

The lowest interatomic distances between any benzene carbon atom and an atom of the surrounding cage are about  $3\frac{1}{2}$  Å.; but any attempt to remove a benzene molecule brings it much closer to cage atoms. A nickel atom of either kind has eight benzene molecules which are equally its neighbours. There is no possibility of any form of chemical linking between nickel and particular atoms of benzene. The planes of the benzene molecules are at right angles to those of the nickel cyanide layers. Any general form of intermolecular attraction directed at right angles to the benzene hexagons would therefore not explain its attachment to the nickel complex. These results, therefore, confirm the assignment of this compound to the clathrate type. The specific character of ammoniacal nickel cyanide as a means of estimating benzene is thus explained; and when further studies of the volume conditions in these structures have been made, it may be possible to make similar materials capable of compound formation with the homologues.

Much information on the nature of the nickel complex can be derived from the fine details of the X-ray diffraction pattern and will be considered elsewhere.

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<sup>1</sup> Hofmann, K. A., and Höchtl, F., *Ber.*, **36**, 1149 (1903). Hofmann, K. A., and Arnoldi, H., *Ber.*, **39**, 339 (1906).

<sup>2</sup> Powell, H. M., *J. Chem. Soc.*, **61** (1948).

### Double Orientation and Infra-Red Dichroism in Polymers

IN continuation of our studies on the orientation of polymer molecules<sup>1</sup>, we have examined several rolled polymer sheets with polarized infra-red radiation using a selenium polarizer<sup>2</sup> and a lithium fluoride prism to give high dispersion in the 3-micron region.

Double orientation has been observed by Bunn and Garner<sup>3</sup> in X-ray photographs of rolled sheets of nylon. We have detected double orientation in nylon and polyvinyl alcohol by examining the spectrum of the rolled material with polarized infra-red radiation passing through the material at an angle of  $54^\circ$  to the plane of the sheet.

The phenomenon is most marked in the case of nylon, where, with suitable orientation of the material, the symmetrical and antisymmetrical  $\text{CH}_2$ -stretching modes are found to have a change of dipole moment respectively in, and perpendicular to, the plane of the sheet. Glatt and Ellis<sup>4</sup>, working in the overtone region, were unable to detect this effect. They suggest that their result may have been due to the rolling technique employed, which produced insufficient orientation, and this appears to be the case.

From quantitative measurements with polarized radiation, it appears that the direction of change of dipole moment in the N—H bond makes the same

angle to the 010 plane of the nylon crystallite as does the axis of the C—H<sub>2</sub> group. The axis of the C—H<sub>2</sub> group lies in the plane of the carbon chain. From the diagram given by Bunn and Garner<sup>3</sup>, it is possible to estimate the various angles, and it appears that the plane of the carbon chain makes an angle of about  $22^\circ$  with the 010 plane. The N—H bond, therefore, makes an angle of about  $22^\circ$  with the 010 plane. The sense of this angle is not known from infra-red measurements, since the nylon crystallites are oriented in two- but not in three-dimensions. It is reasonable, however, to assume that the N—H bond will be on the same side of the carbon chain as the neighbouring C=O on the same chain. This arrangement allows the hydrogen bonding between adjacent chains to take place with the least deformation of the N—H bond. If this is the case, since the C=O makes an angle of about  $4^\circ$  to the 010 plane<sup>5</sup>, then the angle between the C=O and N—H bonds is about  $18^\circ$ , and has been reduced by the hydrogen bonding forces from  $39^\circ$  (corresponding to the nitrogen valency angle).

In hot-rolled sheets of polyvinyl alcohol, the  $\text{CH}_2$  stretching frequencies show the same evidence of double orientation as in nylon, though to a smaller extent. This shows that there is a tendency for the planes of the carbon chains to be oriented parallel to the rolled sheet, as would be expected from the structure for the polymer proposed by Bunn<sup>6</sup>.

Although considerable dichroism is shown by the  $\text{CH}_2$  frequencies, the very broad O—H band shows no dichroism whatever, whether the radiation be normal to the rolled sheet or inclined so as to approximate to the direction of the extended polymer chains. This is entirely in agreement with Bunn's structure<sup>3</sup> and is conclusive evidence that the earlier views of Mooney<sup>6</sup> are incorrect; for if the O—H bonds were confined to the plane of the carbon chain, as Mooney proposed, strong dichroism of the O—H bands should appear when the radiation direction approximates to the chain direction. Our earlier results, obtained with infra-red radiation normal to the stretched polymer<sup>1</sup>, did not discriminate against the structure proposed by Mooney.

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<sup>1</sup> Elliott, A., Ambrose, E. J., and Temple, R. B., *J. Chem. Phys.*, **16**, 877 (1948).

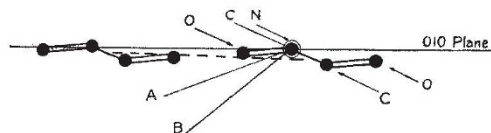
<sup>2</sup> Elliott, A., Ambrose, E. J., and Temple, R. B., *J. Opt. Soc. Amer.*, **38**, 212 (1948).

<sup>3</sup> Bunn, C. W., and Garner, E. V., *Proc. Roy. Soc., A*, **189**, 39 (1947).

<sup>4</sup> Glatt, L., and Ellis, J. W., *J. Chem. Phys.*, **16**, 551 (1948).

<sup>5</sup> Bunn, C. W., *Nature*, **161**, 929 (1948).

<sup>6</sup> Mooney, R. C. L., *J. Amer. Chem. Soc.*, **63**, 2828 (1941).



Nylon crystal seen along the chain axis (Bunn and Garner), showing direction of the N—H bond obtained from infra-red measurements. AN, direction of N—H bond from infra-red measurements; BN, undistorted N—H valency direction

### Reactions in Liquid Sulphur Dioxide

JANDER'S theory<sup>1</sup> of reactions in liquid sulphur dioxide has recently been criticized by Bateman, Hughes and Ingold<sup>2</sup> and, in this connexion, it appeared that some useful information might be obtained by determining whether or not exchange of oxygen occurred between liquid sulphur dioxide and a dissolved alkali sulphite labelled with heavy oxygen. Jander's theory would necessarily require an ex-