl benzoyl peroxide[48], ethylene dibenzoate[49], hippuric acid[50], and 2-hydroxy-4-methoxybenzophenone[51] is respectively 120.1°, 119.7°, 119.9°, 120.1°, and 119.8°. In *N*-diphenylmethyleneaniline[52] the C(C : N) and C(N : C) angles are respectively 119.2° and 119.9°; and in αα-*N*-triphenylnitrone[53] the C(C=N→O) and C(O←N=C) angles are 118.2° and 122.0°: the angle in the benzene ring is larger when the substituents bind through a nitrogen atom than through a carbon atom. Clearly, the nitrone group can act both as a strong σ donor and as a strong σ acceptor.

Table 1. Bond angles C(D, A) and nuclear potentials z^*/r of elements in monosubstituted benzene derivatives.

D, A	C(D, A), °	z^*/r	D, A	C(D, A), °	z^*/r
B	116.7	3.13	Al	116.4 (113.7)	2.78
C	117.5	4.21	Si	116.1	3.55
N	119.4	5.27	P	118.9 (117.6)	4.36
O	120.5	6.23	S	120.2	5.24
F	123.4	7.32	Cl	122.4	6.14
Ga	116.9	3.97			
Ge	118.3	4.62			

With respect to the donor–acceptor characteristics of heteroatoms differing in their electronic nature, Table 1 summarises the C(D, A) bond angles with donor D and acceptor A substituents, and compares them with the nuclear potentials of the elements z^*/r (where z^* is the effective charge on the nucleus and r the covalent radius

of the atom). Values of the angle are given for triphenylborane[54], tetraphenylmethane[25], aniline[55], phenol[56], fluorobenzene[57], di-μ-phenylbisdiphenylaluminium[58], tetraphenylsilane[59], pentaphenylphosphorane[60], diphenyl disulphide[61], chlorobenzene[62], triphenylgallane[63], and tetraphenylgermane[64,65].

The general rule is that the cyclic angle at the substituted carbon atom C(D,A) increases with the nuclear potentials of the substituents along a series in the Periodic System:

$$C(B)<C(C)<C(N)<C(O)<C(F)$$

$$C(Al)<C(Si)<C(P)<C(S)<C(Cl).$$

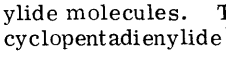
The C(D,A) angles of elements in the third and fourth periods are smaller than those in the second and fourth periods. The reason for such behaviour is that z^*/r increases monotonically along a period, and changes abruptly within a group[66,67].

In the main, Table 1 correctly reflects the trends in the variation of the bond angles of the elements. These tendencies can be revealed by analysing the experimental results for complicated structures. As examples the C(Si) angles in phenyl-triphenylsilyldiazomethane[68], chlorobis-π-cyclopentadienyl-triphenylsilylzirconium(IV)[69], 2,2-diphenyl-2-silaindane[70], and acetyltriphenylsilane[71] are respectively 117.1°, 117.0°, 117.6°, and 117.5°; the C(P) angles in *p*-dimethylaminophenyldiphenylphosphine[72], bisdiphenylphosphinoacetylene[73], and dimethylphenylphosphine[74] are 118.1°, 118.8°, and 117.7°; the C(Ge) angles in acetyltriphenylgermanium[75] and triphenylgermanium *p*-t-butylphenyl sulphide[76] are 118.3° and 118.9°; and the C(N,N) angles in tetraphenylhydrazine[27] and 1-phenyl-thiosemicarbazide[77] are 119.1° and 119.2°. The number of known structures containing elements of the fifth series as substituents is still small.

The formation of double bonds with carbon, oxygen, and sulphur atoms increases the σ-acceptor power of heteroatoms. This is observed in the structures of methylenetriphenylphosphorane[78] (in which the C(P:C) angle is 119.1°), bistriphenylphosphoranylidenemethane[79] C(P:C:P) 119.2°, triphenylphosphine oxide[80] C(P:O) 118.9°, *p*-chloro- and *p*-bromo-phenyldiphenylphosphine oxides[81,82] and the corresponding phosphine sulphides[83,84]—C(P:O) 119.1° and 119.7°; and C(P:S) 119.5° and 119.2°—phenylsulphinylacetamide[85] C(S:O) 121.6°, diphenyl disulphone[86] $C(SO_2.SO_2)$ 122.5°, and 3-methyl-3-phenylsulphinylbutan-2-ol[87] C(S:O) 120.3°.

A significant increase in σ-acceptor power occurs with increase in the positive charge on the heteroatom. In the case of the nitrogen atom, however, the same effect may be produced by loss of π conjugation with the benzene ring due to steric hindrance. We note increases in the C(N.C:O) angle in *N*-phenylacetanilide[88], (+)-benzylmethyl-1-methyl-2-*N'*-phenylpropionamidoethylammonium bromide[30], *N*-methylacetanilide[89], and isonitrosoacetanilide[90] (120.2°, 120.2°, 122.8°, and 120.2°); and the C(N.C:S) angle in 4-phenyl-thiosemicarbazide[91] is larger than the C(N.N) angle in 1-phenyl-thiosemicarbazide[77] (121.1° and 119.2°).

The fact that the charges on substituents influence the deformation of the benzene ring has been established in ylide molecules. The structure of triphenylphosphonium cyclopentadienylide[92] shows an increase in the



angle 119.6° in conformity with the charge on the phosphorus atom of +0.69 e, found by phostoelectronic spectroscopy. Still larger increases in angles have been established in triphenyl-*N*-toluene-*p*-sulphonyliminophosphorane[93] C($P^+.N^-$) 120.1° and *SS*-diphenyl-*N*-toluene-*p*-sulphonylsulphidimine[94] C($S^+.N^-$) 121.1°.

The C(As^+) angle of 121.7° in tetraphenylarsonium triiodide[95] and the C(P^+) angles of 119.9° and 120.0° in tetraphenylphosphonium[96] and methyltriphenylphosphonium bistetracyanoquinodimethanes[97] suggest that positively charged arsenic and phosphorus atoms lose their σ-donor properties. The positively charged iodine atom in diphenyliodonium nitrate[98] remains a strong σ acceptor with C(I^+) 122.4°, but negatively charged boron and indium atoms remain strong σ donors, as is indicated by C(B^-) angles of 114.1° and 116.3° in π-cyclopentadienyl-η-ruthenium(II) tetraphenylborate[99] and bis(trimethyl phosphito)-rhodium(I) tetraphenylborate[100] and by a C(In^-) angle of 118.2° in sodium tetraphenylindate[101]. The dependence of the C(P) angles on the partial charges on the phosphorus atoms in substituted benzenes has been reported[102].

The accurate experimental data that have now accumulated are still insufficient as a basis for quantitative conclusions on the σ bonds of all metals in the Periodic System. Evidence that the atoms of transition metals are among the strongest σ donors is provided e.g. by the angles C(Zn) 115.8°, C(Ni) 115.9°, and C(Cr) 115.2° in bis[phenyl(acetylacetonato)zinc]-bis(acetylacetonato)zinc[103], phenyl-(π-cyclopentadienyl)(triphenylphosphine)nickel[104], and *cis*-diphenylbis-2,2'-bipyridylchromium iodide[105].

2. Disubstituted Benzene Derivatives

It is of interest to trace the changes in structural characteristics as the number of substituents is successively increased. The donor–acceptor characteristics of disubstituted benzenes differ according to the orientation of the substituents. The structures of *para*-substituted benzenes have been the most thoroughly studied.

para-Disubstituted derivatives

As in monosubstituted benzene derivatives the angles at the carbon atoms in *para*-disubstituted derivatives indicate that alkyl substituents are strong σ donors. Thus the $C(CH_3)$ and $C(CH_2)$ angles in di-*p*-tolyl disulphide[106], *p*-bitolyl[107], toluic acid[108], nitrotoluene[109], cresol[110], 1,1-di-*p*-tolylethylene[111], di-*p*-tolylcarbodi-imide[112], the enolic form of ω-*p*-tolylacetophenone[113], β-*p*-tolylthio-*trans*-cinnamic acid[39], ethyl *N*-methyl-*N*-*p*-tolylsulphonylmethylcarbamate[114], (+)-methyl *p*-tolyl sulphoxide[115], propenyl *p*-tolyl sulphone[116], triphenyl-*N*-toluene-*p*-sulphonyliminophosphorane[93], [8]paracyclophane-4-carboxylic acid[117], trisdiphenylmethane-*pp'*-diamine[118], and acetotoluidine[119] are respectively 117.3°, 117.8°, 118.5°, 117.5°, 117.8°, 118.0°, 117.7°, 118.2°, 117.8°, 118.8°, 118.2°, 118.6°, 117.5°, 117.6°, 118.6°, and 117.5°. Similarly to monosubstituted benzene derivatives, the C(C≡C) angle of 119.4° in *p*-diethynylbenzene[120] is larger than the C(C:C) angle in the presence of a vinyl group in 1,1-di-*p*-tolylethylene[111], diethylstilboestrol[121], [2.2](2,6)pyridinoparacyclophane-1,9-diene[122], and 1,6-di-*p*-chlorophenyl-3,4-dimethylhexatriene[123]—117.9°, 118.2°, 117.5°, and 118.0°.

