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The Electronic Structure of Furan-quinones. Polymorphism in Dinaphtho[2,1-2′,3′]furan-8,13-dione

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Abstract—Three polymorphic modifications, a stable orthorhombic form (α) and two metastable monoclinic forms (β and γ), of Dinaphtho[2,1-2′,3′]furan-8,13-dione were identified by single crystal X-ray diffraction. Heats of transformation, measured calorimetrically, for β→α and γ→α are 2.33 cals/gram and 2.07 cals/gram, respectively.

The long wavelength absorption spectrum of the α form and the fluorescence spectra of the three polymorphs are reported. The optical properties of the polymorphs indicate an increase in intermolecular interaction on going from the α to β to γ crystal.

1. Introduction

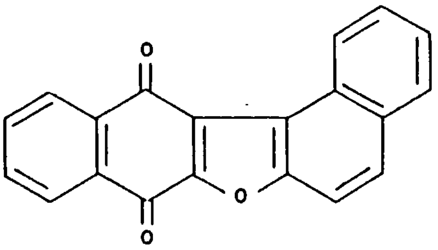
Susich(1,2) in his X-ray diffraction studies of organic dyestuffs reported the X-ray powder patterns of several modifications of the quinoid dye indanthrone. A phase change between two of the modifications was observed in the beam of an electron microscope by Hamm and Norman,(3) while the crystal structure of the stable α form was subsequently reported by Bailey.(4) More recently, Warwicker(5) has shown that polymorphism is a common phenomenon with anthraquinone vat dyes.

Two monoclinic modifications of 1,4-anthraquinone have been reported(6) and certain charge-transfer complexes, containing a quinone as the acceptor moiety, have also been reported to exist in more than one modification.(7,8)

The crystal phase(s) of furan-quinones has received little experimental attention, though derivatives of this class of molecule have been shown to be suitable as vat dyes.(9) Reported here is an X-ray and optical characterization of three crystal modifications observed for Dinaphtho[2,1-2′,3′]furan-8,13-dione (I).

2. Experimental

Dinaphtho[2,1-2′,3′]furan-8,13-dione (I) (Fig. 1) was synthesized by refluxing 2,3-dichloro-1,4-naphthoquinone with β-naphthol in anhydrous pyridine.(10) The quinone was recrystallized from methanol several times, then vacuum sublimed. The melting point was 271 °C, literature value 271 °C. Microanalysis gave H, 3.60% and C, 80.64%, the molecular formula $C_{20}H_{10}O_3$ requires H, 3.40% and C, 80.50%.



I

Figure 1. The molecular structure of dinaphtho[2,1-2′,3′]furan-8,13-dione.

Crystals were grown by vacuum sublimation. Three crystal modifications were obtained by this method, one as yellow platelets (α), and the other two as yellow (β) and orange (γ) rods, respectively.

X-ray diffraction patterns were recorded on precession and Weissenberg cameras with CuKα radiation. Polaroid high speed film was employed in the precession camera and Kodak or Ilford X-ray film in the Weissenberg camera. Measurements on precession photographs enabled lattice parameters to be determined to an estimated accuracy of 0.3% in the distance and 0.1° in the angles. Crystals ranging in thickness from 0.03 to 0.1 mm were used for the measurements.

Calorimetry was carried out using a Dupont Differential Thermal Analyzer (Model 900) with a Differential Scanning Calorimeter attachment. Weighed samples were crimped sealed in aluminium pans. Areas under transition peaks in the thermograms were measured with a K and E compensating polar planimeter.

Ultra-violet and visible absorption and emission spectra were recorded on a Cary 14 Recording Spectrophotometer and an Aminco-Kiers Spectrophotofluorometer, respectively. Emission spectra were corrected for variations in the detector sensitivity with wavelength. All spectra were recorded at ambient temperatures.

3. Results

X-ray Diffraction Studies

The three modifications of the furan-quinone I, namely the yellow platelet (α), the yellow rod (β) and the orange rod (γ) were ascertained to belong to three distinct polymorphic phases. The pertinent cell data for the three polymorphs are given in Table 1.

