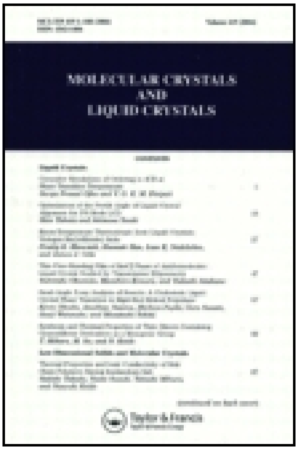

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The Temperature Dependence of the Electrical Conductivity, Density and Tautomerism of Solid Anthrone

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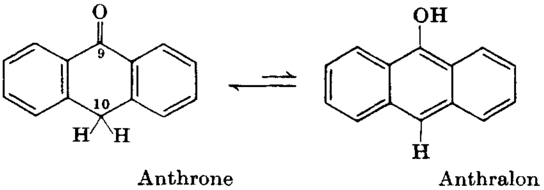
Abstract—The electrical conductivity, density and tautomerism of solid anthrone have been measured as a function of temperature. The coefficient of volume expansion increases by a factor of about 2.3 above 84° C; at or near the same temperature there is an increase in the energy of activation for conduction (E) and in the rate of tautomerism of anthrone to its enol form, anthranol. E and the temperature at which it changes abruptly are independent of the anthranol content of the solid. We conclude that near 84°C an order–disorder transition occurs which produces the observed results.

The conductivity of anthrone (in pressed pellet form) as a function of temperature has been previously studied by Rust *et al.*,[1] who found a break in the logarithmic conductivity versus $1/T$ curve (T = absolute temperature) in the 80–90° C region. The activation energy E derived from the expression for the conductivity $\sigma = \sigma_0 \exp(-E/kT)$ was greater in the higher temperature region and was attributed to an intrinsic carrier generation process which, in the lower temperature region, was obscured by impurity effects. In view of the fact that anthrone is known[2] to tautomerize in the solid state to form anthranol, we considered the possibility that the impurity effects observed by Rust *et al.*[1] were due to the presence of anthranol. The equilibrium is shown in (1) below:



(1)

The equilibrium is in favor of anthrone, particularly in the solid state at temperatures below about 80° C as will be shown later. Above this temperature the tautomeric equilibrium is shifted somewhat to the right in (1) so that the equilibrium concentration of anthranol in the solid is higher than in the lower temperature range, but is still low (less than 1%).

We made dark conductivity measurements on both pressed powder pellets and single crystals, the results being qualitatively the same in both. The activation energy for semiconduction undergoes a discontinuous change in the vicinity of 85° C, being greater in the higher temperature range, as was found by Rust *et al.*[1] We have further found that the rate of anthranol formation rises sharply and that the volume expansion coefficient increases abruptly in the same temperature region (near 84° C). A consideration of these three phenomena, conductivity, rate of anthranol formation and density as a function of temperature, has led us to conclude that near 84° C anthrone undergoes a second-order (or order–disorder) transition which affects its electrical conductivity and rate of tautomerism. Such order–disorder transitions are characterized by a discontinuity in the volume expansion coefficient at the transition temperature.[3] The volume expansion coefficient in anthrone is roughly doubled at the transition point and so is the activation energy for conduction. The change in activation energy is not directly related to the anthranol content of anthrone, since conductivity measurements equilibrate thermally within an hour, whereas the anthranol concentration does not attain equilibrium within days. We believe that the change in the activation energy for conductivity is brought about by a weakening of intermolecular forces at the transition point: this also facilitates tautomerism.

Experimental

The d.c. electrical measurements were made in the usual manner. The anthranol concentration in solid anthrone was measured by making use of the fact that anthranol is fluorescent and absorbs in the 400–420 mμ region, whereas anthrone does not fluoresce and begins to absorb only below 400 mμ. The volume changes of single crystals as a function of temperature were determined by a density gradient technique.

