

the model is built with an O_2-O_1 separation of 2.9 Å. A direct application of the correlation graph of Nakamoto, Margoshes and Rundle⁴ to the observed frequency gives an O—O separation of 2.90 Å, but we do not place too much reliance on this value because of the unusual pattern of hydrogen bonds.

The only crystal structure determination we have found in the literature which provides oxygen valence angle data for hydroxyl groups is in the neutron diffraction study of sucrose by Brown and Levy⁵. The oxygen valence angles of 106° to 112° at the hydroxyl groups given by these authors would give rise to a value of about 40° for the angle θ (see Fig. 1).

We thank Professor C. A. Coulson for informal discussions about our triad hydrogen bond arrangement and Dr Eva Frei for preparing an orientated specimen of *Penicillus dumetosus*.

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Received August 16, 1968.

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BIOLOGICAL SCIENCES

Electron Spin Resonance Linewidths in Met Myoglobin

WE have published¹ a detailed account of the variation of electron resonance linewidth in both acid met myoglobin and met myoglobin azide as a function of orientation. We explained the results in terms of a random misorientation of the molecular axes within the single crystals, and showed that, because of the large g value anisotropy in the acid met derivative, a standard deviation of only 1.6° in angular distribution is sufficient to explain the results obtained. These measurements were carried out at Q -band frequencies and the slight deviations from the expected variations were adequately explained in terms of residual broadening mechanisms such as spin-spin interaction and unresolved hyperfine structure. It can be shown¹ that the misorientation produces a linewidth in an axially symmetric system given by

$$\Delta H = \frac{h\nu}{\beta} \frac{(g_{\perp}^2 - g_{\parallel}^2)}{2g_0^3} \sin 2\theta \sin 2\Delta\theta + K \quad (1)$$

In this expression θ is the angle to the haem normal or symmetry axis, $\Delta\theta$ is the standard deviation and K is a constant which includes all the residual broadening mechanisms. In practice at 3 cm and 8 mm wavelengths, the residual mechanisms give a linewidth of about 50 gauss when $\theta = 90^\circ$.

These measurements have now been extended to 4 mm wavelengths and some very interesting effects observed. The spectrometer is a newly designed 4 mm system with a reflexion cavity and a Philips YK 1010 klystron, and will be described in detail elsewhere. The magnetic field is produced by a 50 kgauss superconducting solenoid and the orientation of the crystal relative to the field is achieved by rotating the crystal within the cavity from outside the cryostat. All the measurements were made at 4.2° K, but the linewidths were checked for temperature dependence at 20° K and 77° K using a conventional electromagnet. The variation in linewidth over a 65°

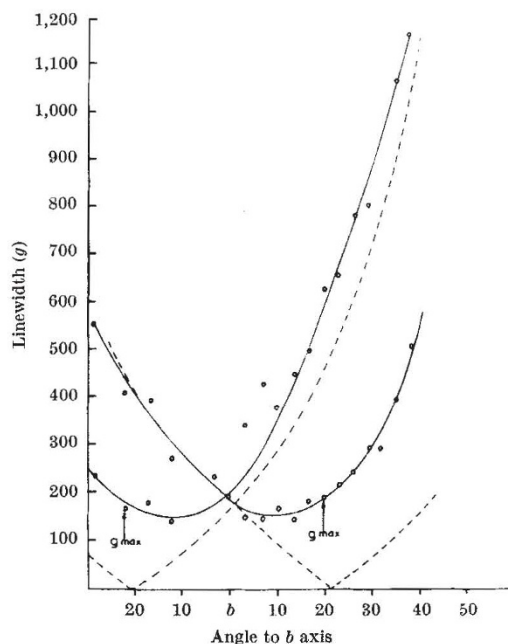


Fig. 1. Variation in line width in the ab plane. —, Experimental curve; ---, theoretical curve.

rotation in the ab plane is shown in Fig. 1. The rotation is at present limited to 65° by the design of the cryostat and the fact that the superconducting magnet has to be used to observe resonance lines with g values approaching the free spin value at 4 mm wavelength. The dotted curve in Fig. 1 is a plot of equation (1), and it can be seen that the theory provides a reasonable fit at angles removed from the haem plane ($\theta = 90^\circ$). The discrepancy near the haem plane is very marked, however, and two points are particularly noticeable. First, the minimum linewidth does not coincide with the maximum g value (g_{\perp}) as would be expected from the simple theory. Second, the deviation of the minimum linewidth from zero, which was previously attributed to residual line broadening mechanisms, has increased in proportion to the increase in frequency.

A scatter in the azimuthal angle and a variation in g_{\perp} was used to explain the linewidth variation in the azide derivative with considerable success¹.

The anisotropy in g_{\perp} in the acid met derivative is so small²⁻⁴ that a scatter of 50° would be necessary if the same mechanism were to be used to explain these results. A variation in linewidth around the haem plane was observed at Q -band and in order to explain these results it must be assumed that this variation is also frequency dependent. The mechanism by which the residual broadening occurs remains obscure, because all the normal broadening mechanisms except g value variation are independent of frequency. Further investigation of these linewidths in different conditions is therefore planned.

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Received September 4, 1968.

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