

place in a temperature range of about 2 deg. C. The deposit evaporates completely at  $-105^{\circ}\text{C}$ . These results differ from those found by König in two respects. The transition point is substantially higher and better defined, and the layer evaporates completely at a much lower temperature.

To examine this point, deposits were formed from residual vapour in the camera, this being possible if the pumping period is not as prolonged as usual. When 'Formvar' or collodion was used as a base, results were obtained similar to those of König, including the transition from the cubic to the hexagonal form at  $-80^{\circ}\text{C}$ . With other bases, the layers evaporated completely at about  $-105^{\circ}\text{C}$ .; these bases were silica and amorphous germanium in the transmission work and silver in reflexion experiments. These and other experiments suggest strongly that the tenacious character of the deposits is associated with some contamination, which in its turn is associated with the organic bases.

The spacing of the cubic ice was measured at  $-120^{\circ}\text{C}$ ., using thallium chloride and rocksalt as standards, the known spacings at room temperature being extrapolated to  $-120^{\circ}\text{C}$ ., using expansion data at room temperature, Grüneisen's law and specific heat data.

The cube spacing of the diamond-type form of ice is found to be  $6.351 \pm 0.007$  angstroms, at  $-130^{\circ}\text{C}$ ., a value which is slightly lower than that found by König.

Experiments were also carried out using heavy water (of purity 99.72 per cent). The same three types of deposit were found as for ordinary water, the temperatures involved being only a few degrees higher than those characteristic of ordinary water.

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N. D. LISGARTEN  
M. BLACKMAN

Department of Physics,  
Imperial College of Science and Technology,  
London, S.W.7. May 31.

<sup>1</sup> König, H., *Z. Kristal.*, **105**, 279 (1943).

<sup>2</sup> Tschudin, K., *Helv. Phys. Acta*, **19**, 91 (1946).

### Symmetry of Azulene Crystals

THE problem of the symmetry of azulene crystals was first put to me by Dr. H. H. Günthard<sup>1</sup> in 1949. He gave me some of the material from which I prepared, by sublimation, extremely pleochroic crystals.

The crystals showed the forms  $\{001\}$  and  $\{110\}$ , but in addition every crystal showed one, and only one, form of the plane (100). In other words, one acute corner of every diamond-shaped crystal was truncated. This seemed to me a strong indication that there was no axis of symmetry and that the space group was  $Pa$  and not  $P2_1/a$ . It is interesting to find from the communication of Prof. J. M. Robertson and Dr. H. M. M. Shearer<sup>2</sup> that X-ray statistical tests confirm the indications of classical crystallography.

J. D. BERNAL

Birkbeck College, Malet Street,  
London, W.C.1.

<sup>1</sup> Günthard, H. H., *Helv. Chim. Acta*, **38**, 1918 (1955).

<sup>2</sup> Robertson, J. M., and Shearer, H. M. M., *Nature*, **177**, 885 (1956).

### Geometrical Isomerism of some Nitrophenylhydrazones of Benzoyl Formic Acid and their Infra-red Spectra

RECENTLY, papers<sup>1,2</sup> have appeared describing *cis*- and *trans*-2:4-dinitrophenylhydrazones of some aliphatic  $\alpha$ -keto acids. The structural assignment of the hydrazones as geometrical isomers was confirmed by means of infra-red spectra. Previously<sup>3</sup> we separated 2:4-dinitrophenylhydrazone of benzoyl formic acid into two forms, using a salting-out process, and found that the *trans*-form is changed into the *cis*-form by sunlight.

We have now investigated further this hydrazone, as well as mono nitrophenylhydrazones of the acid; it was found in each case that the *cis*-form sodium salt, from the isomeric mixture, could also be precipitated by salting-out with sodium carbonate. Each *cis*-isomer had a higher  $R_F$  value (on a silica gel chromatostrip<sup>4</sup> buffered by sodium phosphate), a longer  $\lambda_{\text{max}}$ , and a lower melting point (except for the 2:4-compound). These constants and infra-red data agree well with Isherwood's results<sup>1</sup> (Table 1). All these isomers were isomerized in carbonate solution, or by sunlight or heat.

*Separation of the geometrical isomers.* Well-powdered hydrazones (2 gm.) were suspended in about 80 ml. of N/2 carbonate solution, and various amounts of anhydrous sodium carbonate (0, 1.5, 3, 7 gm.) were then added for the 2:4-dinitro-, *o*-, *p*- and *m*-nitro compounds respectively. The precipitated salt (*cis*-form) was washed with carbonate solution. The filtrate was promptly precipitated with hydrochloric acid, and a pure *trans*-form was obtained by recrystallization from methanol with a small amount of acetone. To obtain a pure *cis*-form, the precipitated salt was dissolved in luke-warm water, and again precipitated by the addition of carbonate, and freed from sodium. Purification was by recrystallization from a mixture of methanol and benzene. The 2:4-dinitro compound was the most sharply separated. Solubilities of sodium salt of this *cis*-form (having 3.5 moles of water) in water and in normal sodium carbonate solution were 0.82 gm./l. and 0.01 gm./l., respectively. The isomer is sensitive to both light and heat.

*Isomerization of the isomers.* Isomerization was carried out in alcoholic aqueous solution, with or without addition of carbonate. Such solutions were either left in the sunlight or in the dark. Isomerization and decomposition were traced by studying, spectrophotometrically, the variations of  $\lambda_{\text{max}}$  and extinction. In carbonate solution, *m*-isomers were isomerized more distinctly, and accompanied by distinct decomposition. The transformation equilibria (starting from both forms) occurred at two different points according to whether the solutions were in the dark or in the light. This may indicate that isomerization occurs in ionic and in photochemical radical processes concurrently. Other isomers, however, isomerized rather slowly under the same conditions. Contrary to the *m*-isomer, the equilibria of the *o*- and *p*-isomers were at nearly the same respective points. The dinitro-compound, on the other hand, was completely converted into a *cis*-form, without decomposition. After exposure to sunlight, from a concentrated solution of the pure *trans*-form of this compound with carbonate, both forms were actually obtained almost quantitatively. Reverse isomerization could not be effected under alkaline or acidic conditions.