An advantage of X-ray structural analysis in comparison with other methods—both physical and chemical—is that comparison of the angles at the carbon atoms in the benzene

ring provides an exceptional opportunity for determining the relative σ donor–acceptor characteristics of different substituents in the same molecule. Thus in tetra-*p*-tolyltin[124] the σ-donor power of the tin atom exceeds that of the methyl group: C(Sn) 116.4° and C(CH_3) 117.3°. The structure of trisdiphenylmethane-*pp'*-diamine-sodium chloride[118], with angles C(CH_2) 118.6° and C(NH_2) 119.2°, shows that methylene is a stronger σ donor than is the amino-group. Examination of the structures of *p*-dimethylaminophenyldiphenylphosphine[72] and *p*-dimethylaminophenyl phenyl sulphide[125] reveals that in the former the phosphorus atom is a stronger σ donor than is the dimethylamino-group, for C(P) 116.9° and C[$N(CH_3)_2$] 117.5°, and that in the latter structure the dimethylamino-group is a stronger σ donor than is the sulphur atom, since C[$N(CH_3)_2$] 117.8° and C(S) 118.4°.

Table 2. Bond angles C(D) and C(A) in *para*-substituted hydroxy- and alkoxy-benzenes.

Compound	D	A	C (D), °	C (A), °
Cresol[110]	CH_3	OH	117,8	120,4
Anisidine[128]	NH_2	OCH_3	118,4	120, 2
Diethylstilboestrol[121]	C=C	OH	118,2	120, 2
trans-pp'-Diethoxyazobenzene[129]	N=N	OC_2H_5	119,5	120,5
Hydroxyacetanilide[130]	N—$COCH_3$	OH	119,8	120,2
Hydroxyacetanilide[131]	COOH	OH	117,7	120,3
Methoxybenzoic acid[132]	COOH	OCH_3	119,7	120,4
Ethoxybenzoic acid[133]	COOH	OC_2H_5	118,7	120,4
n-Butoxybenzoic acid[134]	COOH	OC_4H_7	118,9	120,2
Potassium hydrogen bis-*p*-hydroxybenzoate monohydrate[135]	COOH	OH	119,6	120,7
Pyridinium hydroxybenzoate[136]	COO^-	OH	118,2	119,5

Further, comparison of the angles in terephthalic acid[126] and γ-quinol[127]—C(COOH) 120.4° and C(OH) 121.0°—shows that hydroxyl is a stronger σ acceptor than is carboxyl. This is confirmed by Table 2, which indicates that hydroxyl, methoxyl, ethoxyl, and butoxyl are weak σ acceptors in comparison with such σ donors as methyl, amino, ethylenic, azo, acetylimino, and carboxyl groups.

Table 3. Bond angles C(D) and C(NO_2) in *para*-substituted nitrobenzenes.

Compound	D	C (D), °	C (NO_2), °
Nitrotoluene[109]	CH_3	117,5	122,7
Nitrobenzoic acid[141]	COOH	119,8	122,6
α-Nitrophenol[142]	OH	120,9	122,3
β-Nitrophenol[143]	OH	120,5	122,0
α-Di-*p*-nitrophenyl disulphide[144]	S	119,0	122,7
1,1-Di-*p*-nitrophenylethylene[145]	C=C	118,3	122,2
Nitrobiphenyl[146]	C_6H_4—C_6H_4	118,6	122,2
syn-p-Nitrobenzaldehyde oxime[147]	C=N—OH	119,2	122,7
Nitroacetophenone[148]	$COCH_3$	118,4	121,7
Nitrophenyl acetate[149]	$COOCH_3$	120,7	121,5
D-*p*-nitrophenylcarbodi-imide[150]	N=C=N	120,4	122,1
N-Ethyl-*N*-*p*-nitrophenylcarbamoyl chloride[151]	N(C_2H_5)COCl	120,5	123,8

As in monosubstituted benzene derivatives, the silicon atom is one of the strongest σ donors. Therefore the C(Si) angle in *p*-bistrimethylsilylbenzene[137] is 115.8°. The azoxy-group in *p*-azoxyanisole[138] has a dual role: it acts both as a σ donor with C(N :NO) 119.1° and C(OCH_3) 119.6°, and as a σ acceptor, with C(NO :N) 121.1° and C(OCH_3) 119.9°. The σ-acceptor properties of the azo-group are exhibited in *S*-methyldithiazone[139], with C(N :N) 120.2° and C(N.N) 119.1°, and especially in benzenediazonium-*p*-sulphonate[140], with C(N^+≡N) 125.4° and C(SO_3^-) 121.0°. Data on the C(NO_2) angles in *para*-substituted nitrobenzenes are listed in Table 3.

Sulphonyloxy, sulphonyl, and sulphinyl groups act as σ acceptors: in *cis*-4-t-butylcyclohexyl toluene-*p*-sulphonate[152] C(SO_3) 120.6° and C(CH_3) 117.7°, ethyl *N*-methyl-*N*-*p*-tolylsulphonylmethylcarbamate[114] C(SO_2) 121.1° and C(CH_3) 118.8°, propenyl *p*-tolyl sulphone[116] C(SO_2) 120.7° and C(CH_3) 118.6°, β-sulphanilamide[153] C(SO_2NH_2) 120.5° and C(NH_2) 118.7°, and in (+)-methyl *p*-tolyl sulphoxide[115] C(SO) 120.3° and C(CH_3) 118.2°. However, in *N*-dimethylsulphoniotoluene-*p*-sulphonamide[154] C($SO_2.N^-.S^+$) 119.7° and C(CH_3) 118.9°, and in triphenyl-*N*-toluene-*p*-sulphonyliminophosphorane[93] C($SO_2.N^-.P^+$) 119.7°, so that the sulphonyl group has lost its σ-acceptor properties in structures of the ylide type.

The C($SOCH_3$) angle of 120.3° in (+)-methyl *p*-tolyl sulphoxide, indicating that the sulphinyl group is not a strong σ acceptor, was inconsistent[115] with the Hammett σ_p constants, according to which the acceptor power of the methylsulphinyl group exceeds that of the chlorine atom. This discrepancy remains even with the Taft constants: σ_I(Cl) = +0.40 and σ_I(SO.CH_3) = +0.49. The C(Cl) angle of 122.1° in γ-*p*-chlorobenzene[155] shows that the chlorine atom is a strong σ acceptor. Closely similar C(Cl) angles were obtained in *p*-chlorobenzoic acid[156] C(Cl) 122.1° and C(COOH) 119.9° and in α-chlorophenol[157] C(Cl) 122.4° and C(OH) 121.1°. The C(Cl) angle in the latter compound coincides with C(Br) in 1-*p*-bromophenylbutane-1,3-dione[158]: C(Br) 122.4° and C(C :O) 119.3°.

Table 4. Mean bond angles C(D,A) for elements in the second period.

D, A	C (D, A), °	D, A	C (D, A), °	D, A	C (D, A), °
$B^-(C_6H_5)_3$	114.1	$COCH_3$	118.8	N^+H_3	121.6
$N(CH_3)_2$	117.2	$CONH_2$	119.8	CN	121.8
C_6H_5	117.6	COOH	119.8	NO_2	122.1
CH=CH_2	118.0	OCH_3	119.9	F	123.4
CH_3	118.1	N=N—C_6H_5	120.0	N^+≡N	124.9
NH_2	118.4	OH	120.2		

It is worth noting the mean angles C(D,A) for elements of the second period in the structures of monosubstituted and *para*-disubstituted benzene derivatives (Table 4) given in a paper[17] and in a review[159]. The standard deviations of the angles are 0.1–0.2 deg. However, there are certain discrepancies. In particular, the σ-donor power of the methyl group exceeds that of the vinyl group[7]—$\sigma_I(CH_3)$ = −0.08 and σ_I(CH :CH_2) = +0.01—so that the C(CH_3) angle should be smaller than the C(CH :CH_2) angle.

A linear relation has been reported in a review[160] between the mean C–D and C–A bond lengths and the C(D) and C(A) angles for elements in the third period: silicon (1.8683 Å, 116.98°), phosphorus (1.8276–1.7908 Å, 118.50–119.78°), sulphur (1.708–1.7534 Å, 119.73–121.19°), and chlorine (1.7404 Å, 121.37°). Table 1 shows that the

correlation between C–(D,A) and C(D,A) is due to the increase in the nuclear potential z^*/r caused by the decrease in the radius r and the increase in the effective charge on the nucleus z^* for the atoms along the period.

meta-Disubstituted derivatives

Available data on the structures of *meta*-disubstituted benzene derivatives confirms the σ-donor nature of the methyl group in cresol[161] C(CH_3) 118.7°, the amino-group in nitroaniline[162] C(NH_2) 119.6°, the dimethylamino-group in nitro-*NN*-dimethylaniline[163] C[$N(CH_3)_2$] 117.7°, the carboxy-group in isophthalic acid[164] C(COOH) 119.8°, and the amino-group in *o*-*m*'-trifluoromethylanilinobenzoic acid[165] C(NH) 118.8°. In contrast to this, a σ-acceptor nature has been found for the amino-group in aminophenol[166] C(NH_2) 120.9°, the hydroxy-group in resorcinol[167], cresol, aminophenol, and hydroxybenzamide[168] C(OH) 121.1°, 121.7°, 121.5°, and 120.5°, the chlorine atom in potassium hydrogen bis-*m*-chlorobenzoate[169] C(Cl) 122.4°, the iodine atom in *p*-*m*'-iodophenylbenzoic acid[170] C(I) 121.3° and C(C_6H_4) 117.6°, the ammonio-group in *m*-carboxyanilinium chloride[171] C(NH_3^+) 121.7°, the nitro-group in dinitrobenzene[172], *m*-nitroperchlorylbenzene[173], nitroaniline, and nitro-*NN*-dimethylaniline C(NO_2) 123.6°, 124.1°, 122.3°, and 124.4°, the trifluoromethyl group in *o*-*m*'-trifluoromethylanilinobenzoic acid[165] C(CF_3) 121.8°, and the sulphamoyl group in *m*-sulphamoylanilinium chloride[174] C(SO_2NH_2) 121.7°.

ortho-Disubstituted derivatives

Significant steric hindrance is present between *ortho*-substituents. The σ donor–acceptor characteristics of donor D and acceptor A substituents differ more markedly when their mutual orientation is *ortho* than in the *para*- and *meta*-derivatives. The close proximity of the D and A substituents is responsible for an increase in the C(A) angle and a related decrease in the C(D) angle. Thus among the cresols the difference between these angles diminishes on passing from the *ortho*- to the *meta*- and the *para*-isomers: C(OH) 121.7°, 121.7° and 120.4° respectively; and C(CH_3) 117.0°, 118.7°, and 117.8°.[175] In *o*- and *p*-nitrobenzoic acids[176] the C(NO_2) angle is respectively 123.7° and 122.8°, while C(COOH) is 116.2° and 121.2°: i.e. the difference between corresponding angles C(A) and C(D) increases on passing from the *para*- to the *ortho*-derivative, although the angle φ of rotation of the plane of the nitro-group relative to that of the benzene ring is larger in the *ortho*- than in the *para*-isomer (54.3° and 24.1°).

