

A STUDY OF THE PHASE BEHAVIOUR OF METAL-FREE PHTHALOCYANINE IN A DIFFERENTIAL SCANNING CALORIMETER

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ABSTRACT

The phase behaviour of metal-free phthalocyanine (H_2Pc) has been studied in a differential scanning calorimeter. The effect of the thermal history of samples on the DSC curves was investigated to obtain data concerning the phase transition which appeared on α as well as β forms of H_2Pc over the temperature range from 250 to 340 K. To characterize the α metal-free phthalocyanine at low temperatures, the capacitance of an $Ag(H_2Pc)Al$ sandwich was measured as a function of the temperature. The specific heats of the α and β forms of H_2Pc and the heat of the $\alpha \rightarrow \beta$ polymorphic transition were measured. Kinetic parameters of the $\alpha \rightarrow \beta$ polymorphic transition have been derived from the calorimetric results.

INTRODUCTION

Phthalocyanines represent an ideal model system of organic semiconductors since the chemical constitution and the solid-state structure can be influenced by a change of the porphyrazine system, the central atom or the crystal modification. These compounds are known to exist in several polymorphic forms and the crystal modification influences strongly their electrical and optical properties. H_2Pc has at least three polymorphic forms from which the α form occurring at vacuum evaporation and the β form arising as a single crystal have become important. The transformation of the α to the β phase in thin films has been investigated by Lucia and Verderame¹, Sharp and Miller² as well Griffiths and Walker³. A first-order ferroelectric phase transition has been reported by Vidadi et al.⁴ on the α form and by Dudreva and Grande⁵ on the β form of H_2Pc .

The purpose of the present work is a detailed study of the phase behaviour of H_2Pc in a differential scanning calorimeter.

EXPERIMENTAL

A Perkin-Elmer Model DSC-2 differential scanning calorimeter (DSC) was

used for our measurements with the addition of a subambient accessory at low temperatures. The instrument was calibrated for temperature using cyclohexane, indium and lead. For the specific heat measurements, samples of synthetic sapphire were used to calibrate the ordinate displacement of the instrument. During the specific heat measurements to optimize the sensitivity, an aluminium sample with heat capacity comparable to the heat capacity of the H_2Pc sample was placed into the reference holder. Calibration for energy was made by measurements on samples of high purity indium taken to have a heat of fusion of 6.80 cal g^{-1} . The calorimeter was connected to a perforator and peak area measurements were made by computer. The standard materials and the organic samples were encapsulated in aluminium sample pans.

Measurements were performed with H_2Pc purified by sublimation four times. The obtained crystalline material, according to measurements with a Unicam SP 200G infrared spectrometer, was in the β form. The α form was produced by precipitation from concentrated sulphuric acid by addition of water⁶ or by vacuum evaporation⁶ and was identified by its infrared spectrum⁷.

RESULTS AND DISCUSSION

Specific heat measurements

The specific heats of the α and β forms of H_2Pc were measured by DSC in different temperature ranges, at a heating rate of $10^\circ\text{C min}^{-1}$ on samples of an average weight of 20 mg. As the shape of the thermograms obtained at low temperatures depended on the thermal history of the sample, measurements were made with a high cooling rate and the samples were kept at low temperature for a short time. The results are summarized in Table I. The measurements made on different samples of H_2Pc and synthetic sapphire show that the error of our specific heat measurements does not exceed $\pm 2.5\%$. A series of thermograms run on one sample showed a very good reproducibility of ordinate displacement (with an error less than $\pm 1\%$), and the instrument was able to measure the difference of specific heats between the α and β crystalline forms. The measured values of specific heats on an α - H_2Pc sample and on the β form of the same sample are listed in columns 2 and 3, respectively, of Table I. (The $\alpha \rightarrow \beta$ polymorphic change was made in the DSC.) The differences between the specific heats of the two crystalline forms do not exceed the value of $\pm 2.5\%$ in the investigated temperature range.

The effect of the thermal history of the samples on the DSC curves was investigated to obtain data concerning the ferroelectric phase transition of both crystalline forms of H_2Pc reported by Vidadi et al.⁴ and by Dudreva and Grande⁵. Figure 1, Run 1, shows the behaviour of a sample of α H_2Pc on heating at $2.5^\circ\text{C min}^{-1}$ immediately after cooling to 270 K at a cooling rate of $320^\circ\text{C min}^{-1}$. Run 2 was obtained by scanning the same sample at the same heating rate after cooling to 160 K at $0.31\text{--}1.25^\circ\text{C min}^{-1}$ and holding it at 160 K for 30 min. Figure 2 shows the DSC curves measured on a sample of the β form cooled rapidly (Run 1) and slowly (Run 2). According to thermograms of Figs. 1 and 2 it can be assumed that a slow,