TABLE 1 Lattice Parameters and Space Group Data for the Polymorphs of Dinaphtho[2,1-2′,3′]furan-8,13-dione†

Polymorph	$a(A)$	$b(A)$	$c(A)$	β(deg)	$V(A^3)$	ρ(g/cc)	N	Sp. Gp.
α	5.44_6	6.11_6	39.7_9	90	1325	1.495	4	$P2_12_12_1$
β	23.4_8	3.85_3	7.62_7	104.4	668.3	1.482	2	$P2_1$
γ	12.3_8	15.2_8	7.42_6	107.5	1340	1.479	4	$P2_1$ or $P2_1/m$

† a, b, c are the unit cell dimensions; β is the monoclinic angle, V the volume of the unit cell and ρ the density deduced from the X-ray data; N is the number of monomeric units per unit cell and Sp. Gp. is the most probable space group.

Space Group Determination

α form: The lattice is orthorhombic. The conditions limiting possible reflections, namely $h00 : h = 2n$, $0k0 : k = 2n$ and $00l : l = 2n$, define the space group unambiguously as $P2_12_12_1$. The calculated unit cell volume yields a reasonable crystal density if 4 molecules are contained in the unit cell or 1 molecule in the asymmetric unit.

β form: The lattice is monoclinic. The only observed condition on possible reflections, $0k0 : k = 2n$, limits the space groups to $P2_1$ or $P2_1/m$. The latter, however, can be excluded on the basis of packing requirements. The unit cell volume then requires 2 molecules per unit cell or 1 molecule per asymmetric unit.

γ form: The crystal lattice is monoclinic. Again, the only observed condition on possible reflections, $0k0 : k = 2n$, limits the space groups to $P2_1$ or $P2_1/m$. However, now the packing requirements cannot distinguish between the two possibilities since there must be 4 molecules per unit cell and hence 2 molecules per asymmetric unit if the space group is $P2_1$ and 1 molecule per asymmetric unit if the space group is $P2_1/m$. Furthermore, disorder is present in the structure, as evidenced by the occurrence of diffuse spots which destroy the perfect periodicity of the lattice in the **b** direction. The disorder shows all the characteristics of a simple type of stacking fault first described by Wilson.(11)

In its present manifestation, zones of reflections for which l is odd are diffuse whereas those for which l is even are sharp. According to Wilson, such a pattern would result from a displacement disorder in the normal packing arrangement of the molecules by $c/2$ along **c**. Since the diffuse spots occur only at lattice sites, the disorder in the three-dimensional structure is only partial (Wilson describes it in terms of a degree of partial disorder) and, as such, differs markedly from disorder associated with thermal motion. It is important to note that exactly the same type and degree of disorder was found to occur in two different crystals of the γ polymorph selected at random from the same batch. This observation implies that the disorder may be an inherent property of that polymorph.

Crystal Morphology

α form: The crystals grow as large thin plates with the long crystallographic axis **c** perpendicular to the plane of the plate.

β and γ forms: The crystals of these two modifications grow as elongated slabs. The orientation of the crystallographic axes with respect to the external faces is very similar in both types of crystals. The **b** and **c** axes lie in the plane of the slabs and are inclined to the sides of the slabs by an angle θ which is approximately 15 to 20°. However, the crystals of the two polymorphs differ in the direction of elongation, this direction being predominantly along **b** in the β form and along **c** in the γ form. The change in the relative lengths of the **b** and **c** axes accounts for this difference.

Calorimetric Measurements

Weighed samples of the three polymorphs were run in the D.S.C. cell, temperature range 0–600 °C, at a heating rate of 20 °C/minute.

Exothermic peaks were observed in the thermograms for the β and γ polymorphs at 200 °C and 210 °C, respectively. X-ray powder diffraction patterns of samples of these polymorphs thermally quenched from temperatures above the exothermic regions confirmed that both modifications had converted to the α modification. No evidence of a phase change below the melting point was noted in the thermogram of the α polymorph.

Heats of transformation ΔH for the conversions $\beta \rightarrow \alpha$ and $\gamma \rightarrow \alpha$, given in Table 2, were obtained from the corresponding thermograms using the formula(12):

$$\Delta H = \frac{E \,.\, A \,.\, \Delta T_s \,.\, T_s}{M \,.\, a} \qquad [1]$$

where E is the calibration coefficient, A the transition peak area, ΔT_s and T_s the Y-axis and X-axis sensitivities respectively, M the sample mass and a the heating rate. The calibration coefficient was determined by recording thermograms for samples of known heats of fusion under identical conditions to those used for the quinones.