Data on the structure of *o*-ethoxybenzoic acid[177]—C(OC_2H_5) 120.8° and C(COOH) 118.0°—are consistent with results for the *para*-derivatives: i.e. the ethoxy-group surpasses the carboxy-group in σ-acceptor power. This is observed also in salicylic acid[167,178]—C(OH) 119.5° and C(COOH) 119.1°—though the difference is less marked. As was to be expected, a still larger difference between the angles C(OH), C(OCH_3), C(COOH) and the angles C(CH_3), C(CH), C(CH_2) has been established in cresol[175], 1,1,2,2-tetrakis-*o*-methoxyphenylethane[179] C(OCH_3) 120.5° and C(CH) 117.4°, and in toluene-α,2-dicarboxylic acid[180] C(COOH) 120.3° and C(CH_2COOH) 116.1°. In salicylaldehyde oxime[181] the angles are C(OH) 119.6° and C(C :N.OH) 118.0°, since the hydroxyimino-group occupies a position intermediate between the carboxyl and methyl groups. It is noteworthy that, despite the difference between the angles of rotation of the carboxylate groups around carbon-carbon bonds (32° and 71°), both the C(COO^-) angles in diammonium phthalate[182] are 119.3°.

The identity of the cyclic angles at the substituted carbon atoms in *o*-hydroxymethanesulphonanilide[183]—C(OH) 120.6° and C($NHSO_2$) 120.8°—suggests approximate equality of the σ-acceptor powers of the substituents. There are examples of variation in the angles of nitrogen-containing substituents: thus in *trans*-*oo*'-dichloroazobenzene[184] C(N.N) 118.6° and C(Cl) 121.3°, *o*-chlorohydroxyiminoacetanilide[185] C(N.C :O) 118.6° and C(Cl) 121.0°, *o*-ethoxyhydroxyiminoacetanilide[186] C(N.C :O) 120.3° and C(OC_2H_5) 119.8°, *o*-phenylenediamine hydrochloride[187] C(NH_3^+) 122.3° and C(NH_2) 117.1°, *NN*-dimethylanthranilic acid[188] C[$N^+H(CH_3)_2$] 122.5° and C(COO^-) 117.0°, potassium *o*-nitrophenoxide hemihydrate[189] C(NO_2) 122.5° and C(O^-) 115.2°, nitrobenzamide[190] C(NO_2) 122.1° and C($CONH_2$) 118.8°, and 4-acetyl-2'-nitrobiphenyl[191] C(NO_2) 123.3° and C(C_6H_4) 115.6°. Since the iodine atom is a weaker σ acceptor than is the nitro-group, a smaller difference between the angles C(A) and C(D) is observed in *p*-*o*'-iodophenylbenzoic acid[192]—C(I) 122.6° and C(C_6H_4) 117.9°—than in the corresponding nitro-derivative.

The structures of the racemate[193] and an optically active form of (–)-*o*-methylsulphinylbenzoic acid[194], with C(S :O) 119.8°, 119.5° and C(COOH) 118.0°, 118.4°, orthanilic acid[195] C(SO_3^-) 119.2° and C(NH_3^+) 120.6°, and sulphobenzoic acid trihydrate[196] C(SO_3^-) 119.6° and C(COOH) 118.4° clearly show that the sulpho and sulphinyl groups are σ donors.

It is significant that the introduction of two acceptors in the *ortho*-position leads to a mutual weakening of their σ-acceptor power. Thus in *o*-phenylenediammonium dichloride[197] and dibromide[198] the C(NH_3^+) angles are respectively 120.1° and 119.4°. The hydroxyls in catechol[199] are weaker σ acceptors than are those in resorcinol and quinol: C(OH) 119.9°, 121.1°, and 121.0°.

3. Trisubstituted Benzene Derivatives

Trisubstituted benzenes retain the characteristic features of the variation in bond angles inherent in *meta*- and *ortho*-derivatives. Closely similar C(NO_2) angles (123.4° and 123.6°) have been found in 1,3,5-trinitrobenzene[200] and in *m*-dinitrobenzene[172]. The acetyl group remains a weak σ donor in 1,3,5-triacetylbenzene[201] C($COCH_3$) 119.8°. As was to be expected, the σ-acceptor power of nitro- and hydroxy-groups and of fluorine and chlorine atoms is increased by the introduction of σ donors into the *ortho*-position. This is readily seen from a comparison of the C(A) and C(D) angles in *N*-methyl-*m*-nitro-*p*-toluidine[202] with C(CH_3) 114.3°, C(NO_2) 124.1°, and C($NHCH_3$) 117.3°, 2,5-dimethylphenol[203] C(OH) 121.5° and C(CH_3) 116.6° and 117.3°, (±)-2-(2-fluorobiphenyl-4-yl)propionic acid[204] C(CC_6H_5) 117.1°, C(F) 123.9°, and C(C) 119.6°, and 3-chloro-*NN*-dimethyl-4-nitrovinylaniline[205] C(C :C) 113.0°, C(Cl) 125.7°, and C[$N(CH_3)_2$] 116.6°. Another striking fact is that the σ-acceptor power of the bromine atom is diminished by the introduction of an *o*-nitro-group and an *o*-sulpho-group respectively in 4-bromo-*N*-methyl-3-nitroaniline[202], with C(Br) 116.1°, C(NO_2) 122.4°, and C($NHCH_3$) 118.0°, and in the trihydrate of 2,5-dibromobenzenesulphonic acid[206] C(Br) 120.2° and 122.8° and C(SO_3^-) 119.9°, since the C(Br) angle *ortho* to C(SO_3^-) is smaller than the *meta*-C(Br) angle.

Among 1,2,3-derivatives pyrogallol[207]—C(OH) 120.7°, 119.8°, and 121.2°—has C(OH) angles at positions 1 and 3 that are closely similar to those (121.0° and 121.1°) in γ-quinol and resorcinol, whereas the C(OH) angle at position 2 is close to those in catechol (119.9°). In hemimellitic acid dihydrate[208], despite the marked difference in angles of rotation of the planes of the carboxyls relative to that of the benzene ring (the angles φ at positions 1–3 are respectively 9.6°, 87.2°, and 4.1°), the C(COOH) angles are also larger at positions 1 and 3 (119.7° and 120.0°) than at position 2 (118.9°).

Hydroxyl, ethylenic, and methyl groups undergo greater increase in σ-donor power when located between two σ acceptors: in 2,6-dinitrophenol[209] C(OH) 116.0° and C(NO_2) 122.3° and 121.9°; in 1-(2,6-dichlorophenyl)-4-phenylbuta-*trans*-1,*trans*-3-diene[210] C(C :C) 114.6° and C(Cl) 122.8° and 123.9°; and in 3-bromo-2-methylphenol[211] C(CH_3) 114.4°, C(OH) 124.9°, and C(Br) 124.5°.

Comparison of the structures of 2,3-dimethylphenol[211, 202]—C(OH) 122.4° and C(CH_3) 118.1° and 119.7°—and of 2,3-dimethylbenzoic acid[212]—C(COOH) 121.3° and C(CH_3) 117.4° and 120.3°—clearly shows, as a consequence of the location of hydroxy- and carboxy-groups *ortho* to the methyl groups, the sequence OH > COOH > CH_3 according to their σ-acceptor power, which is consistent with conclusions reached from mono- and di-substituted derivatives.

The difference between the C(O) angles is especially clearly developed in the oxygen bridge in 1-t-butyl-2-(2,6-dinitrophenoxy)benzene[213]: *ortho* to the t-butyl group as σ donor C(O) 123.9°, but *ortho* to two σ-acceptor nitro-groups C(O) 116.2°.

4. Tetrasubstituted Benzene Derivatives

Among 1,2,4,5-tetrasubstituted benzene derivatives—tetra-t-butylbenzene[214], durene[215], pyromellitic acid dihydrate[216], and tetracyanobenzene[217]—the σ-acceptor power increases in the sequence

C($C(CH_3)_3$) 115.1°<C(CH_3) 118.2°<C(COOH) 119.7°<C(CN) 121.3°.

In 3,4,5-trimethylbenzoic acid[218], of course, the C(COOH) angle is 119.7°, but when the hydroxyl is located *ortho* to two t-butyl groups in 2,6-t-butyl-4-methylphenol[211], and a carboxyl is *ortho* to two methyl groups in mesitoic acid[219], the C(OH) angle increases to 122.6°, and C(COOH) to 120.7°. Similarly, the arrangement of a nitro-group *ortho* to two methyl groups in 3,5-dimethyl-4-nitrobenzoic acid[220] has increased the C(NO_2) angle to 124.8°, and diminished the C(CH_3) angles to 116.6°. The introduction of two nitro-groups or two chlorine atoms yields the respective angles—in 4-methyl-3,5-dinitrobenzoic acid[221] C(CH_3) 114.1° and C(NO_2) 124.3°, in 2,6-dichloro-4-nitroaniline[222] C(NH_2) 115.2° and C(Cl) 123.0°, and in 2,4,6-trichlorobenzonitrile[223] C(C≡N) 117.6° and C(Cl) 123.6°.

