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C-Cl ... π(Ar) Interactions

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Communication

C-Cl · · · π(Ar) Interactions

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Geometry consistent with C-Cl · · · π(Ar) and C-Cl · · · · · · π(Cp) interactions is shown to occur from a survey of structures in the Cambridge Structural Database. The C-Cl · · · π(Ar) and C-Cl · · · π(Cp) angles vary between about 90° to 180°. These angles are more nearly linear as the perpendicular distance of the chlorine atom from the π-system decreases. Many of the interactions are of the 'edge' rather than the centroid type.

Geometry consistent with a C-Cl · · · π(Ar) interaction has been shown to exist in a wide variety of compounds[1] (from information retrieved from the Cambridge Structural Database).[2] Figure 1 was derived from information about compounds which contain 'trichloromethyl' as part of their name. The Figure in the graphical abstract, showing a molecule that contains two trichloromethyl groups, has been adapted from reference 3.

The angle [C-Cl · · · π(Ar)] between the C-Cl bond and the normal to the aromatic ring varies widely, from about 90° to a more nearly linear arrangement. There is some tendency for the distance of the chlorine atom from the plane of the aromatic ring to be shorter as the angle, [C-Cl · · · π(Ar)] becomes closer to linear, see Figure 1.

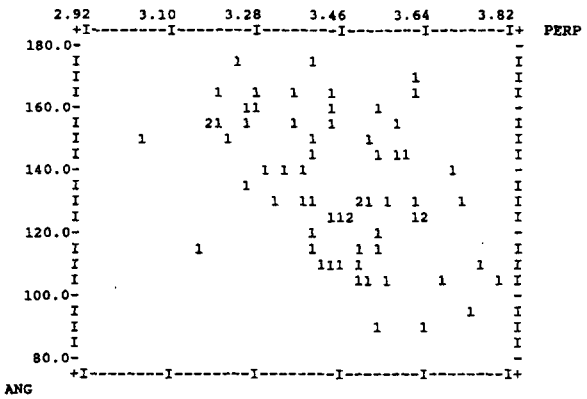

FIGURE 1 Plot of the angle C-Cl · · · π(Ar), (ANG), versus the distance (PERP) of the chlorine atom from the plane of the aromatic ring.

In most of these compounds the C-Cl · · · π(Ar) geometry is of the 'edge' rather than the 'centroid' type.[4–6] i.e. the chlorine atom is closer to one (or two) carbon atom(s) in the aromatic ring rather than to the ring centroid.

Some examples are given in the Table below in which D1 to D6 are the distances, Å, of the chlorine atom from the six carbon atoms in the aromatic ring, given in cyclic order.

CSD REFCODE	PERP	D1	D2	D3	D4	D5	D6
OPTCET	3.24	3.42	3.53	4.25	4.78	4.71	4.09
DUYXUQ	3.27	3.37	3.60	4.31	4.76	4.58	3.92
DUYXUQ	3.28	3.46	3.47	3.59	3.71	3.70	3.57
JUGXAK	3.32	3.41	3.54	3.79	3.91	3.78	3.51
PAGJAI	3.50	3.53	3.65	3.99	4.18	4.05	3.76
YCXINC	3.54	3.55	3.70	4.04	4.24	4.12	3.81

That the C-Cl · · · π(Ar) interaction is widespread is illustrated in Figures 2 and 3. Figure 2 is a plot derived from inclusion compounds that are chloroform solvates but which do not contain chlorine other than in the included chloroform. The same trends are observed here as were noted in the data for Figure 1.

The generality of the C-X · · · π geometry is illustrated by the occurrence of short C-Cl · · · π(cp) distances in some organometallic compounds, see Figure 3.

Analogous geometry for C-Br · · · π(Ar) and C-I · · · π(Ar) has also been noted.[7]

Acknowledgment

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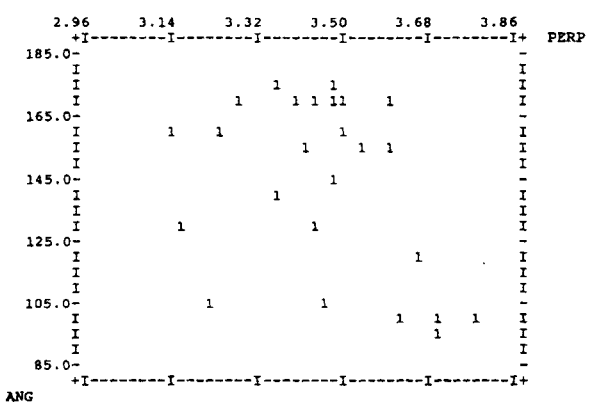

FIGURE 2 Plot of the angle C-Cl · · · π(Ar), (ANG), versus the distance (PERP) of a chlorine atom from the plane of an aromatic ring in the host compound.

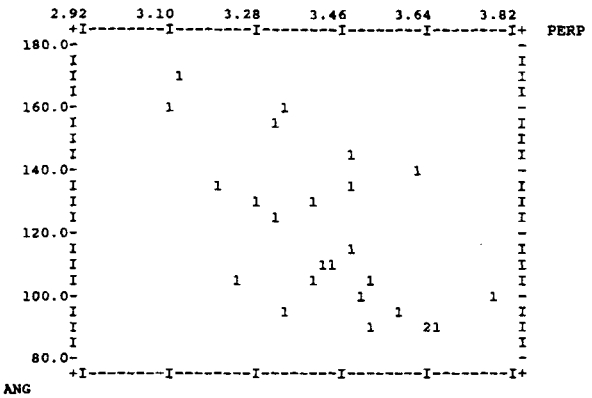

FIGURE 3 Plot of the angle C-Cl · · · π(Cp), (ANG), versus the distance (PERP) of a chlorine atom from the plane of a cyclopentadienyl ring in some organometallic compounds.

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