

Studies of the Isomerization of $[(C_6H_5)_3FC_4]_2$

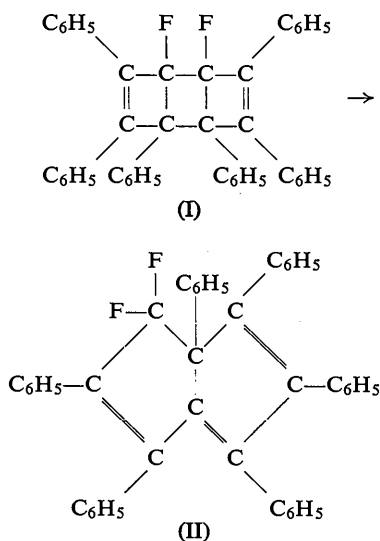
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$[(C_6H_5)_3FC_4]_2$ exists in two isomeric forms (both having triclinic crystal structures), the yellow dichroic form (II) being produced by a rearrangement, in the melt, of the colourless form (I). It was previously observed that (I) turns yellow during prolonged exposure to X-rays, or when heated prior to melting. The present study has shown that some molecules of (II) are formed by heating (I) at temperatures below the melting point (which is a function of heating time) to give a dichroic yellow colour, but, although sufficiently parallel to cause dichroism, the molecules of (II) are situated at random in the matrix of (I), without recrystallization, so that no diffraction pattern for (II) is observed.

Nagarajan, Caserio & Roberts (1964) reported that heating 0.10 g of the liquid compound (I) at 210–215°C for 75 seconds gave a red melt which, on cooling and washing with hexane, afforded 0.085 g of a yellow crystalline powder, which was later shown to have the formula (II).



Compound (II), when recrystallized from acetone, gave bright yellow crystals of m.p. 219–220°C, which are dichroic. The triclinic crystal structure has been fully determined by X-ray diffraction by Beineke & Hughes (1965). They report that the three double bonds in the central skeleton are near enough to coplanarity to give good conjugation, which could account for the intrinsic yellow colour.

The triclinic crystal structure of the colourless compound (I) has been reported briefly by Fritchie & Hughes (1962). The central C skeleton has very closely the symmetry $2/m$ and formula (I) is confirmed. Dr Hughes (private communication to Prof. K. Lonsdale) tells us that a completely untwinned crystal (grown from equal parts of chloroform and absolute alcohol) was never found, but twins occurred with the two indi-

viduals in the ratio of about 1 to 10; seven different crystals of this type had been used (to collect about 5000 non-equivalent reflexions) because during prolonged exposure to X-rays (Cu $K\alpha$) the crystals turned yellow. Nagarajan *et al.* (1964) also reported that compound (I) turned yellow when heated to about 180°C, that is, before melting.

It was suggested by Dr Hughes to Professor Lonsdale that this might be due to the formation of some molecules of (II) in the matrix of (I) and that it would be interesting to find out whether this resulted in the appearance of any kind of one- or two-dimensional substructure such as occurs initially in the solid-state reaction of anthracene peroxide on exposure to prolonged X-rays or on heating (Lonsdale, Nave & Stephens, 1966).

In the latter investigation it was found that the first sign of the reaction was the appearance on Laue, oscillation or Weissenberg photographs (of a single peroxide crystal) of continuous streaks indicating the formation of isolated strings of peroxide molecules parallel to [010]. These subsequently changed to isolated strings of anthraquinone or anthrone molecules, with a different identity distance, and with a mosaic break-up of the peroxide matrix, prior to a recrystallization of a somewhat disorientated single crystal of mixed (anthraquinone, anthrone), of higher density. This decomposition, which released water and other breakdown products randomly into cracks in the final product, occurred entirely in the solid state.

The reaction in $[(C_6H_5)_3FC_4]_2$ occurs in the melt, but is evidently accompanied by some pre-melting phenomenon which produces the yellow coloration. The calculated and measured densities of (I) are given as 1.246 and 1.254 g.cm⁻³ respectively. Those of (II) were given to us by Dr Hughes (private communication) as 1.2498 and 1.25 g.cm⁻³ respectively.

Our own observations were made on crystals of (I) kindly provided by Professor Roberts and Mrs Caserio, through the good offices of Dr E. W. Hughes, and on crystals of (I) and (II) prepared by Mr P. Gaston of this department.

Compound (I) was observed to melt at various temperatures, depending on the rate and duration of heating, to produce a red melt, as follows.

