764. *The Structure of the Hydrogen Maleate Anion : A Symmetric Hydrogen Bond ?*

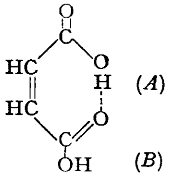
By H. M. E. Cardwell, J. D. Dunitz, and L. E. Orgel.

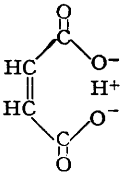
The conditions necessary for the formation of a symmetric hydrogen bond may occur in the acid maleate anion. The infra-red evidence is discussed.

In hydrogen bonds, the hydrogen atom is usually closer to one of the atoms it connects than to the other (Pauling, " Nature of the Chemical Bond," Cornell, Ithaca, N.Y., 1940, p. 301 *et seq.*; Donohue, *J. Phys. Chem.*, 1952, **56**, 502; Davies and Thomas, *J.*, 1951, 2858; Cochran, *Acta Cryst.*, 1953, **6**, 260). Only in very special cases are hydrogen bonds expected to be symmetric and only in one case, potassium hydrogen fluoride, is there unequivocal evidence for such symmetry (Westrum and Pitzer, *J. Amer. Chem. Soc.*, 1949, **71**, 1940; Peterson and Lévy, *J. Chem. Phys.*, 1952, **20**, 704). The possibility that the intramolecular O·H·O bond in nickel and palladium dimethylglyoximes is symmetric has also been discussed recently (Godycki, Rundle, Voter, and Banks, *J. Chem. Phys.*, 1951, **19**, 1205; Rundle and Parasol, *ibid.*, 1952, **20**, 1487). Here we wish to point out that the hydrogen maleate ion provides those conditions under which a symmetric O·H·O bond might exist, and to provide relevant infra-red evidence.

Shahat (*Acta Cryst.*, 1952, **5**, 763) has shown by *X*-ray analysis that in crystalline maleic acid the intramolecular O·H·O distance is abnormally short, 2·46 Å. This distance is fairly close to that, 2·30 Å, expected for a symmetric bond (Donohue, *loc. cit.*), but, nevertheless, the bond distances in the two carboxyl groups show quite conclusively that the hydrogen atom is more firmly associated with one than with the other. The molecule can be represented as in (I). The hydrogen atom of carboxyl group *B* forms an intermolecular hydrogen bond of length 2·75 Å. This atom can be ionised with remarkable ease ($K_1 = 1{\cdot}2 \times 10^{-2}$; compare K_1 for fumaric acid, $9{\cdot}5 \times 10^{-4}$), an effect attributable to the relatively close approach of hydrogen atom *A* to carboxyl group *B*, as Hunter has pointed out (*Chem. and Ind.*, 1953, **17**, 154). Since proton *A* repels proton *B*, it follows that removal of proton *B* to give the acid maleate ion should cause proton *A* to move towards carboxyl group *B*. This suggests that the internal hydrogen bond is more nearly symmetric in the acid maleate ion than in maleic acid itself. Further, from consideration of the electronic structure of the acid maleate ion, one can see that the conjugated system will facilitate the formation of a symmetric bond by favouring the equivalence of the two carboxyl groups. Similar considerations are, of course, applicable to the corresponding phthalic acid case although here the internal O·H·O distance in the acid in unknown.

(I)





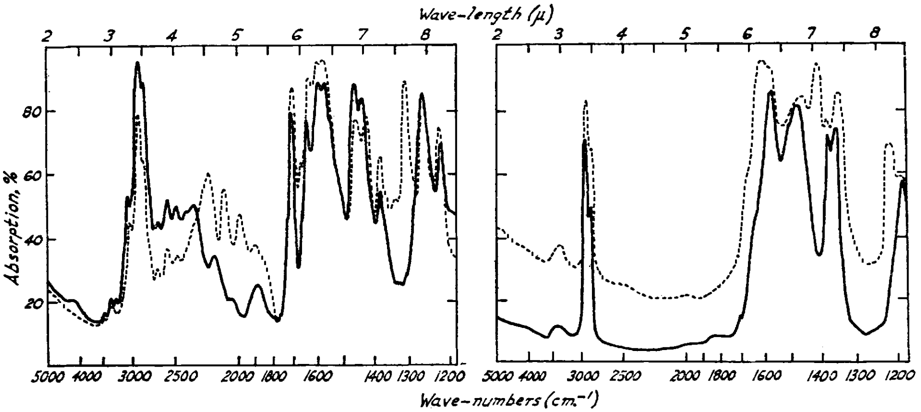
(II)

We have examined the infra-red spectra of maleic acid, anhydrous potassium hydrogen maleate, and some deuterated derivatives, and we find that they are consistent with a more symmetric structure for the hydrogen maleate anion than for the acid. The spectrum of the hydrogen maleate is remarkably simple as compared with that of maleic acid (Figs. 1 and 2). Detailed assignments of the bands cannot be made unambiguously, but nevertheless certain conclusions can be reached. First, the absence of any strong absorption before 1575 cm.$^{-1}$ and at 1260 cm.$^{-1}$ in potassium hydrogen maleate is not compatible with a superposition of carboxyl group and carboxylate ion spectra. The spectrum observed is similar to that of an anion. We may conclude, contrary to Davidson (*ibid.*, p. 408), that the internal hydrogen bond is retained and also that the hydrogen atom is not sufficiently firmly bound to either carboxyl group to produce the characteristic carboxyl group spectrum.

