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Rigid-body refinement: a *caveat*.

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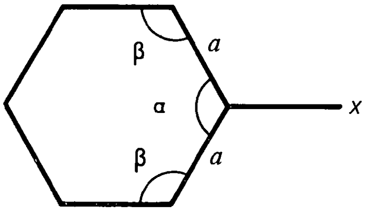
The D_{6h}(6/*mmm*) model usually used in the rigid-body refinement of phenyl groups is not consistent with recent results on the ring geometry of substituted benzene derivatives. Its use with the triphenylphosphite ligand and the tetraphenylborate anion is shown to result in systematic errors on the carbon-substituent bond lengths.

Rigid-body least-squares refinement (Scheringer, 1963; La Placa & Ibers, 1963, 1965; Eisenberg & Ibers, 1965) is used extensively by crystallographers. The technique is applied most frequently to the crystal structure analysis of compounds containing several phenyl groups in the asymmetric unit, assuming that these groups can be treated as rigid bodies of fixed, known geometry.



This assumption is, however, not always correct. A recent analysis (Coulson, Domenicano & Vaciago, 1973; Domenicano, Vaciago & Coulson, 1975*a*) of the best structural data on substituted benzene derivatives has led to the general result that certain geometrical parameters of the carbon hexagon, namely the *a* bonds and the α and β angles, are sensitive to the nature of the substituent. This is especially true for the angle α, the values of which span a rather wide range (114–125°). For a phenyl group bonded to a second-row element, X, the angle α has been shown to be linearly dependent on the electronegativity of X (Domenicano, Vaciago & Coulson, 1975*b*). This correlation has been used to evaluate the true electronegativity of X, as determined by hybridization state and partial charge, in some classes of compounds, and even in individual molecules.

More recently (Colapietro, Domenicano & Vaciago, 1975), evidence has been given for the existence of a small chemical shift of the angle α in Ph_3PX compounds, where X is either a single atom or a group of atoms. This results from the subtle variations in the electronegativity of P induced by the P–X interaction; accurately measured values of α may be used to calculate the partial charge on P, thus providing an insight into the nature of the P–X interaction.

Scattered reports on the occurrence of angular deformations in the phenyl groups of compounds traditionally amenable to rigid-body refinement have appeared in the last few years. Several authors, using conventional, unconstrained refinement of all the atomic parameters, have noticed that the internal angles at the *ipso* carbons in triphenylphosphine derivatives and related compounds are slightly (1–2°) less than 120° (Cotton & Takats, 1970; Hamilton, 1972; Churchill & Veidis, 1972; Churchill, Kalra & Veidis, 1973; Churchill & Kalra, 1974*a*, *b*; Churchill & Chang, 1975). The same angles have been reported to average 114° in the tetraphenylborate anion (Di Vaira & Bianchi Orlandini, 1972; Duggan & Hendrickson, 1974; Randaccio, 1974), and to be about 125° in a triphenylphosphite metal complex (Guss & Mason, 1972).

However, as far as we know, when phenyl groups have been refined by rigid-body techniques the geometry of the carbon hexagons has always been assumed to preserve the full symmetry of unsubstituted benzene. *This cannot be recommended as a correct procedure in the final stages of a crystal structure analysis.* There is no doubt that the conventional, unconstrained refinement of all atomic parameters is to be preferred whenever the data set available is of such a size and quality to warrant the successful determination of the skeletal geometry of the phenyl groups. Unless a correct model for the carbon hexagon is available, rigid-body refinement should only be used with caution when the data set is not of such high standard.

The use of the wrong model in rigid-body refinement is likely to lead to systematic effects in some molecular parameters, especially the lengths of the C–X bonds. Such effects have been observed by Albano & Ciani (1974) in the rigid-body refinement of the structure of tetracarbonylironcarbonyltris(triphenylphosphite)diplatinum. These authors suggest that the rather short C–O bond distances in the triphenylphosphite ligands, $(C_6H_5\text{–}O)_3P$, (average value 1·36 Å, to be compared with 1·40–1·41 Å in four other complexes of the same ligand, the structures of which were refined without constraints) may be due to the inadequacy of the D_{6h} (6/*mmm*) model used for the carbon hexagons.

