# Deviation from Coplanarity of the Carbon Atoms of Fumaric Acid in the Complex: Racemic Fe(CO)$_4$–Fumaric Acid

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IN their model of the platinum–ethylene bond in Zeise's anion, Chatt and Duncanson[1] postulated the non-coplanarity of the hydrogen atoms with the carbon atoms of the olefin due to the repulsion of the hydrogen atoms by the platinum atom.

The principal features of Chatt and Duncanson's model have been confirmed by $X$-ray structure analyses of numerous complexes.[2,3] However, clear experimental evidence of a departure from coplanarity of the atoms adjacent to a double bond co-ordinated to a transition metal has yet to be presented. $X$-Ray structure analyses that have been undertaken have in fact been concerned with complexes containing olefins like ethylene,[2] where it is difficult to determine the exact position of hydrogen atoms, or cyclic diolefins in which any displacement observed may be attributed to strain arising from chelation.[4] In their investigation of Fe(CO$_4$–acrylonitrile, Luxmoore and Truter[5] have found that the CN group is displaced from the plane that contains the two olefinic carbons and is normal to the axis passing through the iron atom and the centre of the double bond. We have examined the structure of racemic Fe(CO)$_4$–fumaric acid.

The crystal data are:

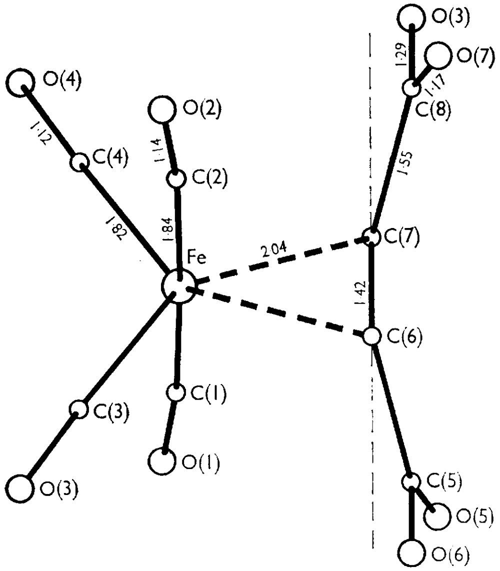
$$a = 6{\cdot}02,\ b = 13{\cdot}42,\ c = 12{\cdot}65\ \text{Å};\ v = 1022\ \text{Å},\ z = 4,\ d_c = 1{\cdot}85\ \text{g. cm}^{-3};\ \text{Space group } Pccn.$$

(Data from Weissenberg photographs, Fe–$K_\alpha$ radiation).

The molecule contains a two-fold crystallographic axis.

The structure consists of hydrogen-bonded molecules; this accounts for the low volatility of the solid.

The molecule consists of five ligands arranged about the iron in the form of a trigonal bipyramid as depicted in the Figure with the fumaric acid in equatorial position.



FIGURE

*Molecular model of racemic* Fe(CO)$_4$*-fumaric acid*

At the present stage of three-dimensional refinement, ($R$-factor 14%) the bond lengths reported in the Figure might still be subject to small variations.

The internal rotation angle C(5)C(6)C(7)–C(6)-C(7)C(8), which should be 180° in fumaric acid, is 145°.

This deviation that may be due to repulsions between non-bonded atoms within the same molecule is also consistent with a hybridization of the carbon atoms C(6) and C(7) with a larger proportion of *p*-character. In our opinion the influence of intermolecular interactions (including the hydrogen bonding between the carboxylic acid groups) on this deviation from a 180° angle is of secondary importance.

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