In 1,2,3,5-tetrasubstituted benzenes containing three nitro-groups the presence of such strong σ acceptors at positions 1 and 3 leads to smaller angles at position 2 substituted by a σ-donor or a weaker σ-acceptor substituent. Therefore in picryl chloride[224], *NN*-difluoro-2,4,6-trinitroaniline[225], 2,4,6-trinitrophenetole[226], *N*-methyl-2,4,6-trinitroacetanilide[227], and in the anion of 2,4,6-trinitrobenzenesulphonic acid tetrahydrate[228] $H_5O_2^+C_6H_2(NO_2)_3SO_3^-$. $2H_2O$, as the angle at position 1 decreases—C(Cl) 117.0°, C(NF_2) 116.8°, C(OR) 116.4°, C(N.C :O) 115.4°, and C(SO_3^-) 115.1°—the angles at positions 2 and 6 correspondingly increase: C(NO_2) 122.4°, 122.6°, 122.8°, 123.5°, and 123.7°.

Variation in σ donor–acceptor characteristics is clearly exhibited in a series of structures containing bridging substituents[229–233]. Thus in methyl 3-nitro-4-(2,4,6-trimethylbenzyl)benzoate, 3-nitro-4-(2,4,6-trimethylbenzoyl)benzoate, 4-mesitylthio-3-nitrobenzoate, 4-mesitylsulphinyl-3-nitrobenzoate, and 4-mesitylsulphonyl-3-nitrobenzoate the C(CH_2), C(C :O), C(S), C(S :O), and C(SO_2) angles are respectively 119.5°, 120.6°, 121.5°, 121.6°, and 121.5° with these groups *ortho* to two methyl groups, but 114.8°, 116.7°, 115.5°, 117.9°, and 117.7° when *ortho* to the nitro-group.

A comparison[227] of structures differing in the angle of rotation of the N–C=O group relative to the plane of the benzene ring—acetanilide[234] (N–C_{Ar} 1.413 Å, C(N.C :O) 119.6°, and φ = 17.6°), *N*-methyl-2,4,6-trinitroacetanilide (1.417 Å, 115.4°, and 61°), and *N*-methylacetanilide (1.481 Å, 122.8°, and 90°)—has shown that the $N^{\delta+}$–C=$O^{\delta-}$ group develops strong σ-acceptor power in the third structure as a consequence of the absence of π conjugation, but in the second structure the overlap of the π orbitals of the nitrogen atom and the ring carbon atom is less than one-quarter of the maximum value (cos 60° = 0.25), so that the decreases in the C(N.C : O) angle and the N–C_{Ar} bond length must be attributed to the σ-acceptor power of the nitro-groups. A similar effect is observed in 2-chloro-4,6-dinitrophenol[235], since the O–C bond is shorter than in phenol (1.333 and 1.383 Å) owing to the decrease in the C(OH) angle from 120.5° to 116.7°. A linear relation has been established between the acid strength pK_a and the C–OH bond length in substituted benzenes[235]. For example, the dissociation constant increases by a factor of 10^8 on passing from phenol to 2-chloro-4,6-dinitrophenol. It may be supposed that an increase in the contribution by the *s* state of the hybrid orbital of the carbon atom in the C–OH bond leads to an increase in the acid strength.

5. Penta- and Hexa-substituted Benzene Derivatives

On passing further sterically overcrowded molecules having five or six substituents in the benzene ring, we again see mainly a trend to preservation of the cyclic angles characteristic of the σ nature of electron-donating and electron-accepting substituents. The typical features of *ortho*-substituents noted in preceding subsections are also maintained.

In 2,4,6-trinitro-1,3-xylene[236] the angles are C(CH_3) 114.2° in the 1 and 3 positions, with C(NO_2) 127.2° (φ = 75.2°) at the 2 position and 122.4° (35.7°) at the 4 and 6 positions; in 4-bromo-*N*-methyl-2,6-dinitro-3-toluidine[237] C($NHCH_3$) 112.0°, C(CH_3) 115.0°, C(Br) 123.5°, and C(NO_2) 127.0° (φ = 73°) and 122.5° at positions 2 and 6. Hence the ring angles at nitro-substituted carbon atoms differ from those at atoms substituted by methyl and by a methylamino-group by 13° and 15° respectively, in agreement with their tendency to maintain the σ-bond angles of D and A substituents. An analogous phenomenon is observed in the structure of 2,4,6-trimethyl-3-pivaloylbenzoic acid[238]: C(CH_3) 117.6°, 117.3°, and 116.7°, C(COOH) 121.7°, and C(CO) 121.8°.

In hexasubstituted benzenes steric hindrance also has a significantly weaker effect than has σ rehybridisation. Thus in pentafluorobenzoic acid[219] the C(COOH) angle of 116.7° has diminished, and the C(F) angles of 121.7° at

positions 2 and 6 are larger than the C(F) angles of 119.9–120.0° at positions 3, 4, and 5; in tetrakispentafluorophenylgermanium[239] C(Ge) 115.6° and C(F) 122.7° and 119.0–120.3°; and in decafluorobiphenyl[240] C(CF_5) 116.3° and C(F) 122.1° and 119.7–120.1°. In 3-amino-6-ethylpyromellitonitrile[241] the angles increase in the sequence C(NH_2) 116.2°, C(C_2H_5) 116.3°, and C(CN) 121.3° and 122.4°.

Further refinement of the structure of hexachlorobenzene[242] has established that the carbon–carbon bond lengths (1.393 ± 0.002 Å, with temperature correction 1.401 Å) differ insignificantly from those in the unsubstituted benzene molecule. The carbon–chlorine bond lengths in substituted aromatic and quinonoid rings[243] are significantly shorter (mean distance 1.709 Å) when in the *ortho*-position and when more distantly separated or when isolated (mean 1.737 Å). The carbon–chlorine bond length in the overloaded hexachlorobenzene molecule (1.715 ± 0.002 Å, with temperature correction 1.722 Å) is shorter than an isolated bond. The steric effect should have increased the bond lengths in the overloaded molecules owing to mutual repulsion of the chlorine atoms. It is more correct to suppose that the possibility of σ rehybridisation is greater for well separated or isolated bonds, since the increase in the proportion of the *p* state of the carbon atom in the bonds is balanced, as a consequence of the strong σ-acceptor power of the chlorine atom, by an increase in the proportion of the *s* state of the carbon atom in the benzene ring. In hexachlorobenzene such a possibility of σ rehybridisation is excluded because all the carbon bonds in the ring are 120.0°, so that the carbon–chlorine bonds remain shortened owing to the excess content of the *s* component of the carbon atom in them. For the same reason the carbon–chlorine bond length should be increased by increase in the C(Cl) angle, as is observed on comparing the structure of picryl chloride C(Cl) 117.0° and C–Cl 1.709 Å with that of 2,6-dichloro-4-nitroaniline 123.0° and 1.743 Å. In decachlorobiphenyl[244], in which the dihedral angle between the phenyl rings is 86.7°, and the bond angles are C($C_6H_5Cl_5$) 118.7° and C(Cl) 121.0°, 118.9°, and 121.7°, the mean carbon–chlorine bond length somewhat exceeds the bond length in hexachlorobenzene (1.718 and 1.715 Å).

Table 5. Bond lengths (Å) and angles (°) in *para*-substituted anilines with the Hammett σ_p constants of the substituents.

Substituent	N–C_1	C_1–C_2	C_2–C_3	C_3–C_4	C_6–C_1–C_6	C_1–C_2–C_3	C_2–C_3–C_4	C_3–C_4–C_5	σ_p
NH_2	1.408	1.389	1.377	1.389	117.1	121.4	121.4	117.1	−0.47
COOH	1.380	1.399	1.375	1.398	119.3	120.8	121.1	118.3	+0.38
SCN	1.376	1.393	1.373	1.385	118.1	121.1	119.8	119.6	+0.52
SO_2NH_2	1.385	1.402	1.381	1.393	118.7	120.8	119.7	120.5	+0.55
NO_2	1.371	1.412	1.375	1.390	118.9	120.5	119.5	121.2	+0.76

IV. X-RAY σ CONSTANTS

It appears reasonable to adopt the structural characteristics of molecules as the basis for constants representing their reactivity. We shall apply the special term "X-ray σ constants" to the C(D) and C(A) bond angles, the problem of which requires special discussion.

A linear dependence exists between the mean bond angles C(D,A)[17,160] and the Taft induction constants σ_I (Fig. 1), values of which have been taken from a monograph[7]. Comparison of these angles in various structures has established relative series of σ-acceptor and σ-donor substituents.

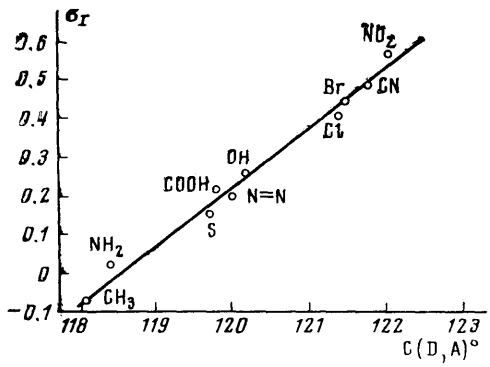


Figure 1. Dependence of induction constants σ_I on bond angles C(D,A).

Insignificant π conjugation of the nitro-group with the benzene ring can be assumed in *p*-nitrotoluene and *p*-nitrobenzoic acid (C–NO_2 1.482 and 1.491 Å). However, the data in Table 5[245–249] are consistent with the view that D and A substituents influence the distribution of C(A) bond angles in *para*-substituted anilines (C–NH_2 1.408–1.371 Å) even when π interaction is superimposed on σ interaction.