Materials

Anthrone (melting point 157–159° C) was obtained from Eastman Organic Chemicals and was further purified by sublimation and two recrystallizations from hot benzene. Commercial grade anthrone contains about 0.1% anthranol and varies slightly from batch to batch. The samples used in the conductivity measurements were either polycrystalline pressed pellets or single crystals. The pellets were prepared by pressing anthrone powder at a pressure of 5000 lb/in^2; the pellets were about 1 mm thick and 1.25 cm^2 in area. The single crystals were grown in a nitrogen atmosphere by slowly allowing a hot supersaturated benzene solution to cool to room temperature; their dimensions were of the order of $\frac{1}{2} \times \frac{1}{2} \times 1$ mm.

Electrical Measurements

Conductivity measurements were carried out in a nitrogen atmosphere. The anthrone sample was placed in a specially constructed sealed chamber (the electrical insulators separating the electrodes and brass chamber protruded about 8 in. above the chamber; thus the electrical insulators were maintained at room temperature while the sample in the chamber was heated). After placing the sample in the chamber, the latter was evacuated for 20 hr at 10^{-4} mm of Hg, filled with nitrogen and then immersed in a thermally regulated oil bath. The chamber was grounded to a Faraday cage which enclosed the oil bath, and a shielded cable was used to connect the sample to the input ($10^{12}\,\Omega$ input resistance) of a Cary 31 vibrating reed electrometer.

Measurements on pellets were carried out with guard rings, but the crystals were too small for successful application of guard rings. The electrodes for the pellets were flat aluminum discs pressed into the pellet; they were evaporated silver films in the case of the single crystals. There was no difficulty in reproducing the conductivity measurements with different pressed pellet samples, but the resistance of many single crystals was often comparable to that of the empty chamber. This was probably due to poor electrode contacts. Silver, evaporated aluminum, indium and aquadag contacts were tried, but the results did not improve—only about one-third of the crystals had a low enough resistance to be useful for conductivity measurements.

The Determination of Anthranol in the Solid State

Anthranol can be formed by heating anthrone powder in a test tube to its melting point and then quickly quenching the melt in a room temperature or ice bath.[2] Near the melting point the rate of anthranol formation is much greater than below 84° C. Below this temperature tautomerization between the two forms in either direction is inhibited. If a quenched anthrone melt is subsequently dissolved in benzene, the solution exhibits a blue fluorescence. Upon standing, the fluorescence of quenched melt benzene solutions decreases slowly (about 50% within 2 hr). The anthranol fluorescence spectrum exhibits maxima at 419 and 440 mμ. The fluorescence of these benzene solutions is directly proportional to their optical density at 400 mμ and the absorption at this wavelength can be used as a criterion of the anthranol concentration. An optical density at 400 mμ of 0.18/mg/ml of dissolved anthrone was found to correspond to a 1% anthranol concentration based on the dry weight of the solid, and followed Beer's law. An extinction coefficient of $\epsilon = 3500$ l mole^{-1} cm^{-1} can be calculated for this wavelength. This standardization was made by titrating solutions containing anthranol with standard iodine solution to an end point determined by the cessation of fluorescence. The fluorescent anthranol reacts rapidly with iodine, whereas the non-fluorescent anthrone reacts very slowly.[2]

Thus, in a determination of anthranol in solid anthrone, the sample was dissolved in benzene and the optical density or fluorescence measurement was made within 5–10 min in order to minimize errors ($\sim$5%) resulting from the reversion of the -ol to the -one form.

Density Measurements

The density of single crystals as a function of temperature was measured by a density gradient technique,[4] using a sucrose solution. The density gradient tube was suspended in an oil bath, which was then slowly heated. The crystals were suspended in the solution and their position as a function of temperature was measured and compared to that of calibrated density Pyrex glass floats.