The substitution of a hydrogen atom in the benzene ring with an $-O-P\!\!<$ moiety is expected to increase the angle α by a few degrees, giving rise to a shortening (by a few hundredths of an ångström) of the $C_{ipso}\cdots C_{para}$ contact distance, d_{ip}, with respect to the value of 2·794 Å calculated for a regular hexagon with a side of 1·397 Å (Domenicano, Vaciago & Coulson, 1975*a*).[†] Constraining the phenyl groups to D_{6h} (6/*mmm*) symmetry unavoidably results in the movement of the *ipso* C towards the respective O atoms, accounting for the shortening of the C–O bonds.

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[†] The mean values of d_{ip} in pentacarbonyltriphenylphosphitechromium (Plastas, Stewart & Grim, 1973) and *trans*-bis(triphenylphosphite)tetracarbonylchromium (Preston, Stewart, Plastas & Grim, 1972) are 2·720 and 2·715 Å respectively, as calculated from the atomic parameters quoted in the original papers. A part of the shortening, however, is probably an artifact resulting from the effects of thermal motion.

An opposite effect is expected with the tetraphenylborate anion, $[(C_6H_5)_4B]^-$, where α is about 114° and d_{lp} is greater than 2·794 Å (Domenicano, Vaciago & Coulson, 1975*a*).* Table 1 shows the mean values of the C–B bond distances in this anion, as observed in a number of salts, the crystal structures of which have been refined by either rigid-body or conventional, unconstrained refinement. As expected, the mean values from rigid-body refinements are greater than the others.

Table 1. *Mean values of the* C–B *bond distances in several salts of the tetraphenylborate anion*

Compound	Ref.	Refinement[a]	C–B (Å)
Tris-(2-aminoethyl)aminochlorozinc tetraphenylborate	*b*	U	1·639 (4)
Isothiocyanato-{*N*,*N*-bis-[2-(diethylamino)ethyl]-2-(diphenylarsino)ethylamine-*N*,*N*,*N*}-nickel tetraphenylborate	*c*	U	1·643 (4)
Potassium tetraphenylborate	*d*	U	1·643 (3)
Tetramethylammonium tetraphenylborate	*d*	U	1·641 (4)
π-Cyclopentadienyl-η-(tetraphenylborato)ruthenium	*e*	U	1·647 (6)
Tris-(2-aminoethyl)aminocyanocopper tetraphenylborate	*f*	U	1·639 (8)
Bis-[*N*,*N*′-ethylene-bis(salicylideneiminato)cobalt]-bis(tetrahydrofuran)sodium tetraphenylborate	*g*	U	1·64 (1)
Nitrosylbis-[1,2-bis(diphenylphosphino)ethane]ruthenium tetraphenylborate acetone	*h*	RB	1·69 (2)
Chugaev's red salt, $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2]^+$ $[(C_6H_5)_4B]^-$	*i*	RB	1·72 (2)

Notes: (*a*) U, unconstrained; RB, rigid-body. (*b*) Sime, Dodge, Zalkin & Templeton (1971). (*c*) Di Vaira & Bianchi Orlandini (1972). (*d*) Hoffmann & Weiss (1974). (*e*) Kruger, Du Preez & Haines (1974). (*f*) Duggan & Hendrickson (1974). (*g*) Randaccio (1974). (*h*) Pierpont & Eisenberg (1973). (*i*) Butler, Enemark, Parks & Balch (1973).

We realize that the choice of a correct model for a phenyl group may sometimes be difficult, since accurate experimental values of the three 'substituent-sensitive' parameters of the carbon hexagon (a, α and β) are not always available. In any case the experimental values of a, as obtained by X-ray diffraction techniques, may be systematically shortened by the effects of thermal motion. Nevertheless, we think that a reasonably constructed model of $C_{2v}(2m)$ symmetry should always prove better than the one of $D_{6h}(6/mmm)$ symmetry.

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* The mean values of d_{lp} in tris-(2-aminoethyl)aminochlorozinc tetraphenylborate (Sime, Dodge, Zalkin & Templeton, 1971) and tris-(2-aminoethyl)aminocyanocopper tetraphenylborate (Duggan & Hendrickson, 1974) are 2·825 and 2·823 Å, respectively, as calculated from the atomic parameters quoted in the original papers. Both values are presumably shortened to some extent by thermal motion.