

CRYSTALLOGRAPHY

Mixed Anthrone—Anthraquinone Crystals

A THREE-DIMENSIONAL refinement of anthrone, $C_{14}H_{10}O$ (recorded m.p. $154^\circ C$) by Srivastava¹ has shown that it is isostructural with anthraquinone, $C_{14}H_{10}O_2$ (recorded m.p. $286^\circ C$) (refs. 2 and 3). The unit-cell dimensions and other crystallographic data are:

$$C_{14}H_{10}O, \text{ m.w. } 194.22, P2_1/a, Z = 2$$

$$a = 15.80, b = 3.998, c = 7.86 \text{ \AA } \beta = 101.7^\circ$$

$$D_x = 1.326 \text{ g cm}^{-3} \text{ (using corrected value)}$$

$$N = 6.02335 \cdot 10^{23}$$

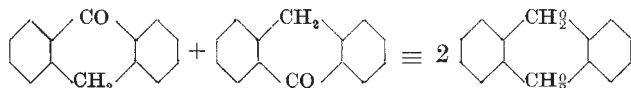
appropriate to the units used)

$$C_{14}H_8O_2, \text{ m.w. } 208.20, P2_1/a, Z = 2$$

$$a = 15.83, b = 3.97, c = 7.89 \text{ \AA } \beta = 102.5^\circ \text{ (at } 20^\circ C)$$

$$D_x = 1.428 \text{ g cm}^{-3} \text{ (corrected)}$$

The similarity between Weissenberg and other photographs of the two compounds is striking. There are small differences, of course, but they have to be looked for. The anthraquinone molecules are centrosymmetrical; the anthrone structure is disordered so that the two molecules in the unit cell each appear to be centrosymmetrical:



The disorder causes the appearance of diffuse layer lines interleaving the 3.998 \AA layer lines in anthrone rotation photographs taken about the b axis. Both structures are markedly pseudo-orthorhombic.

In the course of a solid-state reaction being investigated by X-ray techniques in this laboratory it was found that the main decomposition product gave photographs corresponding with a somewhat fibrous crystal of anthraquinone. Mass spectrometry showed that some anthrone might also be present, although it was not at first certain whether the anthrone was only produced in the mass spectrometer. The fibrous nature of the decomposition product prevented small differences in intensity from being detected, and the presence of disorder and impurity in the final crystals made melting-point determinations a little uncertain. The question then arose as to whether, if anthraquinone and anthrone were both present, they would in any case form mixed crystals.

Attempts to form mixed crystals by recrystallization from solvents were unsuccessful, because anthrone is much more soluble than anthraquinone in all the following

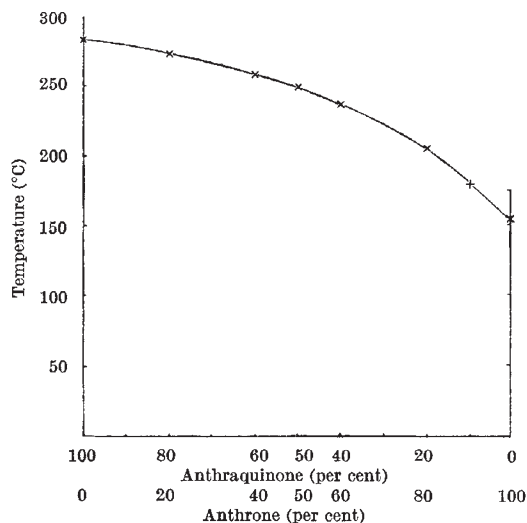


Fig. 1

solvents: ethyl alcohol, acetone, acetic acid, benzene and chloroform. These were all tried, but acicular anthraquinone always came down first. It was found, however, that if anthraquinone and anthrone were melted together in known proportions in a sealed tube and the mixture allowed to cool slowly in a vacuum flask, acicular crystals formed which gave the melting-point/composition curve (Fig. 1). This implies that the crystals at any composition were formed by simple solid solution, no ordered structure appearing at any stage, except for pure anthraquinone.

Weissenberg photographs ($[h0l]$ and $[h1l]$) were taken of a single crystal obtained from the 50:50 melt, the melting-point being checked on another crystal from the same batch. These Weissenberg photographs were compared with similar photographs of the two end members. The crystal in question proved to be a twin on the (201) plane, which is a pseudo-orthorhombic 'axial plane' of the anthraquinone/anthrone structure, and this twinning obscured even the small differences that exist between the two end members of the series. There is no doubt, however, that the structure does correspond closely with that of the end members, anthraquinone and anthrone, and that mixed crystals in any proportions can be formed.

A melting-point determination for the decomposition product mentioned here, carried out in a sealed tube under conditions similar to those used for obtaining the results in Fig. 1, gave $257 \pm 1^\circ C$. This confirmed that the product was not pure anthraquinone (or anthrone) but that it may have contained up to about 45 per cent anthrone or a lesser amount of anthrone together with other impurities.

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¹ Srivastava, S. N., *Acta Cryst.*, **17**, 851 (1964).² Murty, B. V. R., *Z. Kristallog.*, **119**, 445 (1960).³ El Sayed, K., thesis (London, 1965).

CHEMISTRY

Gamma-ray-induced Polymerization of some Vinyltin Compounds

ALTHOUGH much work has recently been carried out on the syntheses of vinylmetallic compounds¹, work on their polymerization has been surprisingly scarce, especially radiation polymerization. Moreover, these compounds seem to be regarded as substances scarcely polymerizable in general. For example, with triethylvinyltin, one of the compounds treated in this communication, Korshak *et al.*² observed the formation of the oligomer, when they heated it with di-*t*-butylperoxide to $120^\circ C$ under pressure as high as 6,000 atm. (ref. 2).

We have irradiated triethylvinyltin and triphenylvinyltin by γ -rays from cobalt-60 in the ordinary state and observed the formation of the polymeric substances from both compounds.

Triethylvinyltin (b.p. 58° – $59^\circ C/13$ mm mercury) and triphenylvinyltin (m.p. 38.5° – $39.5^\circ C$) were synthesized by the reaction of triethyltin chloride and triphenyltin chloride respectively with vinyl Grignard³. The monomers were sealed under 10^{-5} mm mercury after vigorous degassing.

When triethylvinyltin was irradiated by γ -rays from cobalt-60 *in vacuo*, it became turbid, and the mixture of the slightly yellowish viscous product, which occupied the major part, and an insoluble white powder was left behind after pumping out the remaining monomer at room temperature. Yields of the polymeric substances are shown in Table 1.

Fig. 1 shows the infra-red spectra of triethylvinyltin and its soluble polymer. In the $1,100 \sim 3,000 \text{ cm}^{-1}$ region many of the vibrational frequencies of vinyl- and ethyl-substituted organometallic compounds were well