When π conjugation of D and A substituents with the benzene ring is insignificant, the bond angles C(D,A) will obviously determine directly the induction effect σ_I of the substituent. Such π conjugation is most strongly developed among elements in the second period, especially by the nitrogen atom. The plot of carbon–nitrogen bond length against the C(N) angle (Fig. 2) has a straight segment indicating a linear relation between σ rehybridisation and π conjugation. Hammett's equation $\lg(K/K_0) = \rho\sigma$ (where K and K_0 are equilibrium constants of the chemical reaction) is based[252] on the linear relation between changes in free energy. The hypothesis[253] of a linear dependence between σ rehybridisation and π conjugation enables the bond angles C(D,A) to be used instead of Hammett σ constants. The correctness of this approach is supported by the linear correlation of the C(D,A) angles[160] with the nuclear potentials z^*/r for elements in the second, third, and fourth periods (Fig. 3). Hence these angles obey a periodic law. The C(N) and C(O) angles plotted in Fig. 3 relate to compounds in which the contribution of π conjugation is insignificant.

A change of 0.5 deg in the C(N) angle is accompanied by a change in the Hammett σ_p constant[3,7] by ~ 0.2 (Fig. 4). Modern X-ray techniques enable C(D,A) angles to be determined to 0.1–0.3 deg, and C–D,A bond lengths to 0.001–0.003 Å. X-Ray diffraction thus provides the most accurate method for determining constants characterising the reactivities of molecules.

Fig. 2 shows that the linear relation between the carbon–nitrogen bond length and the C(N) angle breaks down in *p*-thiocyanatoaniline and in 2-*p*-dimethylaminobenzylidenindane-1,3-dione, where strong direct polar π conjugation is present, as well as in the presence of the saturation effect in *p*-phenylenediamine. For this reason the Hammett σ constants should be replaced by other parameters.

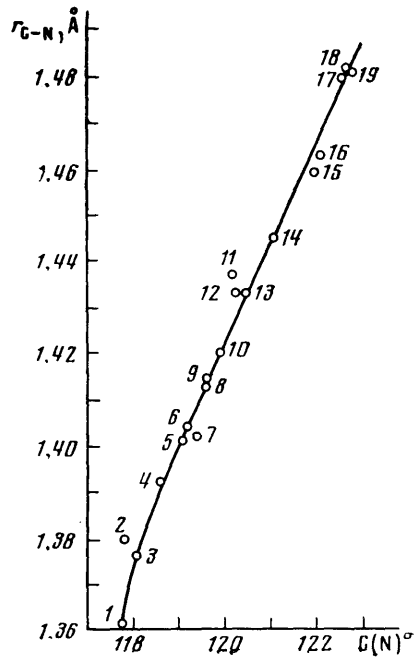
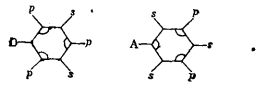


Figure 2. Correlation between C–N bond lengths and C(N) angles for: 1) 2-*p*-dimethylaminobenzylidenindane-1,3-dione; 2) *p*-dimethylaminophenyl phenyl sulphide; 3) *p*-thiocyanatoaniline; 4), 5), 13) anilinophenylphthalimide; 6) 1-phenyl-thiosemicarbazide; 7) aniline; 8) acetanilide; 9) *NN'*-diphenyl-*p*-phenylenediamine[250]; 10) *N*-diphenylmethylenaniline; 11) *N*-phenylacetanilide; 12) azobenzene[251]; 14) 4-phenyl-thiosemicarbazide; 15) $\alpha\alpha N$-triphenylnitrone; 16) mean values for *p*-nitrobenzenes[159]; 17) *p*-nitrobenzoic acid; 18) *p*-nitrotoluene; 19) *N*-methylacetanilide.

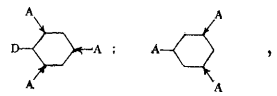
A review[160] has shown that the C(D, A) bond angles (denoted α by the reviewers) of elements in the third period are related to the Pauling[254] electronegativities χ by the linear formula $\alpha = 3.33\,\chi + 111.4$. On Pauling's thermochemical scale, however, the electronegativity sequence of the elements C > Si = Ge = Sn = Pb and N > P > As > Sb = Bi does not correspond to the bond angles and nuclear potentials of the elements.

Considering the structural aspect of the reactivity of the benzene molecule, we note that, according to the scheme of σ rehybridisation of bonds in Section II, increase in the bond angle of a carbon atom in the benzene ring implies an increase in the proportion of the *s* state of this atom in the cyclic carbon–carbon bonds and hence an increase in the proportion of the *p* state of this atom in the exocyclic carbon–hydrogen bond. The distribution of predominant *s* and *p* components of σ-hybrid bonds of carbon atoms in the exocyclic bonds of monosubstituted derivatives can be represented

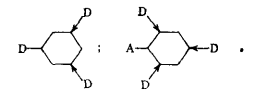


As a result, electrophilic-acceptor substituents will be oriented in conformity with the excess of *p* electrons, and nucleophilic-donor substituents according to the excess of *s* electrons:

electrophilic substitution



nucleophilic substitution



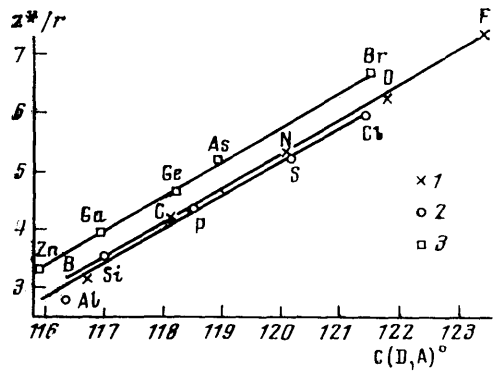


Figure 3. Dependence of bond angles C(D, A) on nuclear potentials z^*/r of elements in different periods: 1) second; 2) third; 3) fourth.

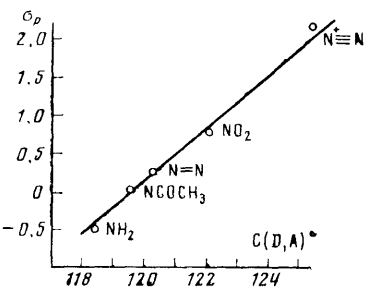


Figure 4. Dependence of the constants $\sigma_p = \sigma_I + \sigma_R$ on the bond angles C(D, A).

Thus the structural scheme of substituted benzenes is fully consistent with experiment: a donor D orients electrophilic substituents to *ortho* and *para*-positions, and nucleophilic substituents to the *meta*-position; but an

acceptor A orients electrophilic substituents to the *meta*-position, and nucleophilic substituents to *ortho*- and *para*-positions. Since σ bonds with excess of the *p* state are less stable than those with excess of the *s* state, electrophilic substitution should occur more readily than nucleophilic substitution. Thus the structural scheme of σ rehybridisation explains the main features of the reactivity of substituted benzenes, and hence σ bonds are of decisive significance for establishing the orienting effect of substituents.

V. COMPARISON OF STRUCTURAL CHARACTERISTICS OF SUBSTITUTED BENZENES AND OF METAL COMPLEXES

It is of interest to compare the structural characteristics found for substituted benzenes with X-ray results obtained for metal complexes containing the same substituents as ligands in the coordination sphere. In the modern theory of the *trans*-effect in complex compounds of metals widespread use is made of the concept of the σ rehybridisation of orbitals of the central metal atom, according to which an increase in the proportion of a given component (*s*, *p*, or *d*) in the hybrid bond of the metal atom implies a decrease in an adjacent bond of the metal[255].

The scheme of population of σ bonds suggested for substituted benzenes D(*p*)–(*s*)A(*p*)– operates also in metal complexes. The *trans*-effect of ligands L, which has been most thoroughly studied in complex platinum compounds, is evident in the lability of the platinum–chlorine bond along the L–Pt–Cl axis: D(*p*)–(*s*,*d*)Pt(*p*)–Cl. Thus the platinum–chlorine bond length should increase on passing from acceptor ligands A to donor ligands D because of the increased fraction of the *p* state of the platinum atom in the platinum–chlorine σ bonds. Table 6 shows that decrease in the C(D,A) bond angle[160] is accompanied by an increase in the platinum–chlorine bond length[256].

Table 6.

L	O	Cl	PR_3	CR_3	SiR_3
Pt—Cl, Å	2.28	2.30	2.37	2.415	2.45
C(D, A)°	121.8	121.4	118.5	118.1	117.0

Several deductions can be made from the above structural characteristics. According to the platinum–chlorine bond lengths the Taft induction constant σ_I for the methyl group should exceed that for a trialkylsilyl group. This is supported by a comparison of the C(C) bond angle in triphenylmethane with C(Si) in tetraphenylsilane (117.8° and 116.1°). These results suggest that the sequence of the σ_I constants of methyl and silyl groups (–0.08 and +0.01)[3] should evidently be refined.

The X-ray spectra of platinum complexes indicate[257] that the polarity of the platinum–chlorine bond is enhanced by the *trans*-effect of a ligand L. This is quite consistent with the concept of σ rehybridisation. The polarity of the platinum–chlorine bond would increase because *p* electrons are more weakly bound to the nucleus than are *s* electrons. Hence the ultimate cause of the enhanced bond polarity is an increase in the proportion of the *p* component of the platinum atom in this bond.

Similar ideas enable us to understand the relative stabilities of bonds involving other metals. For example, more substantial changes in bond lengths involving metal atoms are observed in tin than in platinum complexes[258].

