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Distribution of hydrogen bond angles in molecular crystals

THE structures of hydrogen-bonded molecular crystals have been studied extensively, and the resulting histograms of the distributions of the O–H $\cdots$ O bond angles θ show maxima at approximately 15° from the linear configuration[1-3]. At first sight this seems odd, because theoretically a linear hydrogen bond is stable[4,5]. Kroon and Kanters[3] have indicated, however, that because the number of possible hydrogen bond configurations at any value of θ is proportional to $\sin\theta$, these histograms should not be interpreted to indicate that the configuration of $\theta = 15°$ is, energetically, the most stable. They applied the $\sin\theta$ correction to the statistics of a series of 196 values of hydrogen bond angles in molecular crystals, and showed that the experimental distributions are not inconsistent with an assumed preference for linear hydrogen bonds.

One of us (M.H.)[5] has calculated the potential energy function for the bending of the hydrogen bond O–H–O $\cdots$ O–H$_2$ using the method of CNDO/2, one of the semi-empirical LCAO MO SCF methods which includes all the valence electrons. We intend to show here that the histograms of Kroon and Kanters[3] can be explained by Hasegawa's[5] potential energy function.

The potential function[5] can be represented approximately by the following quadratic form:

$$\Delta E = s\theta^2/2 \qquad (1)$$

in which the linear hydrogen bond is most stable and ΔE represents the strain energy for the bending through θ degrees of the hydrogen bond. The value of the force constant, s, is estimated at 0.4 eV/rad^2. In the case of the hydrogen-bonded water dimer, the dependence on the angle ω of the strain energy ΔE is small, so that factor is neglected here.

If it is assumed that the distribution among configurations in various molecular crystals may be approximated by a Boltzmann distribution, the distribution function $f(\theta)$ for the bending of the hydrogen bonds is represented by

$$f(\theta) = C \sin\theta \, \exp(-s\theta^2/2kT) \qquad (2)$$

where C is the normalisation factor, k is the Boltzmann constant, and T is temperature, taken to be 300 K. The factor, $\sin\theta$, is necessary because the number of possible configurations at a given value of θ is proportional to $\sin\theta$ and the energy dependence on ω is neglected.

The histogram for the distribution of the O–H $\cdots$ O hydrogen bond angles can be calculated using this procedure (Fig. 2).

Figure 2 also shows Kroon and Kanters's histogram[3] of 196 O–H $\cdots$ O hydrogen bond angles observed in molecular

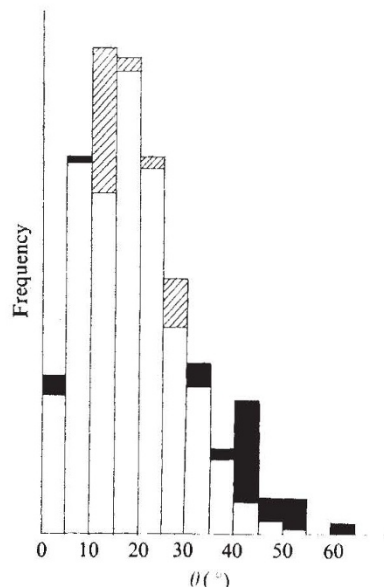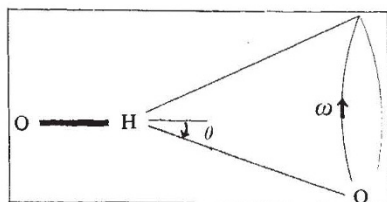Fig. 1 A bent hydrogen-bonded configuration.

Fig. 2 The superimposed histograms of the theoretical and experimental distributions of O–H $\cdots$ O hydrogen bond angles. The experimental histogram is from Fig. 2 of ref. 3. Excess of experimental frequency over theoretical frequency is indicated by solid shading and excess of theoretical frequency over experimental frequency is indicated by hatching. Thus, open column indicates the amount of frequency common to both theory and experiment.

crystals. The two histograms agree quite well with each other: in our calculation the distribution shows a maximum at 14.5°, and the maximum from the molecular crystal data is approximately 15°. The slightly narrower distribution of our theoretical histogram compared with the experimental histogram may be because of the omission of the higher order terms in the right hand side of equation (1).

The hydrogen bond angle is a factor of the molecular structure and molecular arrangement in each crystal. The fact that the distribution of θ, found when the values of the hydrogen bond angle in various crystals are treated statistically, coincides with the distribution for an isolated hydrogen bonded structure, seems to suggest that the perturbation experienced by a structure of O–H $\cdots$ O in molecular crystals is very small.

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Marks of unknown carbonate-decomposing organelles in cyanophyte borings

BLUE-GREEN algae are a major agent of destruction of carbonate rocks and sediments, particularly in the littoral and shallow marine environments. The organisms discussed here are endolithic, that is, the individual algal filaments reside snugly in made-to-measure tunnels of their own, excavated chemically. Data presented here suggest that much of this geologically significant bioerosion is actually caused by what may be called digestion of the mineral substance, and is not,