

## LETTERS TO THE EDITOR

ENANTIOMORPHISM IN HYDROGEN  
PEROXIDE, THE SIMPLEST  
DISSYMMETRIC MOLECULE\*

THE X-ray analysis of the structure of hydrogen peroxide was reported by Abrahams, Collin and Limpscomb<sup>1</sup> and a more detailed analysis including the location of hydrogen atoms using neutron diffraction technique was reported by Busing and Levy.<sup>3</sup> This confirmed that the molecule is essentially non-planar with a  $C_2$  symmetry and a dihedral angle of  $89^\circ \pm 2^\circ$ . The molecule of hydrogen peroxide is of considerable interest from the point of view of rotational isomerism since it may be considered to be the simplest dissymmetric molecule which can show conformational isomerism, a fact, which the author feels, is not adequately emphasized in the normal literature. It is simplest in the sense that it contains the minimum number of atoms namely four. The only other type of molecule which could compete with hydrogen peroxide is perhaps substituted ammonia namely NXYZ, where X,Y,Z are substituents all different from each other. But  $H_2O_2$  may be considered simpler than NXYZ since, in order to show isomerism, the latter requires all the four atoms to be of different species while in the former only two species are present.

The optical inactivity of  $H_2O_2$  at room temperature is due to the relatively small rotational energy barrier namely about 1 to 2 kcal./mole, and hence both isomers will be in equal proportions. To be able to isolate the isomers, the value of the energy barrier for rotation around single bonds, is required to be of the order of 20 kcal./mole or more.<sup>4</sup> It is however of interest to note in this connection that in the solid crystalline state  $H_2O_2$  takes up the non-centrosymmetric and enantiomorphous space group<sup>3,7</sup>  $P4_12_12$  (or  $P4_32_12$ ) which clearly shows that only one particular species of rotamer exists in the lattice. The fact that it takes up the space group  $P4_12_12$  also shows that the two enantiomeric crystalline forms should exist. A reference to literature<sup>1,3,9</sup> shows that no specific observation on this point seems to have been made. Crystals may also be expected to show optical activity since it is uniaxial and the oxygens have relatively large polarisability,

A further interesting aspect of its structure is the possibility of establishing the absolute configuration of the crystal structure which will yield the absolute conformation of the molecule, *i.e.*, the helical sense, and this will yield particularly valuable correlation with its optical activity in the solid state.

This possibility has been considered by us, using the X-ray anomalous dispersion technique,<sup>2</sup> since, recently even with light elements such as oxygen, determination of absolute configuration has been achieved successfully.<sup>6</sup> However, in the case of  $H_2O_2$  the "non-anomalous scatterer" namely the hydrogen is of rather very low scattering power and the possibility of detecting the difference in intensity of the Bijvoet pairs looks rather remote. For instance using the co-ordinates of Busing and Levy<sup>3</sup> and using  $\Delta f_0'' = 0.028$  (Zachariasen<sup>10</sup>) the maximum value of the Bijvoet ratio

$$\frac{[I(H) - I(\bar{H})]}{[I(H) + I(\bar{H})] \cdot 2}$$

turns out to be about 1% for a few reflections. The accuracy, attainable with the available diffractometers, makes it unlikely that the effect could possibly be detected.

It may be remarked in this context that a somewhat similar case of enantiomorphism in the solid state for a dissymmetric molecule was pointed out sometime ago by Robertson<sup>8</sup> in the case of ammonium oxalate, where the oxalate ion in that particular structure lacks the  $\bar{1}$  and  $m$  symmetry and the crystal takes the non-centrosymmetric space group  $P2_12_12_1$ . It may be noted that the oxalate ion normally has a plane of symmetry but in the particular structure mentioned above it becomes dissymmetric due to rotation of one of the COO- planes with respect to the other around the C-C single bond resulting in a dihedral angle of about  $27^\circ$ . This has been attributed to the influence of the  $NH_4^+$  ion which has a strong hydrogen bonding tendency. The case of hydrogen peroxide discussed here may be considered even simpler than the oxalate ion in ammonium oxalate since in the former the entire crystal structure is based purely on the single species of the dissymmetric molecule, not needing any other ions or groups,

Finally, it may be remarked that the possible existence of rotational isomers in disulphides and related compounds has earlier been considered,<sup>5</sup> and in fact some of the crystals containing such structures take up enantiomorphous space groups.<sup>5</sup> Although the dissymmetry in these structures is similar to that of  $H_2O_2$ , these are obviously more complex structures.

Morphological and other optical studies on  $H_2O_2$  crystals are being undertaken and the results will be reported in due course.

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