Results

ELECTRICAL CONDUCTIVITY

The conductivity σ of a typical pressed pellet and single crystal is shown in Fig. 1. A break in the ln σ *vs.* $1/T$ curve appears at about 84° C in both cases. If care is not exercised to remove all air from the samples, another break is exhibited at 65° C. The activation energy calculated from the slopes of the curves in Fig. 1 according to the expression $\sigma = \sigma_0 \exp(-E/kT)$ are $E_1(T < 84°\,\mathrm{C}) =$ 0.41 eV for the pellet and 0.57 eV for the crystal; $E_2(T > 84°\,\mathrm{C}) =$ 1.04 eV for the pellet and 0.95 eV for the crystal. The activation energies of four different pellets have been calculated to average $E_1 = 0.5 \pm 0.1$ eV and $E_2 = 1.1 \pm 0.1$ eV. The average of six crystals also yielded $E_1 = 0.5$ eV and $E_2 = 1.0$ eV, but the variation is considerably greater than in the case of the pellet; thus the minimum value for E_2 was 0.7 eV and the maximum value 1.5 eV. The reproducibility of the activation energies, particularly for the crystals, was not very good, but in all cases there was a break in the ln σ *vs.* $1/T$ curve in the 80–89° C region.

The current readings reached equilibrium after 20 min at each temperature and were ohmic at least up to an applied voltage of 190 V.

In general, the shape of the ln σ *vs.* $1/T$ curves was reproducible for the same pellet, but in a second heating cycle the resistance was uniformly higher (about 50–100%) than during the first run. For single crystals, a given run could not be repeated because of the increase in resistance. This was probably due to a deterioration of the electrode contacts as a result of heating the crystal; it was also noted that at the beginning of a run the crystals were clear, but were cloudy at the end.

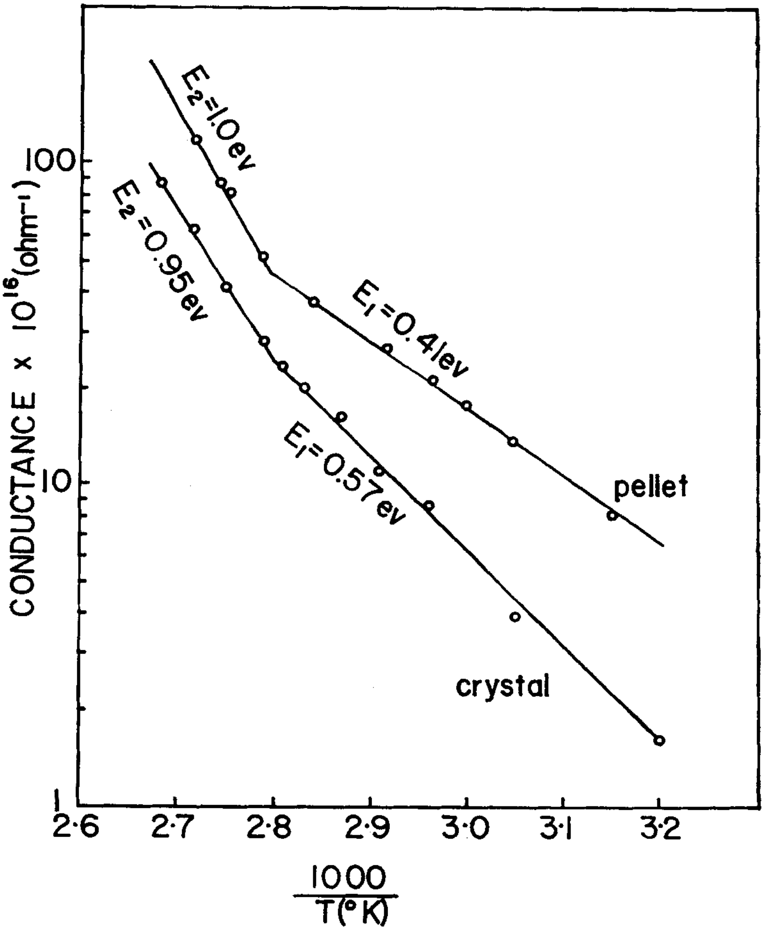


Figure 1. Conductance of anthrone as a function of temperature. Sample dimensions for the pellet are: electrode area, 1.5 cm^2; thickness 0.05 cm. For the crystal: electrode area, 0.1 cm^2; thickness 0.1 cm.

