

suggest that the mean amplitude of the thermal vibration of atoms has the largest component along the c axis and the smallest component along the a axis, since the overall temperature factor is least for the (001) projection (1.1 \AA^2) and maximum for the (100) projection (3.2 \AA^2). This is also indicated by the (010) electron-density projection (Fig. 2) where the atomic contours, especially those of the methyl carbon atom, appear distinctly elongated nearly along the c axis. This can be understood from the orientation of the molecule (x, y, z) with respect to the neighbouring molecules in Fig. 4. The atom O_1 is strongly bonded to the two sodium atoms (x, y, z) and ($x, y, z+1$), and atom O_3 is strongly bonded to the two sodium atoms ($x, y+1, z$) and ($x, y+1, z+1$). The methyl carbon C_3 and keto-group oxygen O_2 are bonded to the neighbouring molecules by weak forces only. The oscillation of the molecule about the line O_1-O_3 should therefore be most likely, and so the components of the thermal

vibration amplitudes of the atoms C_2, C_3 and O_2 will be maximum along the c axis and will be least along the a axis. The bond between $Na(x, y, z)$ and $O_2(x, y, z)$ is quite strong (distance 2.51 \AA), but since the movement of the atom O_2 would take place nearly perpendicular to the $Na-O_2$ bond, the $Na-O_2$ distance is not expected to alter appreciably during the oscillation. Besides, there is a possibility of free rotation about the central C-C bond, so that the plane $C_3-C_2-O_2$ may keep turning suitably during the oscillation so that the $Na-O_2$ distance is not affected.

References

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
 LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, pp. 288, 309. London: Bell.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1961). **14**, 1286

A note on the crystal structure of zirconium pyrophosphate. By H. McD. MCGEACHIN, *Albright and Wilson (Mfg) Ltd., Oldbury, Birmingham, England*

(Received 26 June 1961)

Levi & Peyronel's (1935) structure of zirconium pyrophosphate ZrP_2O_7 , requires that the central P-O-P group of the pyrophosphate ion be linear, lying in fact on a three-fold axis. In both paper and abstract there occurs an unfortunate numerical error by which the P-P distance is incorrectly given as 3.03 \AA which is less than twice 1.56 \AA , the P-O distance. This has led some writers (Hanwick & Hoffmann, 1951; Van Wazer, 1958) to the conclusion that the P-O-P angle is 152° and not 180° . Furthermore it has been felt that since the X-ray scattering is dominated by the zirconium atoms, the determination of the structure of the pyrophosphate ion may not be unequivocal.

The low temperature form of ZrP_2O_7 , crystallizes in a primitive cubic cell of side $a_0 = 8.258 \text{ \AA}$ (Harrison, McKinsty & Hummel, 1954). Levi & Peyronel give the density as about 3.3 g.cm.^{-3} , which corresponds to four formula units per cell. In any such cell at least some of the eight phosphorus atoms must lie on three-fold axes. If $P_2O_7^{4-}$ is a discrete ion and one phosphorus atom lies on a three-fold axis, so must the other, for otherwise the ion would contain four phosphorus atoms; the only sensible way of distributing the seven oxygen atoms is to place one on the axis and six in two symmetrical

groups of three. To preserve four-fold grouping of oxygen atoms round the phosphorus atoms the only possible configuration is one in which the single oxygen atom is placed on the three-fold axis between the phosphorus atoms.

The existence and linearity of the central P-O-P group in ZrP_2O_7 , can thus be confirmed (without detailed knowledge of the structure or even the space group) from considerations of the Bravais lattice, cell size and density, and the assumption that the P_2O_7 ion is discrete. It should be noted, however, that in $Na_4P_2O_7 \cdot 10H_2O$ the P-O-P angle is 134° (MacArthur & Beevers, 1957).

References

- HANWICK, T. J. & HOFFMANN, P. O. (1951). *J. Chem. Phys.* **19**, 708.
 HARRISON, D. E., MCKINSTY, H. A. & HUMMEL, F. A. (1954). *J. Amer. Ceramic Soc.* **37**, 277.
 LEVI, G. R. & PEYRONEL, G. (1935). *Zeit. Krist.* **92**, 190.
 MACARTHUR, D. M. & BEEVERS, C. A. (1957). *Acta Cryst.* **10**, 428.
 VAN WAZER, J. R. (1958). *Phosphorus and its compounds*, vol. 1, p. 617. New York: Interscience Publishers.