TABLE 2 Heats of Transformation for the Polymorphs of Dinaphtho[2,1-2′,3′]furan-8,13-dione

Transformation	ΔH cal/gram	T† °C
$\beta \rightarrow \alpha$	2.33 ± 0.05	200
$\gamma \rightarrow \alpha$	2.07 ± 0.05	210

† Exothermic peak temperature, heating rate 20 °C/minute.

Visible Absorption and Emission Spectra

The long wavelength absorption band in the single crystal spectrum (unpolarized light) of the α-polymorph is shown in Fig. 2; the corresponding molecular absorption band, measured in hexane, is also shown for comparison. The crystal shift of the transition, as given by $\nu_{\mathrm{HEXANE}}-\nu_{\mathrm{CRYSTAL}}$, is 1330 cm^{-1}. The frequency separation between the absorption maximum at 457 nm and the shoulder at approximately 482 nm in the crystal spectrum is 1140 cm^{-1}. This frequency, which corresponds closely to the vibrational spacing of 1100 cm^{-1} observed in the analogous molecular transition, is tentatively associated with the furan C-O-C stretching vibration.(13) Single crystal absorption spectra were not recorded for the β and γ

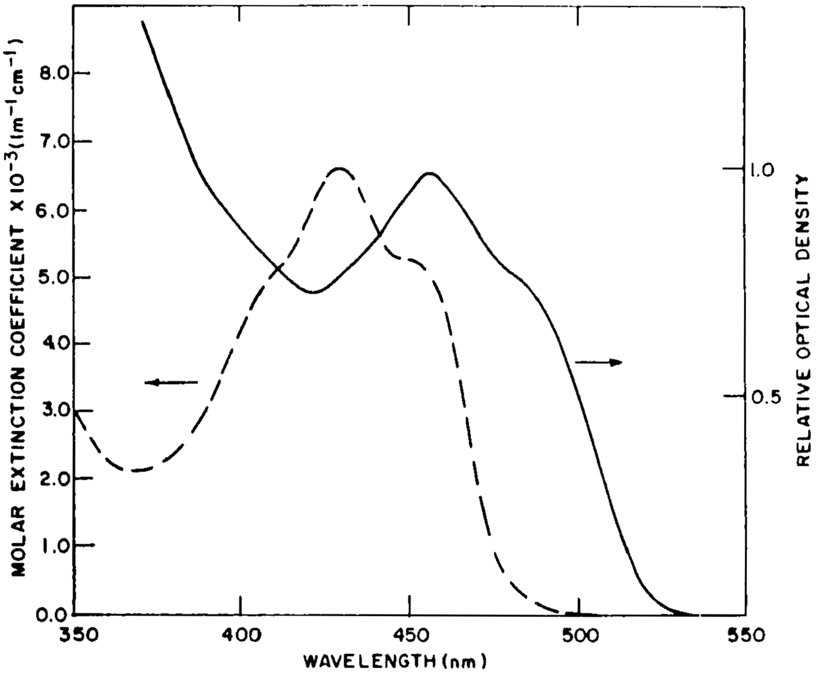


Figure 2. ——— The single crystal visible absorption spectrum of the α polymorph of dinaphtho[2,1-2′,3′]furan-8,13-dione. ------ The long wavelength absorption spectrum of the furan-quinone measured in hexane solvent.

polymorphs due to a lack of suitable crystals. Further, attempts to measure the spectra of these polymorphs as dispersions in a potassium bromide matrix were unsuccessful due to partial conversion of these polymorphs to the stable α form during sample preparation. However, the orange colour of the γ crystals is indicative of a shift to lower energies in the absorption edge of this modification.

In the absence of absorption spectra for the three polymorphs, crystal fluorescence spectra were recorded. Single crystals were mounted on a quartz slide and excited with 350 nm radiation and the fluorescence emission viewed normal to the front surface of the crystal. Fluorescence spectra are shown in Fig. 3, the spectra of the β and γ forms may be somewhat distorted due to fluorescence reabsorption in these crystals which were thicker than those of the α form (3 to 10μ vis 1 to 3μ). The α fluorescence spectrum shows an