TABLE 1

SPECIFIC HEATS OF H₂Pc AT DIFFERENT TEMPERATURES

Temp. (K)	Specific heat of H ₂ Pc (cal g ⁻¹ deg ⁻¹)		
	<i>β</i> form	<i>α</i> form	<i>β</i> form
255	0.205		
260	0.210	0.212	0.208
265	0.215	0.216	0.212
270	0.220	0.220	0.216
275	0.224	0.224	0.219
280	0.229	0.228	0.224
285	0.234	0.233	0.229
290	0.239	0.238	0.234
295	0.243	0.242	0.238
300	0.247	0.247	0.242
305	0.252	0.251	0.246
310	0.257	0.255	0.251
315	0.260	0.259	0.254
320	0.264	0.264	0.258
325	0.269	0.267	0.263
330	0.273	0.272	0.267
335	0.277	0.276	0.271
340	0.282	0.280	0.276
345	0.286	0.284	0.280
350	0.289	0.288	0.283
355	0.294		
360	0.297		
365	0.302		
370	0.306		
375	0.310		
380	0.313		
385	0.317		
390	0.321		
395	0.325		
400	0.329		
405	0.333		
410	0.336		
415	0.339		
420	0.343		

first-order phase transition appears over the temperature range from 250 to 340 K.

To characterize the α -H₂Pc at low temperatures the capacitance of an Ag (H₂Pc)Al sandwich was measured as a function of the temperature. The sandwich structure was prepared by vacuum evaporation, the thickness of the α -H₂Pc film was about 3 μ m, the area of the sandwich was about 20 mm². The measurements of capacitance were carried out in a vacuum chamber evacuated to about 3×10^{-6} Torr, and at a heating rate of 13.2°C min⁻¹. To avoid the effects of contacts, the capacitance of the sandwich structure was measured at a frequency of 1 Mc sec⁻¹ with a direct

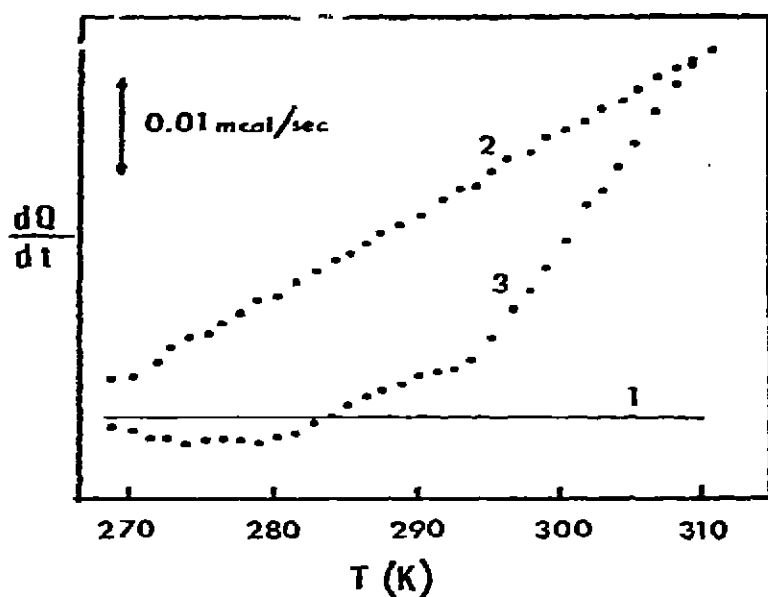


Fig. 1. DSC thermograms of α -H₂Pc. 1 = Baseline scan of empty sample pans. 2 = DSC thermogram of a rapidly cooled sample (from 400 to 270 K at a cooling rate of 320°C min⁻¹); heating rate: 2.5°C min⁻¹, weight of the sample: 29.43 mg; weight of the Al reference: 30.13 mg. 3 = Rescan of the same sample after cooling from 310 to 160 K at a cooling rate of 0.31°C min⁻¹ and holding it at 160 K for 30 min. Heating rate: 2.5°C min⁻¹.