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1. Heating a single crystal to 148°C at 1–2° per minute on a Pt–Pt/10% Rh thermocouple (Meyer, 1965): after 30 minutes (visual observation) the crystal had turned yellow. Further heating at the same rate caused partial melting at 183°C. The crystal completely melted after 15 minutes at this temperature ($182 \pm 3^\circ\text{C}$).

2. Heating a single crystal at 1–2° per minute on a Pt–Pt/10% Rh thermocouple, but finding the temperature of final melting by taking a skidded oscillation photograph (Milledge, 1966): the skidded reflexions disappeared at $181 \pm 5^\circ\text{C}$.

3. Heating a single crystal at 2–3° per minute on a hot-stage microscope (Welch, 1954): a yellow colour appeared at 180°C; continued heating caused the crystal to melt over a period of 20 minutes, the temperature varying between 165 and 185°C. On cooling, the melt solidified over the range 70 to 45°C. Remelting occurred at 70 to 90°C.

4. Heating bulk samples at 2° per minute in a standard metal-block melting-point apparatus: yellow coloration was observed at 160°C, and liquid at $178 \pm 3^\circ\text{C}$. On cooling, the bulk samples solidified at temperatures below 100°C.

Leaving bulk samples in the heater for several hours gave results illustrating the time dependency of the melting. For example, a sample heated for 4 hours showed the formation of some liquid at 157°C. Another sample heated at 155°C for 3 hours turned a deep orange-yellow colour, was considerably sintered, and contained what appeared to be a small amount of liquid.

5. Heating several crystals on a temperature-gradient hot bar: After 40 minutes, the following distribution was observed: liquid, $T > 175^\circ\text{C}$; liquid plus solid, $T = 174^\circ\text{C}$; solid (yellow), $T < 173^\circ\text{C} (\pm 2^\circ\text{C})$.

The temperature dependence of the yellow colour formation was further illustrated by heating several crystals of compound (I) on a hot bar for longer periods at lower temperatures. Those heated at 51° to 54°C showed no change after 71 hours; at 102° to 105°C, a slight yellow was detected after 41 hours; at 128° to 131°C, a definite yellow colour was observed after 41 hours.

The yellow crystals of compound (I), resulting from heat treatment, are dichroic. The maximum intensity is observed when a crystal is viewed perpendicular to the (011) face, the electric vector making an angle of $35^\circ \pm 10^\circ$ with a_0 in the direction of the (011) face normal.

Several samples of compound (I), both bulk and single crystal, were examined by X-ray diffraction during and after heating for various lengths of time to produce the yellow coloration. Bulk samples, heated in glass capillaries prior to exposure, gave only the powder pattern of compound (I). Single crystals, heated either on a thermocouple during exposure or on a hot bar prior to exposure, also gave a pattern indicative of compound (I) only. Samples previously melted showed only a low-order diffuse ring; after recrystal-

lization from acetone, however, the powder pattern characteristic of compound (II) was obtained. $0kl$ and $1kl$ layer reflexions of an untwinned crystal, heated for 1 hour at 147°C to produce a pronounced yellow colour, were compared before and after heating, but no changes in intensity were observed.

The data outlined above suggest that the yellow colour produced by heating compound (I) is due to the formation of some molecules of (II), these being sufficiently parallel to cause dichroism, but situated at random in the matrix of compound (I) without recrystallization so that no diffraction pattern for (II) is obtained.

The existence of compound (II) was confirmed by examining a solution of crystals heated until they were quite yellow (158 to 162°C for 1 hour) in an ultraviolet spectrophotometer. An absorption peak at 373 μ , characteristic of compound (II) (Nagarajan *et al.*, 1964), resulted, indicating a concentration of ca. 3.5% of (II) in the crystals of (I). That this small amount of (II) can give such a pronounced colour effect is consistent with the fact that no changes in intensity were observed for a crystal heated for the same length of time at an even lower temperature.

No attempt was made to do so, but possibly the solid solution of (II) formed in (I) could be studied by heating compound (I) for long periods of time, at low enough temperatures, so that a liquid phase is not formed. There might, however, be a limit to the amount of (II) that could be formed without a break-up of the (I) structure.

I am grateful to Dr E. W. Hughes for drawing our attention to this problem, to Professor J. D. Roberts and Mrs M. C. Caserio for a specimen of compound (I) and to Mr P. Gaston for the preparation of compounds (I) and (II). My thanks are also due to Professor Kathleen Lonsdale and to Dr Judith Milledge for laboratory facilities and advice, to Miss Supanich Pramatus for intensity measurements and to the National Research Council of Canada for a Postdoctoral Research Fellowship. We are indebted to Ferranti Ltd. and to International Computers and Tabulators for the gift and servicing of the computer PEGASUS on which the greater part of the computing was carried out.

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