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**Planarity of the dicarboxylic acid dimer configuration.** By J. H. ROBERTSON, *University of Leeds, England*

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In their recent communication, Jeffrey & Sax (1963) pointed out that the carboxylic acid pair, hydrogen bonded about a centre of symmetry, need not be planar as a whole and is often not so in fact. The planes of individual carboxyl groups are in some cases as much as 0.5 Å apart.

The fact remains, however, that these 8-membered rings are approximately planar. A displacement of even 0.5 Å rotates the O...O vector by only 10° out of the plane. Further, in a significant proportion of cases — to which we may now add propionic and butyric acids (Strieter, Templeton, Schenerman & Sass, 1962; Strieter & Templeton, 1962) — they are *exactly* planar. The fact that overall planarity is not crystallographically required renders more significant the degree of planarity which is found.

We may go some way towards explaining the phenomenon in the light of known characteristics of hydrogen bonding. The acid proton is not merely attracted to the electronegative oxygen atom as such, but is specifically drawn towards its lone pairs of electrons. This situation has been discussed in detail for H<sub>2</sub>O and HF by Schneider (1955), who also made some reference to carboxylic acids. In the carboxyl group the *sp*<sup>2</sup> hybridization of the carbon atom demands *sp*<sup>2</sup> hybridization of the carbonyl oxygen atom also; consequently its two lone pairs extend at 120° to the C=O bond (Fig. 1) and are coplanar with it and the other carbon-oxygen bond. It is the presence of these lone pairs and their interaction

with the hydrogen bonding protons that determines the tendency to overall planarity.

Planarity of a carboxylic acid dimer is thus an ideal towards which the hydrogen bonding of the dimer strives. In the gas phase, the ideal is fully achieved (Costain & Srivastava, 1961; Karle & Brockway, 1944). In the solid, planarity cannot be the rule because of the relative feebleness of hydrogen bonding and the fact that other packing considerations interfere. Benzenhexacarboxylic acid (Darlow, 1961) affords a particularly striking example of such interference because each molecule bears six adjacent carboxyl groups, ideal linkages for all of which would be impossible. Even so, all dimerize; and of the four crystallographically distinct dimers, only one is very much twisted, one is slightly twisted and two are almost planar.

An interesting demonstration of the stereochemical importance of lone pairs in the hydrogen bonding of carboxyl groups (though not in a dimer) is provided by ammonium oxalate, where the oxalate ion is twisted by 28° out of its usual planar form (Hendricks & Jefferson, 1936; Jeffrey & Parry, 1952). Three-dimensional refinement has shown (Robertson, 1964) that, in its deformed configuration, the oxalate nion is in excellent relationship with the protons of both the NH<sub>4</sub><sup>+</sup> and the H<sub>2</sub>O molecule in the crystal, achieving planarity and approximate trigonal symmetry (of the C-O bond and the two O...H contacts) at each of the carbonyl groups.

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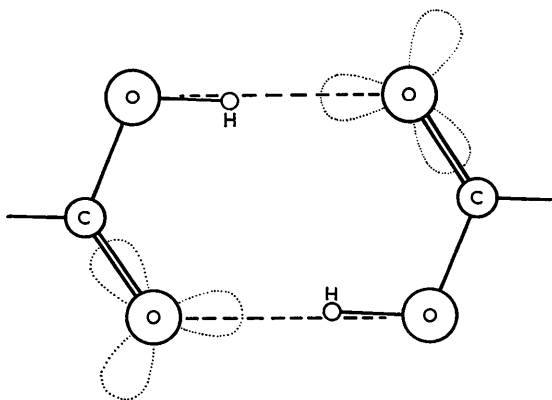


Fig. 1. Configuration of carboxylic acid pair.