Further support for this interpretation is given by a more detailed but tentative discussion of the more prominent features of the spectrum. Increase in hydrogen-bond strength is accompanied by weakening, broadening, and shifting to longer wave-length of the O–H band (Rundle and Parasol, *loc. cit*; Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166). In maleic acid the doublet centred at 2000 cm.$^{-1}$ has been assigned to O–H (Lord and Merrifield, *loc. cit.*), and it is certainly in a region in which deuteration produces changes. On the other hand, deuteration of the hydrogen maleate produces no marked change above 1600 cm.$^{-1}$. We may infer that the hydrogen bond in the latter is particularly strong. In the acid the rather strong band at 1630 cm.$^{-1}$ may be the C=C stretching frequency. If so, its disappearance in the salt would be consistent with a more symmetric structure. Since the band at 1700 cm.$^{-1}$ in maleic acid can be assigned with confidence to C=O stretching of the carboxyl group which forms the external hydrogen bond, the only reasonable alternative for the 1630 cm.$^{-1}$ band is C=O stretching of the other carboxyl group, in which case its disappearance in potassium hydrogen maleate is even stronger evidence for a very strong hydrogen bond.

Infra-red spectra (2—8·5 μ) *in paraffin.*

FIG. 1. FIG. 2.



——— *Maleic acid.*
- - - - *Deuteromaleic acid.*

——— *Potassium hydrogen maleate.*
- - - - *Potassium deuterium maleate.*

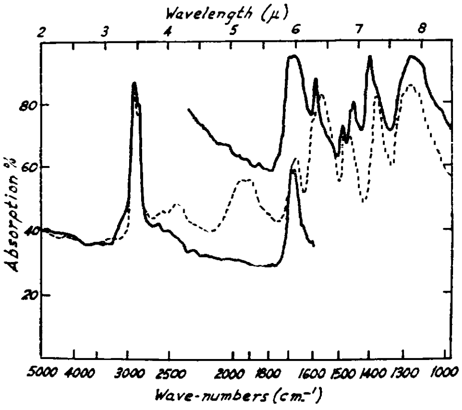


FIG. 3. *Infra-red spectra* (2—8·5 μ) *of phthalic acid* (——) *and potassium hydrogen phthalate* (- - - -) *in paraffin.*

Our results, therefore, establish the existence of an exceptionally strong hydrogen bond in potassium hydrogen maleate. It is tempting to postulate a structure in which a proton lies between two carboxyl anions to form the symmetric anion (II), but it seems wiser to await the results of *X*-ray and neutron-diffraction studies before coming to any definite conclusions.

The infra-red evidence (Fig. 3) for phthalic acid and its corresponding derivatives has also been examined. Considerations similar to those outlined above indicate that the internal hydrogen bond in potassium hydrogen phthalate is stronger than in phthalic acid, but not as strong as in potassium hydrogen maleate.

EXPERIMENTAL

Deuteromaleic acid was prepared (*a*) by distillation of a solution of maleic acid in 99·75% deuterium oxide, and (*b*) by dissolution of maleic anhydride in warm deuterium oxide and evaporation at room temperature *in vacuo*. The two specimens gave identical infra-red spectra.

Potassium deuterium maleate was prepared by dissolution of anhydrous potassium hydrogen maleate in deuterium oxide and concentration as in (*a*) and (*b*) above. The two specimens gave identical infra-red spectra.

X-Ray powder photographs showed that no change in crystal structure occurs on deuteration of either maleic acid or potassium hydrogen maleate.

Potassium hydrogen maleate, prepared by evaporation of an aqueous solution of potassium hydrogen carbonate and maleic acid, is anhydrous, contrary to the description as a hemihydrate by Büchner (*Annalen*, 1844, **49**, 62). The crystals occur as orthorhombic needles or tablets with $a = 4{\cdot}54$ Å, $b = 7{\cdot}78$ Å, $c = 15{\cdot}95$ Å. The space group is either C_{2v}^{5} (Pbc2_1) or D_{2h}^{11} (Pbcm), probably the former. The density, determined by flotation in ethylene dibromide-benzene, is 1·82 g. cm.$^{-3}$, leading to a molecular weight of 154 [Calc. for $KH(C_4H_2O_4)$: *M*, 154), for 4 molecules in the unit cell.

Infra-red spectra on paraffin and perfluorokerosene mulls were recorded on a Perkin–Elmer double-beam spectrophotometer Model 21 by Dr. F. B. Strauss with the technical assistance of Mr. F. H. L. Hastings.

UNIVERSITY MUSEUM, OXFORD.

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