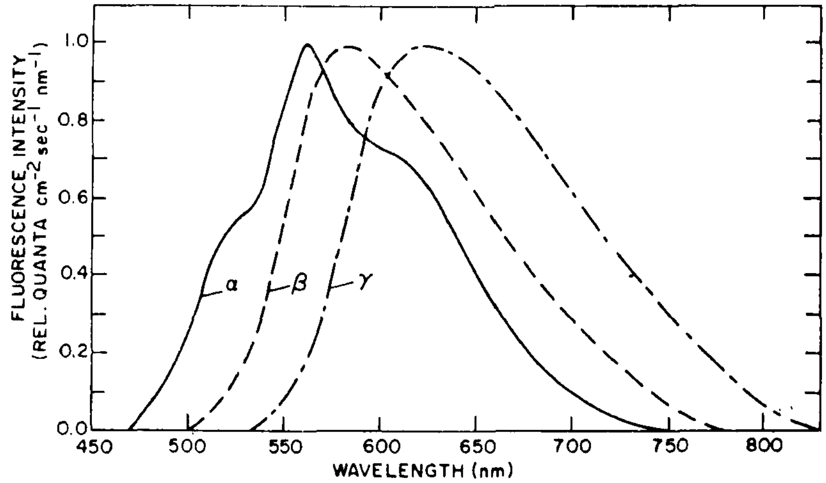


Figure 3. The crystal fluorescence spectra of the α, β and γ polymorphs of dinaphtho[2,1-2′,3′]furan-8,13-dione.

approximate mirror image relationship with the long wavelength absorption band of the crystal. The vibrational spacing is comparable to that observed in absorption. The emission of the β and γ forms are shifted to longer wavelengths in the order $\alpha < \beta < \gamma$. No structure was observed in these spectra (resolution approximately 2 nm).

4. Discussion

The lattice parameters determined for the crystal modifications of Dinaphtho[2-1-2′,3′]furan-8,13-dione, grown by vacuum sublimation, confirm the existence of at least three polymorphic forms of this furan-quinone. The orthorhombic α modification, with four molecules per unit cell, is the stable form in the temperature range studied, i.e. 20–270 °C. The monoclinic β and γ modifications, with two and four molecules per unit cell, respectively, are metastable forms which rapidly convert to the α form at temperatures above 170 °C. Heats of transformation for $\beta \rightarrow \alpha$ and $\gamma \rightarrow \alpha$ of 2.33 cals/gram and 2.07 cals/gram respectively reflect the similar stabilities of the β and γ polymorphs. These observations are consistent with predictions based on the calculated X-ray densities of the polymorphs.(14)

The α form having a greater density than those of the β and γ forms is expected to be the more stable polymorph, while the latter two forms with approximately the same densities are expected to have similar stabilities. A density of 1.46 grams/cc was measured by flotation for the α polymorph, which is in fair agreement with the X-ray density of this form.

Emission spectra of organic crystals are extremely sensitive to the presence of impurities and crystal defects.(15) Distortions in the recorded fluorescence spectral distribution may also arise from reabsorption of the emission in the crystal. The latter effect is most evident when using thick crystals and weakly absorbed excitation and when there is a strong overlap of the crystal absorption edge with the emission band. Repeated purification of the quinone by crystallization from methanol and then vacuum sublimation produced no change in the fluorescence spectra. This appears to exclude the possibility that the emission is due to impurities in the crystal. The disorder in the crystal structure of the γ polymorph may result in defect emission contributing to the fluorescence of this crystal form. Fluorescence reabsorption was minimized in this work as mentioned earlier. In this case it would appear that the fluorescence emission spectra recorded for these crystals (Fig. 3) are characteristic of the respective polymorph.

The shift in crystal fluorescence maxima to longer wavelengths in the order $\alpha < \beta < \gamma$ indicates an increase in inter-molecular interaction, possibly resulting from a closer molecular spacing or greater overlap of adjacent molecules, on going from the α to β to γ crystal structure. The electron affinity (molecular) of the furan-quinone has been estimated, from aromatic hydrocarbon-quinone charge-transfer spectra, as 1.58 eV(16) relative to a value of 1.4 eV for *p*-benzoquinone.(17) The molecular ionization potential of the molecule has been calculated by Kuder, using molecular orbital theory, as 8.3 eV.(18) In this case intermolecular charge-transfer interactions may contribute to the decrease in energy of the first electronic transition in the β and γ crystals. Complete crystal structures are required for any further interpretation of intermolecular interactions in the α, β and γ polymorphs.

Polymorphism has also been observed for the isomeric furan-quinone Dinaphtho[1,2-2′,3′]-furan-7,12-dione and for several derivatives of both molecules. These observations indicate that polymorphism may be a general phenomena with furan-quinones.

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