

expectation and, in fact, the result of the catalytic hydrogenation of  $\beta$ -ergosterol (II) strongly suggests that rings *C* and *D* are in *cis* relation. Laucht<sup>3</sup> has shown quite conclusively that the double bond in this substance occupies the C<sub>14:15</sub> position. The original stereochemical configuration of the *C* and *D* rings has, therefore, been destroyed, yet, on catalytic hydrogenation in neutral solution<sup>4</sup> and even in acetic acid<sup>5</sup> (a solvent known to favour the formation of a *cis* configuration),  $\beta$ -ergosterol yields the same ergostanol as that obtained by the complete reduction of ergosterol. Ergostanol must, therefore, include a *cis* fusion of the *C* and *D* rings. As ergostanol is known to possess the *allo*-cholanolic configuration, it would appear from this line of evidence that the *C* and *D* rings in the sterols and the bile acids are in *cis* relation also.

This result also supplies confirmatory evidence of the *trans* fusion of rings *B* and *C*, since, in the wandering of the double bond from ring *B* to ring *D*, the former two rings would be expected from known analogies to adopt their more stable configuration. This is further supported by the fact that inversions of 7-keto derivatives analogous to the facile isomerization of dehydrohydrodesoxycholic acid to 3:6-diketo*allo*-cholanolic acid have never been observed:

D. A. PEAK.

Dyson Perrins Laboratory,  
University, Oxford.  
July 8.

<sup>1</sup> Wieland and Dane, *Z. physiol. Chem.*, **216**, 91 (1933).

<sup>2</sup> Wieland and Schlichting, *Z. physiol. Chem.*, **134**, 276 (1924).

<sup>3</sup> Laucht, *Z. physiol. Chem.*, **237**, 236 (1935).

<sup>4</sup> Reindel and Walter, *Ann.*, **452**, 45 (1927). Heilbron and Wilkinson, *J. Chem. Soc.*, 1708 (1932).

<sup>5</sup> Hart and Emerson, *J. Amer. Chem. Soc.*, **54**, 1073 (1932).

### The *Cis*-form of Azobenzene

DURING determinations of the solubility of azobenzene, in which a photometric method of analysis was used, an apparent lack of reproducibility was traced to an increase both in the light absorption of standard solutions and in the concentration of saturated solutions, on exposure to light. The increases reached steady values after several days' exposure in a thermostat tank in a north-lit room. The increase of adsorption was shown to be nearly independent of light intensity, solvent and concentration, but was reached much more rapidly in bright sunlight—a few minutes sufficing for a *M*/2000 solution in a glass bottle. The phenomenon, persisting after repeated recrystallization of the azobenzene, seemed consistent only with a reversible formation of a polymer or isomer, both forward and backward reactions being activated by light and the thermal reaction being very slow at ordinary temperatures.

The second form was found to be distributed between immiscible solvents much more in favour of the more polar one than is ordinary azobenzene and a method of separation based on this property was devised. 5 gm. of azobenzene were dissolved in 250 c.c. of acetone and the solution exposed to sunlight for several hours. The following operations were then carried out in dim light. 350 c.c. of water were added, the mixture cooled, filtered and extracted with 40 c.c. of light petroleum. The azobenzene left in the aqueous layer would have been extremely small if the acetone solution had not been exposed to light. That actually remaining was

extracted by chloroform. The procedure was several times repeated and the chloroform extracts united, dried and evaporated down *in vacuo*. The product was crystallized from light petroleum between 25° and -15° C.

Solutions of successive crystal fractions were made up in acetone. The first few fractions had a constant absorption coefficient for the blue light used (that transmitted through a Kodak 'Wratten No. 47' gelatin filter) and this was 2.17 times that of ordinary azobenzene. On exposure to sunlight, the absorption of these solutions fell to a constant fraction, 0.61, of the original value. That of ordinary azobenzene rises on exposure to 1.32 of the original, the exposed solutions thus having identical absorption. It was assumed that the first crystal fractions were the pure second form. The equilibrium mixture would contain, therefore, about 27 per cent of the second form.

The melting point of the second form is at least one or two degrees higher than that of the normal form (68° C.). Successive determinations on the same sample gave melting points progressively lower at first, passing through a minimum at about 35°, and then rising to 68° C. Some thermal reversion may have occurred before the first determination, and the exact melting point is therefore in doubt. Thermal reversion is undoubtedly quicker in the liquid than the solid state, but some reversion had occurred in crystals that had been exposed to strong sunlight. In a sealed tube, with a mercury manometer attached, in which the azobenzene occupied about 1/10 of the enclosed air space, thermal reversion took place at 100° C. without change of pressure.

The polar character of the second form, which proves almost conclusively that it is the *cis*-isomer, a suggestion first due to Prof. S. Sugden, is indicated by its greater solubility, despite the higher melting point, in polar solvents, and smaller solubility in petroleum. Determinations of the dipole moment in benzene solutions, made by Dr. R. J. W. Le Fèvre, give a value of 3.0 Debye units. The apparent moment of the ordinary *trans*-form increased on exposure of a solution to light from zero to 1.4-1.5 while that of the *cis*-form decreased to the same value. The change indicates that the equilibrium solution contains between 20 and 25 per cent of the *cis*-form, in good agreement with an approximate estimate of 21 per cent by the photometric method, this value, in a c. 1 per cent solution in benzene, being somewhat lower than that, 27 per cent, found in much more dilute solution in acetone.

G. S. HARTLEY.

Sir William Ramsay Laboratories  
of Inorganic and Physical Chemistry,  
University College,  
London.

### Transformation of Hydrate Cellulose into Native Cellulose

IF cellulose is precipitated from solution or liberated from its compounds with sodium hydroxide, the space lattice ( $a=8.14$  A.,  $b=10.3$  A.,  $c=9.14$  A.,  $\beta=62^\circ$ ) differs from that of native cellulose ( $a=8.35$  A.,  $b=10.3$  A.,  $c=7.9$  A.,  $\beta=84^\circ$ ). In this form it is known as hydrate cellulose, although it is in fact of the same analytical composition as the native form, and is free from water. Hitherto it has not been possible to convert one modification directly into the other; it was possible to pass from native cellulose via alkali cellulose to hydrate cellulose, and from this