LETTERS TO THE EDITORS

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Absorption Spectra with Polarized Infra-Red Radiation

Elliott and Ambrose[1] have described measurements with polarized infra-red radiation. In a previous paper[2], we have explored the use of polarized radiation in studying the absorption spectra of oriented polymers. We have now extended this work by a much-improved technique, using large selenium mirrors to obtain the polarization, and have measured the spectra of many substances between 2 and 15 μ. Particularly interesting results have been found with crystalline solids such as simpler amides, dibenzyl, benzyl and diphenyl acetylene. A small amount of the solid is melted between a pair of rock-salt plates and allowed to crystallize so as to obtain so far as possible a linear orientation of the crystal growth.

When examined in polarized radiation with the direction of crystal growth successively parallel and perpendicular to the plane of polarization, marked spectral changes were found. Bands which are weak in one case are strong in the other; it is probable that the differences would be even more marked and informative if the crystalline orientation could be made more complete. The reality of the effects is proved by replacement of the selenium polarizing mirror by a plane aluminium mirror, when all the bands appearing in either of the other two cases appear together.

A very interesting feature is noticed with some of the amides, where the stretching vibration bands of the C=O and N—H bonds at 1655 cm.$^{-1}$ and 3250 cm.$^{-1}$ appear strong when that of the N—H deformation at 1545 cm.$^{-1}$ is weak, and *vice versa*. This could at once be explained if the amides are associated through hydrogen bridges of the type usually accepted and confirmed spectroscopically[3], namely, involving the link —C=O⋯H—N—. In different amides, which may differ in their internal crystal structure and hence in the arrangement of the bridges, the effect observed varies in degree. The results therefore confirm this type of association, and also provide a new reason for attributing the band at 1545 cm.$^{-1}$ to the deformation of the N—H bond, about which there has recently been some doubt. Moreover, they suggest that it may be possible to use this method in studying the structure of polyamides.

We are extending this work to unstretched and stretched rubbers, derivatives of cellulose, and nylons, with which similar changes have been found, and we are also applying it to peptides and proteins such as myosin. A detailed account will be published later elsewhere.

J. MANN
H. W. THOMPSON

Physical Chemistry
Laboratory,
Oxford.
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[1] *Nature*, **159**, 641 (1947).
[2] Thompson and Torkington, *Proc. Roy. Soc.*, A, **184**, 3 (1945); *Trans. Farad. Soc.*, **41**, 260 (1945).
[3] Richards and Thompson, *J. Chem. Soc.*, in the press.

Polarized Infra-Red Radiation as an Aid to Crystal Analysis

THE optical properties of crystals have been widely used as subsidiary data in X-ray structure analysis. Recent advances in infra-red spectroscopy now make it possible to extend the optical measurements into the region of molecular vibrational frequencies. Since certain infra-red absorption bands of organic molecules can be assigned to vibrations largely localized in certain substituent groups, or to vibrations of the molecule as a whole, a study of infra-red dichroism gives information about the orientation of the groups or molecules in the crystal. For example, if all the molecules in a crystal are equally oriented with respect to the crystal axes, then the minimum absorption of polarized infra-red radiation will be observed when the plane of polarization contains the direction of the change of electric moment produced by the molecular vibration responsible for the absorption. If the crystal contains two sets of mutually inclined molecules, the maximum absorption occurs when the plane of polarization bisects the obtuse angle between the two planes containing the directions of the electric moments and the incident beam. From the ratio of the maximum to minimum optical densities, the angle between the planes can be calculated. Information of this sort can be obtained with the aid of an extremely simple polarizing attachment to a standard infra-red spectrophotometer.

A polarizer was constructed from two surface-aluminized concave mirrors and a plane selenium mirror. The latter was made by melting selenium between a metal plate and a plane glass plate; on cooling, the glass plate was removed, leaving a highly reflecting selenium surface. The first concave mirror was arranged to throw a parallel beam of light from a Nernst filament on to the selenium mirror at the polarizing angle, and the second mirror to condense it on to the crystal sample placed in the usual position relative to the spectrophotometer. The electric vector in the polarized beam was parallel to the length of the slit, and the sample could be rotated about the axis of the beam. The samples were prepared as thin sheets between rock-salt plates by crystallizing from the melt until a parallel growth of crystals was obtained.

The efficiency of the polarizer may be judged from the fact that the transmission of a sample of succinic acid at 2,900 cm.$^{-1}$ decreased from 75 to 1·5 per cent as the plane of polarization was rotated from the [c] axis to a perpendicular direction. The [c] axes of the acicular crystals in this sample, which was a high-temperature form of unknown crystal structure, were parallel to one another, but the crystals assumed two different orientations about this axis. The great change in absorption of the broad band extending from 3,250 cm.$^{-1}$ to 2,300 cm.$^{-1}$, due to hydrogen-bonded hydroxyl groups, indicates that the O—H bonds must all be nearly parallel to one another and to the [c] axis. This is known to be the case in the form stable at room temperature[1].

In the case of a sample of *p*-benzoquinone, tabular on the (100) face, none of the bands showed very intense dichroism. In the crystal structure of benzoquinone determined by X-ray methods[2], the angle between the [b] axis and the projection of the C=O bonds on the (100) plane is approximately 33°. Several of the absorption bands, including those associated with the C=O and C—H fundamental