Acta Cryst. (1962). **15**, 619

Proton magnetic resonance study of the structure of ammonium oxalate monohydrate.

By R. Chidambaram, *Department of Physics, Indian Institute of Science, Bangalore 12, India*

(*Received* 28 *December* 1961 *and in revised form* 20 *February* 1962)

Ammonium oxalate monohydrate, $(NH_4)_2C_2O_4.H_2O$, belongs to the space group $P2_12_12$ with two molecules in the unit cell. A proton magnetic resonance study of the hydrogen bonds from the water molecules in the structure of this crystal has been carried out using a slightly modified Pound–Knight type of NMR spectrometer at 14·85 m.c./s. Resonance signals were recorded for a single crystal for 13 angular orientations of the magnetic field H_0 in the a–b plane at intervals of about 15°.

For all the orientations, an intense central peak is obtained due to the reorienting ammonium ions, as found in all ammonium salts without exception at room temperature. In addition, there are two pairs of doublet lines due to the two non-parallel **p**–**p** (inter-proton) vectors of water molecules. These doublet lines are resolved from the central ammonium peak for some of the orientations and the doublet separation ΔH could be measured for these. The values of ΔH thus obtained were fitted into the Pake equation (Pake, 1948) by the method of least squares to determine the **p**–**p** separation and the orientations of the two water molecules. The **p**–**p** separation is $1·60 \pm 0·015$ Å. The two non-parallel **p**–**p** vectors lie in the (001) plane (as is to be expected from space-group considerations) and are oriented at $\pm(14° \, 40' \pm 1°)$ to the a-axis.

As suggested by Jeffrey & Parry (1952, 1954) on the basis of their X-ray structure analysis, the water molecules are seen to link the oxalate ions by means of $O–H \cdots O$ hydrogen bonds into linear chains parallel to the a-axis. From the atomic parameters determined by these authors, the water–oxygen to carboxyl–oxygen $(O_w \cdots O)$ distance is 2·78 Å, the angle $O \cdots O_w \cdots O$ is 126°, and the inclination of the $O \cdots O$ vectors to the a-axis is $\pm 13·5°$. If we assume an O–H distance of 1 Å (generally found for $O–H \cdots O$ bonds of this length), the $H–O_w–H$ angle is 106·5° for a **p**–**p** distance of 1·60 Å. Thus the $H–O_w–H$ angle is close to the value of 104·5° found in the water–vapour molecule. The angle between the **p**–**p** vector and the $O \cdots O$ vector is only 1°; hence the atoms in the hydrogen-bond system, $O \cdots H–O_w–H \cdots O$, lie in a plane within the limits of experimental error. But in this plane, the $O–H \cdots O$ bonds are bent with an angle of 10° between the O_w–H and $O_w \cdots O$ directions. It has been shown elsewhere (Chidambaram, in press) that, in all the hydrated crystals so far investigated by neutron diffraction and proton magnetic resonance, when the angle at the donor water oxygen subtended by the acceptor oxygens deviates from the vapour $H–O_w–H$ angle value of 104·5°, bent hydrogen bonds are formed in preference to distortion of the $H–O_w–H$ angle.

It may be added that there is no direct evidence from this investigation regarding the non-planarity of the oxalate ion in this structure discovered by Hendricks & Jefferson (1936).

The author is grateful to Prof. R. S. Krishnan for his kind interest and encouragement and to Dr G. Suryan for some useful discussions. He also thanks the Department of Atomic Energy for a Senior Research Fellowship.

References

Chidambaram, R. (1962). *Jour. Chem. Phys.* (Under publication.)

Hendricks, S. B. & Jefferson, M. E. (1936). *Jour. Chem. Phys.* **4** 102.

Jeffrey, G.A. & Parry, G.S. (1952). *Jour. Chem. Soc.*, p. 4864.

Jeffrey, G. A. & Parry, G. S. (1954). *Jour. Amer. Chem. Soc.* **76**, 5283.

Pake, G. E. (1948). *Jour. Chem. Phys.* **16**, 327.

Acta Cryst. (1962). **15**, 619

Unit cell and space group of 2.2′ dinitrobiphenyl,

By R. Hulme, *Chemistry Dept., King's College, London, W. C. 2, England*

(*Received* 26 *February* 1962)

During the course of other studies crystals of 2.2′ dinitrobiphenyl $(C_{12}H_8N_2O_4)$ were examined. A chloroform solution of the material yields pale yellow acicular crystals, m.p. 126 °C., which show oblique extinction, the needle axis being c. Weissenberg photographs using Cu $K\alpha$ radiation show the unit cell to be monoclinic,

$$a = 12·71 \pm 0·05,\ b = 8·23 \pm 0·02,\ c = 14·55 \pm 0·07\ \text{Å}\,,$$
$$\beta = 134·8 \pm 0·04°,\ U = 1079\ \text{Å}^3.$$

The cell contains four molecules ($D_m = 1·48$ by flotation, $D_c = 1·50$ g.cm.$^{-3}$). The observed systematic absences correspond to the space group $Cc\ (C_s^4)$, or $C2/c\ (C_{2h}^6)$.

These results are in fair agreement with the morphological data of Groth quoted in the Barker Index (1956). There the axial ratios are 1·293:1:0·909 with an angle of 121·6°. With $a' = [\bar{1}0\bar{1}]$, $b' = b$, $c' = c/2$, the present ratios are 1·288:1:0·884, β' being 121·8°.

No further work on this compound is contemplated.

Reference

The Barker Index of Crystals (1956). Vol. II, Pt. 3, M2405. Cambridge: Heffer.