We note in conclusion that the variation of the effect of substituents in benzene derivatives is paralleled by that of the *trans*-effect of the corresponding ligands in metal complexes. This is due to the important role of σ bonds in both classes of chemical compounds, resulting from the influence of donor–acceptor substituents (ligands) on the σ rehybridisation of (D,A)–C and (D,A)–M bonds. As a result, the influence of such donors D or acceptors A is apparent in the thermodynamic lability or stability of the C–H and M–L bonds involved in substitution. The reason for such behaviour of substituents (ligands) lies in the general rule that the length of a D–A bond decreases with fall in the nuclear potential z^*/r of the donor atom D and rise in that of the acceptor atom A.[66,67]

REFERENCES

1. A.I.Kitaigorodskii, "Molekulyarnye Kristally" (Molecular Crystals), Nauka, Moscow, 1971.
2. B.M.Mikhailov, Uspekhi Khim., 40, 2121 (1971) [Russ.Chem.Rev., No.12 (1971)].
3. L.M.Yagpol'skii, A.Ya.Il'chenko, and N.V.Kondratenko, Uspekhi Khim., 43, 64 (1974) [Russ. Chem.Rev., No.1 (1974)].
4. L.P.Hammett, "Fundamentals of Physical Organic Chemistry" (Translated into Russian), Mir, Moscow, 1972.
5. R.W.Taft, Jnr., "Separation of Polar, Steric, and Resonance Effects in Reactivity", Chapter in "Steric Effects in Organic Chemistry" (Edited by M.S.Newman) (Translated into Russian), Inostr. Lit., Moscow, 1960.
6. M.J.S.Dewar and P.J.Grisdale, J.Amer.Chem. Soc., 84, 3539 (1962).
7. Yu.A.Zhdanov and V.I.Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Organic Chemistry), Izd.RGU, 1966.
8. E.G.Cox, D.W.J.Cruickshank, and J.A.S.Smith, Proc.Roy.Soc.A, **247**, 1 (1958).
9. G.E.Bacon, N.A.Curry, and S.A.Wilson, Proc. Roy.Soc.A, 279, 98 (1964).
10. "Tables of Interatomic Distances and Configurations in Molecules and Ions", Special Publication No.18, The Chemical Society, London, 1965.
11. "International Tables for X-Ray Crystallography", The Kynoch Press, Birmingham, 1968, Vol.3.
12. J.Trotter, Tetrahedron, 8, 13 (1960).
13. A.S.Bailey and C.K.Prout, J.Chem.Soc.(A), 4867 (1965).
14. O.L.Carter, A.T.McPhail, and G.A.Sim, J.Chem. Soc.(A), 822 (1966).
15. W.C.Hamilton, Acta Cryst., Suppl., A28, 106 (1972).
16. Z.V.Zvonkova, "I Vsesoyuznoe Soveshchanie po Organicheskoi Kristallokhimii, Tezisy Dokladov" (First All-Union Conference on Organic Crystal Chemistry—Abstracts of Papers), Zinatne, Riga, 1975, p.128.
17. A.Domenicano, P.Mazzeo, and A.Vaciago, Acta Cryst., Suppl., A31, 117 (1975).
18. Z.V.Zvonkova and A.N.Khvatkina, Kristallografiya, 10, 734 (1965).

19. H.A.Bent, J.Inorg.Nuclear Chem., 19, 43 (1961).
20. W. von Niessen, Theor.Chim.Acta, 29, 29 (1973).
21. "Structure Reports", Oosthoek, Utrecht, Vol.1–35B.
22. "Molecular Structure and Dimensions", Oosthoek, Utrecht, Vol.1–6.
23. "Interatomic Distances", Oosthoek, Utrecht, Vol. A1.
24. "Itogi Nauki, Kristallokhimiya" (Progress in Science—Crystal Chemistry), VINITI, Moscow.
25. A.Robbins, G.A.Jeffrey, J.P.Chesick, J.Donohue, F.A.Cotton, B.A.Frenz, and C.A.Murillo, Acta Cryst., B31, 2395 (1975).
26. C.Riche and C.Pascard-Billy, Acta Cryst., B30, 1874 (1974).
27. A.Hoekstra and A.Vos, Acta Cryst., B31, 1722 (1975).
28. P.Argos, R.E.Barr, and A.H.Weber, Acta Cryst., B26, 53 (1970).
29. J.J.Guy and T.A.Hamor, J.Chem.Soc.Perkin Trans., II, 101 (1974).
30. P.Singh and F.R.Ahmed, Acta Cryst., B25, 1901 (1969).
31. F.Iwasaki and H.Iwasaki, Acta Cryst., B28, 3370 (1972).
32. J.Bernstein, Acta Cryst., B31, 418 (1975).
33. P.G.Evrard, P.Piret, G.Germain, and M. van Meerssche, Acta Cryst., B27, 661 (1971).
34. C.J.Finder, M.G.Newton, and N.L.Allinger, Acta Cryst., B30, 411 (1974).
35. B.Schmelter, H.Bradaczek, and P.Luger, Acta Cryst., B29, 971 (1973).
36. Y.Sasada, H.Shimanouchi, H.Nakanishi, and M.Hasegawa, Bull.Chem.Soc.Japan, 44, 1262 (1971).
37. L.Fallon, H.L.Ammon, A.G.Anderson, J.O.Currie, and R.A.LaBar, Acta Cryst., B30, 531 (1974).
38. R.L.Harlow, R.A.Loghry, H.J.Williams, and S.H.Simonsen, Acta Cryst., B31, 1344 (1975).
39. F.S.Stephens, J.Chem.Soc.(A), 1843 (1970).
40. D.Rabinovich, J.Chem.Soc.(B), 11 (1970).
41. P.Groth, Acta Chem.Scand., 27, 3302 (1973).
42. J.Donohue and J.P.Chesick, Acta Cryst., B31, 986 (1975).
43. G.P.Charbonneau and Y.Delugeard, Acta Cryst., B32, 1420 (1976).
44. H.M.Rietveld, E.N.Maslen, and C.J.B.Clews, Acta Cryst., B26, 693 (1970).
45. Y.Delugeard, J.Desuche, and J.L.Baudour, Acta Cryst., B32, 702 (1976).
46. A.E.Jungk and G.M.J.Schmidt, Chem.Ber., 104, 3272 (1971).
47. C.C.F.Blake and R.W.H.Small, Acta Cryst., B28, 2201 (1972).
48. N.J.Karch, E.T.Koh, B.L.Whitsel, and J.M.McBride, J.Amer.Chem.Soc., 97, 6729 (1975).
49. S.Perez and F.Brisse, Acta Cryst., B32, 470 (1976).
50. H.Ringertz, Acta Cryst., B27, 285 (1971).
51. B.W.Liebich and E.Parthe, Acta Cryst., B30, 2522 (1974).
52. P.A.Tucker, A.Hoekstra, J.M.Ten Cate, and A.Vos, Acta Cryst., B31, 733 (1975).
53. J.N.Brown and L.M.Trefonas, Acta Cryst., B29, 237 (1973).
54. F.Zettler, H.D.Hausen, and H.Hess, J.Organometallic Chem., 72, 157 (1974).
55. D.G.Lister, J.K.Tyler, J.H.Hog, and N.W.Larsen, J.Mol.Structure, 23, 253 (1974).
56. T.Sakurai, Acta Cryst., B24, 403 (1968).
57. L.Nygaard, I.Bojesen, T.Pedersen, and J.Rastrup-Andersen, J.Mol.Structure, 2, 209 (1968).
58. J.F.Malone and W.S.McDonald, J.Chem.Soc. Dalton Trans., 2646 (1972).
59. C.Glidewell and G.M.Sheldrick, J.Chem.Soc.(A), 3127 (1971).
60. P.J.Wheatley, J.Chem.Soc., 2206 (1964).
61. M.Sacerdoti, G.Gilli, and P.Domiano, Acta Cryst., B31, 327 (1975).
62. D.Andre, R.Fourme, and M.Renaud, Acta Cryst., B27, 2371 (1971).
63. J.F.Malone and W.S.McDonald, J.Chem.Soc.(A), 3362 (1970).
64. P.C.Chieh, J.Chem.Soc.(A), 3243 (1971).
65. A.Karipides and D.A.Haller, Acta Cryst., B28, 2889 (1972).
66. Z.V.Zvonkova, Kristallografiya, 4, 668 (1959).
67. Z.V.Zvonkova, "Problemy Fizicheskoi Khimii" (Problems of Physical Chemistry), Goskhimizdat, Moscow, 1959, p.9.
68. C.Glidewell and G.M.Sheldrick, J.Chem.Soc. Dalton Trans., 2408 (1972).
69. K.W.Muir, J.Chem.Soc.(A), 2663 (1971).
70. J.P.Vidal and J.Falgueirettes, Acta Cryst., B29, 263 (1973).
71. P.C.Chieh and J.Trotter, J.Chem.Soc.(A), 1778 (1969).
72. W.Dreissig and K.Plieth, Z.Krist., 135, 294 (1972).
73. J.C.J.Bart, Acta Cryst., B25, 489 (1969).
74. C.Krüger and P.J.Roberts, Cryst.Struct.Comm., 3, 707 (1974).
75. R.W.Harrison and J.Trotter, J.Chem.Soc.(A), 258 (1968).
76. M.E Cradwick, R D. Taylor, and J.L. Wardell, J.Organometallic Chem., 66, 43 (1974).
77. M.Czugler, A.Kalman, and G.Argay, Cryst. Struct.Comm., 2, 655 (1973).
78. J.C.J.Bart, J.Chem.Soc.(B), 350 (1969).
79. A.T.Vincent and P.J.Wheatley, J.Chem.Soc. Dalton Trans., 617 (1972).
80. G.Ruban and V.Zabel, Cryst.Struct.Comm., 5, 671 (1976).
81. W.Dreissig and K.Plieth, Acta Cryst., B27, 1146 (1971).
82. W.Dreissig and K.Plieth, Acta Cryst., B27, 1140 (1971).
83. W.Dreissig and K.Plieth, Acta Cryst., B28, 3478 (1972).
84. W.Dreissig, K.Plieth, and P.Zäske, Acta Cryst., B28, 3473 (1972).
85. L.Leiserowitz, Z.Berkovitch-Yellin, and M.Weinstein, Cryst.Struct.Comm., 4, 93 (1975).
86. C.T.Kiers and A.Vos, Rec.Trav.chim., 91, 126 (1972).
87. F.H.Allen, O.Kennard, and G.M.Sheldrick, Acta Cryst., B32, 274 (1976).
88. W.R.Krigbaum, R.J.Roe, and J.D.Woods, Acta Cryst., B24, 1304 (1968).
89. B.F.Pedersen, Acta Chem.Scand., 21, 1415 (1967).
90. J.L.Brianso, C.Miravitlles, and M.Font-Altaba, Cryst.Struct.Comm., 2, 319 (1973).
91. A.Kalman, G.Argay, and M.Czugler, Cryst. Struct.Comm., 1, 375 (1972).