Tautomerism in the Solid State

Evacuated ampoules containing anthrone were kept at different temperatures (25–118° C) for different lengths of time ranging from

1 hr to 6 days and the solid was then analyzed for its anthranol content. There was no measurable change in anthranol concentration in the 25–75° C range, but above this temperature the rate of tautomerization to the -enol form increases appreciably. For example, three samples of anthrone kept respectively at 85, 90 and 96° C for 1 hr, were then dissolved in benzene. The fluorescence of the solutions containing equal amounts of anthrone had increased by 10, 15 and 24% respectively over that of an unheated sample. Only, after an equilibration time of 5 days is there virtually no additional anthranol formed; at 94° C, for example, keeping the powder an additional day at this temperature increases the anthranol content by 2% only, which is within the experimental error. A plot of % anthranol *vs.* $1/T$ for an equilibration time of 5 days is shown in Fig. 2. Assuming that equilibrium has been attained, a heat of reaction for tautomerism in the solid state of $\Delta H = 14.5$ kcal/mole can be calculated from the slope, for $T > 85°$ C.

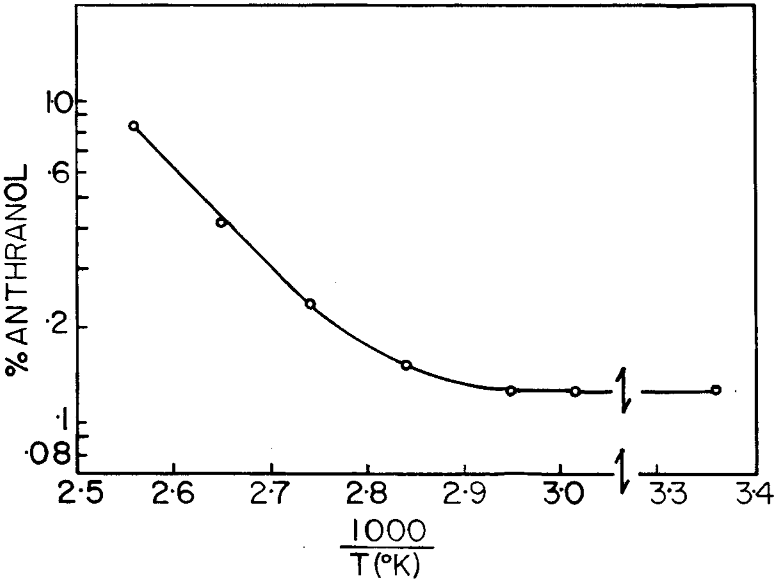


Figure 2. Concentration of anthranol in solid anthrone after a 5-day equilibration period, as a function of temperature.

Bansho and Nukada have found heats of activation for the anthrone ↔ anthranol tautomerism of 5.8 and 12.2 kcal/mole in methanol and benzene solutions respectively.[5] Our value of 14.5 kcal/mole is consistent with these values, since one would expect a higher activation energy for this reaction in the solid state than in solution.

The Density as a Function of Temperature

The change in density of anthrone with increasing temperature can be conveniently measured in a density gradient tube. The volume expansion coefficient α is defined as $(1/V)/(\partial V/\partial T)$ or $\rho[\partial(1/\rho)/\partial T]$ where V is the volume and ρ the density. Thus, a plot of $-\ln\rho$ *vs.* T yields a straight line with α as the slope (Fig. 3).

