Shortening of the Carbon–Chlorine Interatomic Distance in *ortho*-Substituted Aromatic Compounds

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Summary The carbon–chlorine bond distance in aromatic compounds is significantly shorter for two *ortho* bonds than for *meta, para,* or isolated bonds.

DURING the analysis of the results of a single-crystal *X*-ray diffraction study of tetrachlorophthalic anhydride (TCPA)[1] it was noted that the carbon–chlorine bond lengths were significantly shorter than those reported for a number of similar polychlorinated compounds. Although this effect has been noted in several individual instances, sufficient experimental evidence has not previously been available to permit any generalizations. The observed carbon–chlorine distances in a number of similar molecules are listed in the Table. The data indicate that the C–Cl distances in compounds containing *ortho*-chlorine atoms are close to 1·709 Å, while "isolated" C–Cl distances (even when *para* to each other) are close to 1·737 Å. This leads to the important conclusion that, in the case of aromatic or partially aromatic compounds, each of two adjacent C–Cl bonds is shorter than a lone C–Cl bond.

Bersohn,[2] in a discussion of the double-bond character of conjugated carbon–chlorine bonds, stated that the decrease of double-bond character and consequent increase of the nuclear quadrupole coupling constant of a carbon–chlorine bond upon the introduction of another chlorine atom in a resonating system is a small high-order effect. He did not distinguish between *ortho-*, *meta-*, and *para*-substitution. However, if we use nuclear quadrupole resonance data as a measure of the double-bond and/or ionic character of the bond, then an increase in the resonance frequency will indicate a decrease in the ionic character of the bond, an increase in the double-bond character, and a shortening of the bond length. The data given for a series of chlorinated benzene compounds[2] show that there is a small increase for the *meta-* and *para*-substituted dichlorobenzenes, and a significantly larger increase for *o*-dichlorobenzene.

While no detailed quantitative explanation has been attempted, a plausible approach would seem to be on the basis of a van der Waals attraction of the London type between the adjacent chlorine atoms. Bastiansen and Traetteberg[3] reported that attractive van der Waals forces are stronger than the repulsive forces in determining the configuration of the 2,2′-dihalogenobiphenyl molecules.

TABLE 2

Average carbon–chlorine bond distances (Å) *in several chlorinated compounds*

Compound	Distance
2,5-Dichloroaniline[a]	1·744
1-(2,6-Dichlorobenzyl)-6-hydroxy-1,4,5,6-tetrahydronicotinamide[b]	1·743
Ammonium chloroanilate monohydrate[c]	1·741
1,4,5,8-Tetrachloronaphthalene[e]	1·740
4-Acetyl-2′-chlorobiphenyl[e]	1·738
o-Chlorobenzoic acid[f]	1·737
trans-pp′-Dichloroazobenzene[g]	1·737
4,4′-Dichlorodiphenyl sulphone[h]	1·736
TMPD–Chloranil[i]	1·714
Tetrachloro-*p*-benzoquinone[j]	1·714
Tetrachlorohydroquinone[k]	1·712
Pentachlorophenol[a]	1·707
TCPA[l]	1,705
TCPC[m]	1·705
TCBF[n]	1·705

[a] T. Sakurai, M. Sundaralingam, and G. Jeffrey, *Acta Cryst.*, 1963, **16**, 354; [b] H. Hope, *ibid.*, 1969, B**25**, 78; [c] E. Krogh-Anderson, *ibid.*, 1967, **22**, 196; [d] G. Gafner and F. Herbstein, *ibid.*, 1962, **15**, 1081; [e] H. Sutherland and T. Hoy, *ibid.*, 1968, B**24**, 1207; [f] G. Ferguson and G. Sim, *ibid.*, 1961, **14**, 1262; [g] H. Hope and D. Victor, *ibid.*, 1969, B**25**, 1849; [h] J. Sime and S. Abrahams, *ibid.*, 1960, **13**, 1; [i] J. de Boer and A. Vos, *ibid.*, 1968, B**24**, 720; [j] S. Chu, G. Jeffrey and T. Sakurai, *ibid.*, 1962, **15**, 661; [k] Ref. 6; [l] Ref. 1; [m] H. Shimanouchi, *et al.*, *ibid.*, 1969, B**25**, 1890; [n] Y. Nishi, *et al.*, *Bull. Chem. Soc. Japan*, 1966, **39**, 818.

Thus they found that 2,2′-dihalogenobiphenyl compounds exist in the near *cis-*, rather than the *trans-*, conformation, in spite of the obstacles presented by molecular overcrowding. They attribute this to a predominantly halogen–halogen interaction. Coulson[4] reported that indications of attractive forces between nonbonded atoms such as the halogens in 2,2′-dihalogenobiphenyls have been found. He also showed that important factors in discussing the bonding in *o*-dichlorobenzene are the attractions due to resonance with structures showing a Cl–Cl single bond and the dispersion forces of attraction between the chlorine atoms.

On the other hand, Morino *et al.*,[5] ascribe this to an induction effect. In an isolated carbon–chlorine bond, the bonding electrons are displaced toward the more electronegative chlorine; in polychloro *ortho*-derivatives the attractive forces of the other chlorine atoms counteract that of the one in question to produce a decrease in the ionic character of the carbon–chlorine bond.

It would be helpful to determine if the observed shortening of the bond is due to an actually shorter internuclear distance or to an effect caused by an anisotropic electron cloud distribution about the chlorine atom. A comparison of neutron and *X*-ray diffraction data would be of help in clarifying this point. A search of the literature revealed only one suitable compound that had been studied by neutron diffraction. Sikka and Chidambaram[6] found that the C–Cl bond lengths in tetrachlorohydroquinone have an average bond-length of **1·712** Å and that all carbon–carbon bond lengths are within one estimated standard deviation (e.s.d.) of **1·390** Å. On this basis, the observed C–Cl bond lengths, which are within one e.s.d. of **1·709** Å, are in agreement with those observed for TCPA and related *ortho*-substituted polychloro-compounds. However, it is felt that these data are not sufficient to permit one to distinguish between actual shortening of the bond and apparent shortening due to electron-cloud distortion. Neutron diffraction investigations of other polychlorinated compounds are needed.

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[2] R. Bersohn, *J. Chem. Phys.*, 1954, **22**, 2078.

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[4] C. A. Coulson, *Tetrahedron*, 1962, **17**, 256, 260.

[5] Y. Morino, M. Toyama, K. Itoh, and S. Kyono, *Bull. Chem. Soc. Japan*, 1962, **35**, 1667.

[6] S. K. Sikka and R. Chidambaram, *Acta Cryst.*, 1967, **23**, 107.