92. H.L.Ammon, G.L.Wheeler, and P.H.Watts, J. Amer.Chem.Soc., 95, 6158 (1973).
93. A.F.Cameron, N.J.Hair, and D.G.Morris, Acta Cryst., B30, 221 (1974).
94. A.Kalman, B.Duffin, and A.Kucsman, Acta Cryst., B27, 586 (1971).
95. J.Runsink, S.Swen-Walstra, and T.Migchelsen, Acta Cryst., B28, 1331 (1972).
96. P.Goldstein, K.Self, and K.N.Trueblood, Acta Cryst., B24, 778 (1968).
97. A.T.McPhail, G.M.Semeniuk, and D.B.Chesnut, J.Chem.Soc.(A), 2174 (1971).
98. W.B.Wright and E.A.Meyers, Cryst.Struct. Comm., 1, 95 (1972).
99. G.J.Kruger, A.L.du Preez, and R.J.Haines, J.Chem.Soc.Dalton Trans., 1302 (1974).
100. M.J.Nolte and G.Gafner, Acta Cryst., B30, 738 (1974).
101. K.Hoffmann and E.Weiss, J.Organometallic Chem., 50, 25 (1973).
102. M.Colapietro, A.Domenicano, and A.Vaciago, Acta Cryst., Suppl., A31, 117 (1975).
103. A.L.Spek, Cryst.Struct.Comm., 2, 535 (1973).
104. M.R.Churchill and T.A.O'Brien, J.Chem.Soc.(A), 266 (1969).
105. J.J.Daly, F.Sanz, R.P.A.Sneeden, and H.H.Zeiss. J.Chem.Soc.Dalton Trans., 73 (1973).
106. L.G.Vorontsova, Z.V.Zvonkova, and G.S.Zhdanov, Dokl.Akad.Nauk SSSR, 172, 57 (1969).
107. G.Casalone, C.Mariani, A.Mugnoli, and M.Simonetta, Acta Cryst., B25, 1741 (1969).
108. M.G.Takwale and L.P.Pant, Acta Cryst., B27, 1152 (1971).
109. J.V.Barve and L.M.Pant, Acta Cryst., B27, 1158 (1971).
110. C.Bois, Acta Cryst., B26, 2086 (1970).
111. G.Casalone, A.Gavezzotti, C.Mariani, A.Mugnoli, and M.Simonetta, Acta Cryst., B26, 1 (1970).
112. A.T.Vincent and P.J.Wheatley, J.Chem.Soc. Perkin Trans, II, 687 (1972).
113. K.Kato, Acta Cryst., B27, 2028 (1971).
114. I.J.Tickle and J.B.F.N.Engberts, J.Chem.Soc. Perkin Trans.II, 2031 (1973).
115. U.de la Camp and H.Hope, Acta Cryst., B26, 846 (1970).
116. A.H.Klazinga and A.Vos, Rec.Trav.chim., 92, 360 (1973).
117. M.G.Newton, T.J.Walter, and N.L.Allinger, J. Amer.Chem.Soc., 95, 5652 (1973).
118. J.W.Swardstrom, L.A.Duvall, and D.P.Miller, Acta Cryst., B28, 2510 (1972).
119. H.Maeda, N.Kamijyo, and K.Fukui, Cryst.Struct. Comm., 5, 129 (1976).
120. N.A.Ahmed, A.I.Kitaigorodsky, and M.I.Sirota, Acta Cryst., B28, 2875 (1972).
121. C.M.Weeks, A.Copper, and D.A.Norton, Acta Cryst., B26, 429 (1970).
122. L.H.Weaver and B.W.Matthews, J.Amer.Chem. Soc., 96, 1581 (1974).
123. C.H.Stam and L.Riva di Sanseverino, Acta Cryst., 21, 132 (1966).
124. A.Karipides and K.Wolfe, Acta Cryst., B31, 605 (1975).
125. G.Bandoli, D.A.Clemente, and E.Tondello, J. Chem.Soc.Perkin Trans.II, 157 (1974).
126. M.Baily and C.J.Brown, Acta Cryst., 22, 387 (1967).
127. K.Maartmann-Moe, Acta Cryst., 21, 979 (1966).
128. Z.P.Povet'eva, S.L.Ginzburg, and Z.V.Zvonkova, Zhur.Strukt.Khim., 16, 1078 (1975).
129. J.L.Galinge, Acta Cryst., B26, 1977 (1970).
130. M.Haisa, S.Kashino, and H.Maeda, Acta Cryst., B30, 2510 (1974).
131. K.Fukuyama, K.Ohkura, S.Kashino, and M.Haisa, Bull.Chem.Soc.Japan, 46, 804 (1973).
132. R.F.Bryan, J.Chem.Soc.(B), 1311 (1967).
133. R.F.Bryan and J.J.Jenkins, J.Chem.Soc.Perkin Trans.II, 1171 (1975).
134. R.F.Bryan and L.Fallon, J.Chem.Soc.Perkin Trans.II, 1175 (1975).
135. L.Manojlovic, Acta Cryst., B24, 326 (1968).
136. K.Fukuyama, S.Kashino, and M.Haisa, Acta Cryst., B29, 2713 (1973).
137. G.Menczel and J.Kiss, Acta Cryst., B31, 1787 (1975).
138. W.R.Krigbaum, Y.Chatani, and P.G.Barber, Acta Cryst., B26, 97 (1970).
139. J.Preuss and A.Gieren, Acta Cryst., B31, 1276 (1975).
140. C.Romming, Acta Chem.Scand., 26, 523 (1972).
141. S.S.Tavle and L.M.Pant, Acta Cryst., B27, 1479 (1971).
142. P.Coppens and G.M.J.Schmidt, Acta Cryst., 18, 62 (1965).
143. P.Coppens and G.M.J.Schmidt, Acta Cryst., 18, 654 (1965).
144. J.S.Ricci and I.Bernal, J.Amer.Chem.Soc., 91, 4078 (1969).
145. G.Casalone and M.Simonetta, J.Chem.Soc.(B), 1180 (1971).
146. G.Casalone, A.Gavezzotti, and M.Simonetta, J. Chem.Soc.Perkin Trans.II, 342 (1973).
147. F.Bachechi and L.Zambonelli, Acta Cryst., B29, 2598 (1973).
148. J.K.S.Kim, E.R.Boyko, and G.B.Carpenter, Acta Cryst., B29, 1141 (1973).
149. R.Guttormson and B.E.Robertson, Acta Cryst., B28, 2702 (1972).
150. A.T.Vincent and P.J.Wheatley, J.Chem.Soc. Perkin Trans.II, 1567 (1972).
151. P.Ganis, G.Avitabile, S.Migdal, and M.Goodman, J.Amer.Chem.Soc., 93, 3328 (1971).
152. V.J.James and C.T.Grainger, Cryst.Struct. Comm., 1, 111 (1972).
153. A.M.O'Connell and E.N.Maslen, Acta Cryst., 22, 134 (1967).
154. A.F.Cameron, N.J.Hair, and D.G.Morris, J. Chem.Soc.Perkin Trans.II, 1951 (1973).
155. G.L.Wheeler and S.D.Colson, Acta Cryst., B31, 911 (1975).
156. R.S.Miller, I.C.Paul, and D.Y.Curtin, J.Amer. Chem.Soc., 96, 6334 (1974).
157. M.Perrin and P.Michel, Acta Cryst., B29, 253 (1973).
158. R.D.G.Jones, Acta Cryst., B32, 301 (1976).
159. A.Domenicano, A.Vaciago, and C.A.Coulson, Acta Cryst., B31, 221 (1975).
160. A.Domenicano, A.Vaciago, and C.A.Coulson, Acta Cryst., B31, 1630 (1975).
161. C.Bois, Acta Cryst., B29, 1011 (1973).
162. A.C.Skapski and J.L.Stevenson, J.Chem.Soc. Perkin Trans.II, 1197 (1973).
163. Y.Delugeard and J.C.Messager, Acta Cryst., B31, 2809 (1975).