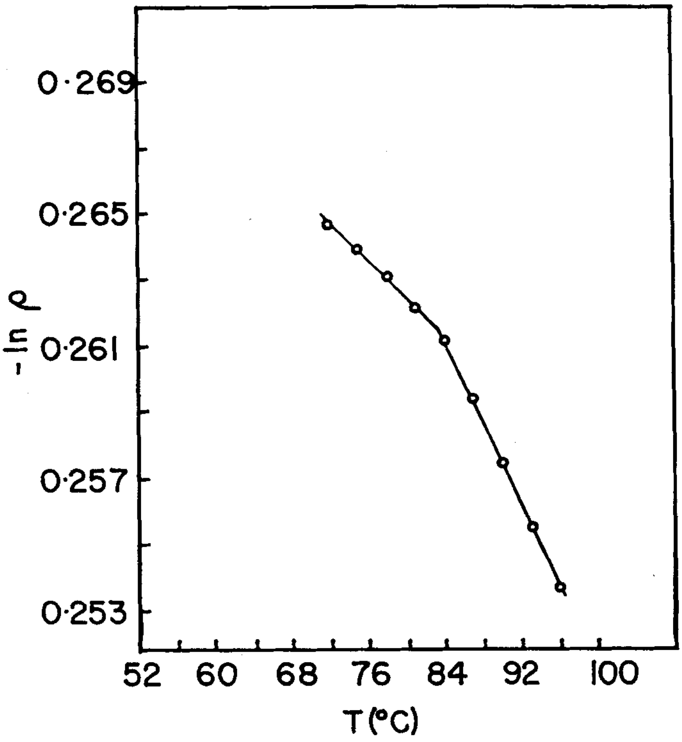


Figure 3. Temperature dependence of the density of anthrone crystal.

There is an abrupt change in α at 83.5°; below this temperature $\alpha = 2.5 \times 10^{-4}$ deg$^{-1} \pm 15\%$ and above 83.5° $\alpha = 5.8 \times 10^{-4} \pm 15\%$. This change in slope has been verified for six other crystals and usually occurs at 84° C; this break occurs during consecutive and repeated heating cycles for the same crystal, which indicates that a reversible phase change takes place at 83–84° C. The density at 25° C found by extrapolating the $T < 84°$ C curve in Fig. 3 is 1.32 g/cc, which compares well with the value of 1.33 given by Srivastava.[6]

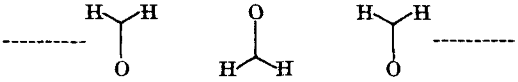
Discussion

From an examination of the temperature coefficient of the conductivity, tautomerism and density, it appears that these three phenomena are related, since relatively abrupt changes in these three properties occur in the vicinity of 84° C. In view of the difficulties encountered in making the electrical measurements, we consider the absolute value of the conductivity and the energy of activation to be of less significance than the relative changes that take place around the temperature of 84° C. On the other hand, the measurements of volume expansivity and anthranol content have an absolute significance.

In view of the long time required to achieve equilibrium in the tautomerism reaction, relative to the short time required to attain equilibrium in the conductivity and density measurements, we conclude that the tautomerism is not the cause of the change in activation energy of conductivity in anthrone. Furthermore, if anthranol played a significant role as an impurity one would expect the temperature at which bulk conductivity takes over from impurity conductivity to depend on the impurity concentration, and such is not the case. A pellet made from anthrone that was kept at 105° C, for 5 days and had a 0.4% anthranol content showed the same transition temperature as a sample with a 0.1% anthranol content.

The change in α is effected in the same time as is the change in E, and is in the direction to cause the observed change in E. Changes in σ can occur through changes in carrier density and carrier mobility. An increase in α should increase the activation energy for carrier mobility and carrier generation. Since α is a strong measure of the degree of intermolecular interaction, it is reasonable to expect correspondingly distinct changes in those properties that depend strongly on intermolecular coupling, such as the electrical conductivity.