164. R. Alcala and S. Martinez-Carrera, Acta Cryst., B28, 1671 (1972).
165. J. F. McConnell, Cryst. Struct. Comm., 3, 459 (1973).
166. C. de Rango, S. Brunie, G. Tsoucaris, J. P. Declercq, and G. Germain, Cryst. Struct. Comm., 3, 485 (1974).
167. G. E. Bacon and R. J. Jude, Z. Krist., 138, 19 (1973).
168. Y. Katsube, Y. Sasada, and M. Kakudo, Bull. Chem. Soc. Japan, 39, 2576 (1966).
169. A. L. Macdonald and J. C. Speakman, J. Chem. Soc. Perkin Trans. II, 1564 (1972).
170. H. H. Sutherland and M. J. Mottram, Acta Cryst., B28, 2212 (1972).
171. S. K. Arora, M. Sundaralingam, J. S. Dancz, R. H. Stanford, and R. E. Marsh, Acta Cryst., B29, 1849 (1973).
172. J. Trotter and C. E. Williston, Acta Cryst., **21**, 285 (1966).
173. G. J. Palenik, J. Donohue, and K. N. Trueblood, Acta Cryst., B24, 1139 (1968).
174. M. Le Bars, M. Alleaume, and C. Hauw, Cryst. Struct. Comm., 3, 383 (1973).
175. C. Bois, Acta Cryst., B28, 25 (1972).
176. S. S. Tavale and L. M. Pant, Acta Cryst., B29, 2979 (1973).
177. E. M. Gopalakrishna and L. Cartz, Acta Cryst., B28, 2917 (1972).
178. M. Sundaralingam and L. H. Jensen, Acta Cryst., 18, 1053 (1965).
179. J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, J. Chem. Soc. Perkin Trans. II, 1614 (1972).
180. M. P. Gupta and M. Sahu, Acta Cryst., B28, 2887 (1972).
181. C. E. Peluger and R. L. Harlow, Acta Cryst., B29, 2608 (1973).
182. R. A. Smith, Acta Cryst., B31, 1773 (1975).
183. H. P. Klug, Acta Cryst., B26, 1268 (1970).
184. M. Komeyama, S. Yamamoto, N. Nishimura, and S. Hasegawa, Bull. Chem. Soc. Japan, 46, 2606 (1973).
185. C. Miravitlles, F. Plana, J. L. Brianso, and M. Font-Altaba, Cryst. Struct. Comm., 3, 439 (1974).
186. J. L. Brianso, C. Miravitlles, F. Plana, and M. Font-Altaba, Cryst. Struct. Comm., **2**, 551 (1973).
187. C. Stalhandske, Acta Chem. Scand., 26, 2962 (1972).
188. N. N. Dhaneshwar and L. M. Pant, Acta Cryst., B29, 2980 (1973).
189. E. Krogh Andersen and I. G. Krogh Andersen, Acta Cryst., B31, 391 (1975).
190. K. Fujimori, T. Tsukihara, Y. Katasube, and I. Yamamoto, Bull. Chem. Soc. Japan, 45, 1564 (1972).
191. H. H. Sutherland, J. H. C. Hogg, and D. J. Williams, Acta Cryst., B30, 1562 (1974).
192. H. H. Sutherland, Acta Cryst., B26, 1217 (1970).
193. B. Dahlen, Acta Cryst., B29, 595 (1973).
194. B. Dahlen, Acta Cryst., B30, 642 (1974).
195. S. R. Hall and E. N. Maslen, Acta Cryst., **22**, 216 (1967).
196. R. Attig and D. Mootz, Acta Cryst., B32, 435 (1976).
197. C. Stalhandske, Acta Cryst., B30, 1586 (1974).
198. C. Stalhandske, Acta Chem. Scand., 26, 3029 (1972).
199. H. Wunderlich and D. Mootz, Acta Cryst., B27, 1684 (1971).
200. C. S. Choi and J. E. Abel, Acta Cryst., B28, 193 (1972).
201. B. H. O'Connor and F. H. Moore, Acta Cryst., B29, 1903 (1973).
202. A. Chiaroni, Acta Cryst., B27, 448 (1971).
203. A. Neuman and H. Gillier-Pandraud, Acta Cryst., B29, 1017 (1973).
204. J. L. Flippen and R. D. Gilardi, Acta Cryst., B31, 926 (1975).
205. T. S. Cameron and J. E. Thompson, Cryst. Struct. Comm., 3, 503 (1973).
206. J. O. Lundgren, Acta Cryst., B28, 475 (1972).
207. P. Becker, H. Brusset, and H. Gillier-Pandraud, Compt. rend., C274, 1043 (1972).
208. F. Takusagawa and A. Shimada, Bull. Chem. Soc. Japan, 46, 2998 (1973).
209. F. Iwasaki, M. Sato, and A. Aihara, Acta Cryst., B32, 102 (1976).
210. D. Rabinovich and Z. Shakked, Acta Cryst., B31, 819 (1975).
211. M. Maze-Baudet, Acta Cryst., B29, 602 (1973).
212. P. Smith, F. Florencio, and S. Garcia-Blanco, Acta Cryst., B27, 2255 (1971).
213. K. Gurtu, W. D. Chandler, and B. E. Robertson, Canad. J. Chem., 53, 2093 (1975).
214. C. H. Stam, Acta Cryst., B28, 2715 (1972).
215. E. Prince, L. W. Schroeder, and J. J. Rush, Acta Cryst., B29, 184 (1973).
216. F. Takusagawa, K. Hirotsu, and A. Shimada, Bull. Chem. Soc. Japan, 44, 1274 (1971).
217. C. K. Prout and I. J. Tickle, J. Chem. Soc. Perkin Trans. II, 520 (1973).
218. F. H. Cano, S. Martinez-Carrera, and S. Garcia-Blanco, Acta Cryst., B26, 972 (1970).
219. V. Benghiat and L. Leiserowitz, J. Chem. Soc. Perkin Trans. II, 1778 (1972).
220. M. C. Apreda, P. Smith-Verdier, and S. Garcia-Blanco, Acta Cryst., B29, 2658 (1973).
221. D. F. Grant and J. P. G. Richards, Acta Cryst., B25, 564 (1969).
222. D. L. Hughes and J. Trotter, J. Chem. Soc. (A), 2181 (1971).
223. V. B. Carter and D. Britton, Acta Cryst., B28, 945 (1972).
224. J. S. Willis, J. M. Stewart, H. L. Ammon, H. S. Preston, R. E. Gluyas, and P. M. Harris, Acta Cryst., B27, 786 (1971).
225. P. Batail, D. Grandjean, F. Dudragne, and C. Michaud, Acta Cryst., B31, 1367 (1975).
226. C. M. Gramaccioli, R. Destro, and M. Simonetta, Acta Cryst., B24, 129 (1968).
227. G. G. Christoph and E. B. Fleischer, Acta Cryst., B29, 121 (1973).
228. J. O. Lundgren, Acta Cryst., B28, 1684 (1972).
229. S. P. N. van der Helijden, W. D. Chandler, and B. E. Robertson, Canad. J. Chem., 53, 2121 (1975).
230. S. P. N. van der Helijden, W. D. Chandler, and B. E. Robertson, Canad. J. Chem., 53, 2127 (1975).
231. S. P. N. van der Helijden, W. D. Chandler, and B. E. Robertson, Canad. J. Chem., 53, 2102 (1975).
232. S. P. N. van der Helijden, W. D. Chandler, and B. E. Robertson, Canad. J. Chem., 53, 2108 (1975).
233. S. P. N. van der Helijden, W. D. Chandler, and B. E. Robertson, Canad. J. Chem., 53, 2115 (1975).
234. C. J. Brown, Acta Cryst., **21**, 442 (1966).

235. E.Krogh Andersen and I.G.Krogh Andersen, Acta Cryst., B31, 387 (1975).
236. J.H.Bryden, Acta Cryst., B28, 1395 (1972).
237. S.Abrahamsson, M.Innes, and B.Lamm, Acta Chem.Scand., 21, 224 (1967).
238. C.A.Bear, A.L.Macdonald, and J.Trotter, Acta Cryst., B29, 2617 (1973).
239. A.Karipides and R.H.P.Thomas, Cryst.Struct. Comm., 2, 275 (1973).
240. W.B.Gleason and D.Britton, Cryst.Struct.Comm., 5, 483 (1976).
241. K.Folting, J.C.Huffman, and L.L.Merritt, Cryst. Struct.Comm., 4, 705 (1975).
242. G.M.Brown and O.A.W.Strydom, Acta Cryst., B30, 801 (1974).
243. R.Rudman, Acta Cryst., B27, 262 (1971).
244. B.F.Pedersen, Acta Cryst., B31, 2931 (1975).
245. Z.P.Povet'eva and Z.V.Zvonkova, Kristallografiya, 20, 69 (1975).
246. T.F.Lai and R.E.Marsh, Acta Cryst., 22, 885 (1967).
247. I.V.Isakov, E.E.Rider, and Z.V.Zvonkova, Cryst. Struct.Comm., 5, 95 (1976).
248. A.M.O'Connell and E.N.Maslen, Acta Cryst., 22, 134 (1967).
249. K.N.Trueblood, E.Goldish, and J.Donohue, Acta Cryst., 14, 1009 (1961).
250. Z.P.Povet'eva, L.A.Chetkina, and V.V.Kopylov, Kristallografiya, 21, 313 (1976).
251. C.J.Brown, Acta Cryst., 21, 146 (1966).
252. V.A.Pal'm, Uspekhi Khim., 30, 1069 (1961) [Russ. Chem.Rev., No.9 (1961)].
253. Z.V.Zvonkova and N.S.Magomedova, Zhur.Strukt. Khim., 18, 92 (1977).
254. L.Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960.
255. E.M.Shustorovich, Zhur.Strukt.Khim., 15, 123 (1974).
256. Yu.N.Kukushkin, Uspekhi Khim., 43, 1689 (1974) [Russ.Chem.Rev., No.10 (1974)].
257. M.A.Porai-Koshits and V.I.Nefedov, Vestnik Akad. Nauk SSSR, No.8, 33 (1972).
258. G.G.Mather, G.M.McLaughlin, and A.Pidcock, J.Chem.Soc.Dalton Trans., 1823 (1973).

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