The question arises as to the nature of the change in the solid that causes the change in α. The crystal structure of anthrone has been studied extensively by Srivastava.[6] Anthrone is monoclinic and belongs statistically to the space group C_{2h}^5—P_{1a}^2 with two molecules per unit cell; this structure requires a center of symmetry which the anthrone molecule does not possess and which has been interpreted by Srivastava as follows: the molecules are arranged in a regular manner in the 010 plane along the *b* axis in such a way that statistically it appears as if each molecule has 1/2 (O + 2H) at each the 9 and 10 positions, indicating an alternate arrangement of the molecules along the *b* axis, as shown schematically below:



(2)

If hydrogen bonding of the type C—H...O were to exist in anthrone, as has been shown to be the case in some organic crystals,[8] it would be possible to form definite conclusions about the nature of the 84° C transition. Second-order transitions involving hydrogen-bonding equilibria are well known in the case of polyamides and polyvinyl alcohols.[9] These transitions are marked (at constant pressure) by a discontinuous change in the heat capacity and coefficient of volume expansion and are interpreted in terms of hydrogen-bonding equilibria: above the transition temperature a variation in temperature is followed by a shift between bonded and non-bonded hydrogen bonding sites. The relaxation times are small and equilibrium sets in a very rapidly. Below the transition temperature relaxation times are very long and equilibrium is not achieved. Eley and Spivey[10] measured the conductivity of hydrogen-bonded polyamides and found two activation energies, the transition from one region to the other occurring near 100° C which they related to hydrogen-bonding.

However, the possibility of hydrogen-bonding in anthrone is unlikely as becomes evident from an examination of Srivastava's crystal structure data.[6] The closest distance between C and O atoms situated on adjacent molecules is given as 3.388 Å, whereas Sutor[8] states that 3.4 Å is the normal van der Waals' separation and that hydrogen bonding can be assumed to exist only if the C...O distance is significantly less than 3.4 Å.

From the observations of Srivastava[6] it is evident that an order–disorder transition is possible in anthrone, in which the regular arrangement shown in (2) is randomized. This rearrangement may also be accompanied by the appearance of a previously inhibited vibrational mode in which there is a slight out of plane vibration of the 9 and 10 carbon atoms allowing the hydrogen atoms at the 10 position (see (1)) to approach closer to the oxygen atom. Thus, a weakening of the intermolecular van der Waals' forces should facilitate the tautomerism if this process is monomolecular and involves a hydrogen atom transfer within the same molecule. This reaction has been shown to be monomolecular in solution,[5] which is probably also the case in the solid state. However, elucidation of the exact nature of the 84° C change will have to await a detailed X-ray study at temperatures above this transition point.

Attempts to link polymorphic changes in conductivity in organic materials have been made previously. Hexamethylbenzene undergoes a reversible transition from a triclinic crystal below 109° to an orthorhombic lattice. Kronick and Labes, however, did not find a change in the conductivity at the transition point[11] and furthermore, were not able to reproduce the change in conductivity as a function of temperature in chlorpromazine, which had been previously reported by Gutmann and Netschey.[12] Keyzer[13] recently measured the volume expansion of chlorpromazine as a function of temperature and found no change at the reported conductivity transition temperature.[12] A change in the logarithmic dependence of the conductivity of phthalocyanine as a function of $1/T$ has been reported,[14] but has since been attributed to impurities.[11] However, in anthrone it appears that the conductivity change is linked to a polymorphic change.

Similar results have been reported for inorganic materials. Thus, the conductivity[15] and volume expansion coefficient α of sodium nitrite[16] and sodium nitrate[17] have been measured over a temperature range that includes a second order transition. For these materials, it was found that the conductivity obeys the relation $\sigma = \sigma_0 \exp(-E/kT)$, and that σ and the density ρ were continuous through the transition temperature, but that the values of E and α changed abruptly at that temperature. The difference between anthrone and these inorganic materials is that the latter exhibited a gradual variation in α above the transition temperature (in the case of sodium nitrate also below this temperature), whereas E remained constant and changed abruptly only at the transition temperature. Thus, the causes underlying the changes in E and α in anthrone and the inorganic salts may be different.

Acknowledgments

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