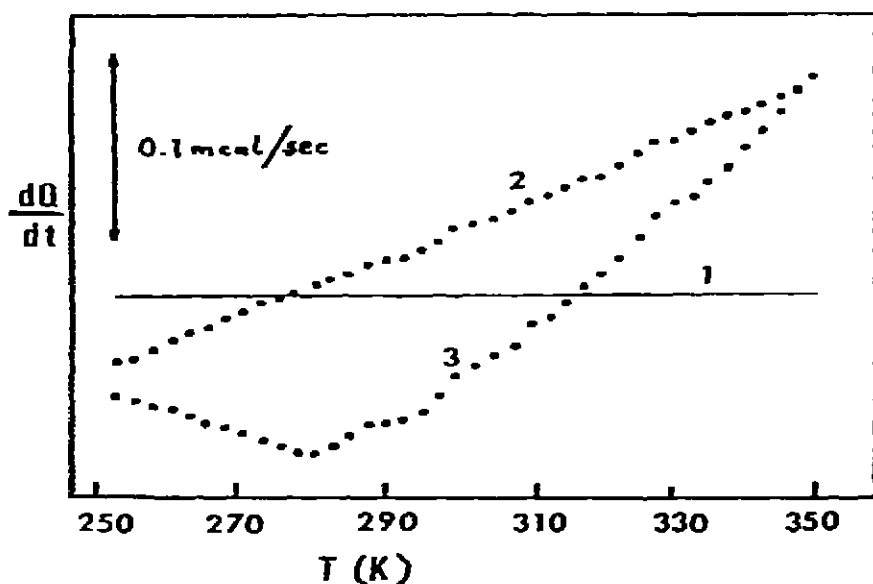


Fig. 2. DSC thermograms of β -H₂Pc. 1 = Baseline scan of empty sample pans. 2 = DSC thermogram of a rapidly cooled sample (from 400 to 250 K at a cooling rate of 320°C min⁻¹); heating rate: 5°C min⁻¹, weight of the sample: 29.16 mg; weight of the Al reference: 30.13 mg. 3 = Rescan of the same sample after cooling from 350 to 160 K at a cooling rate of 0.31°C min⁻¹ and holding it at 160 K for 30 min. Heating rate: 5°C min⁻¹.

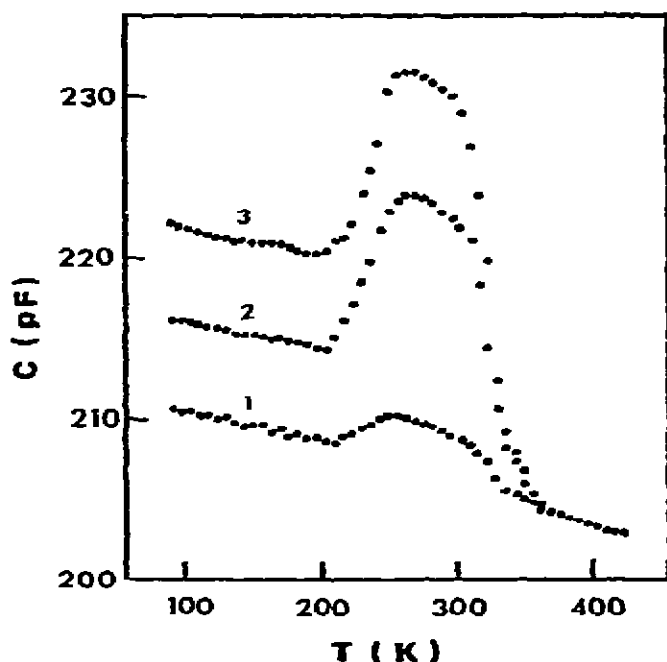


Fig. 3. Capacitance versus temperature curves of an Ag(α H₂Pc)Al sandwich, 1 -- after cooling from 420 to 90 K at a cooling rate of 40°C min⁻¹; 2 -- after cooling from 420 to 90 K at a cooling rate of 2°C min⁻¹; 3 -- after cooling from 420 to 160 K at a cooling rate of 2°C min⁻¹, holding the sample at 160 K for 30 min and cooling it from 160 to 90 K at 2°C min⁻¹.

capacitance bridge, Model 750 (Boonton Electronics Co.). The results are drawn in Fig. 3, where curve 1 shows the capacitance of a rapidly cooled sample versus temperature. Curves 2 and 3 were obtained for the same sandwich structure when the cooling was slow and when the slow cooling was followed by a heat treatment at 160 K for 30 min, respectively. It is seen, that (1) the dielectric constant of the H₂Pc layer increases in the low temperature range with decreasing cooling rate, or by holding the sample at low temperature for a long time and it is independent of heat treatment at high temperature; (2) in a given broad temperature range, a maximum of the capacitance, i.e., a maximum in the dielectric constant, appears. Both facts make the presence of a ferroelectric phase probable at low temperature. Whereas the transition to ferroelectric phase is slow, the changes of enthalpy or dielectric constant shown in Figs. 1-3 do not characterize the total phase transformation.

The heat of the $\alpha \rightarrow \beta$ polymorphic phase transition

The $\alpha \rightarrow \beta$ polymorphic phase transition was investigated in the temperature range of 400-600 K at different heating rates. In Fig. 4 the thermograms of H₂Pc between 420 and 530 K are drawn. The thermogram shows two exothermic peaks occurring over the ranges 450 to 475 K and from 485 to 510 K. According to our infrared spectroscopic investigations the sample which was heated at a scanning rate of 5°C min⁻¹ to 480 K and was cooled quickly to room temperature remained in its α

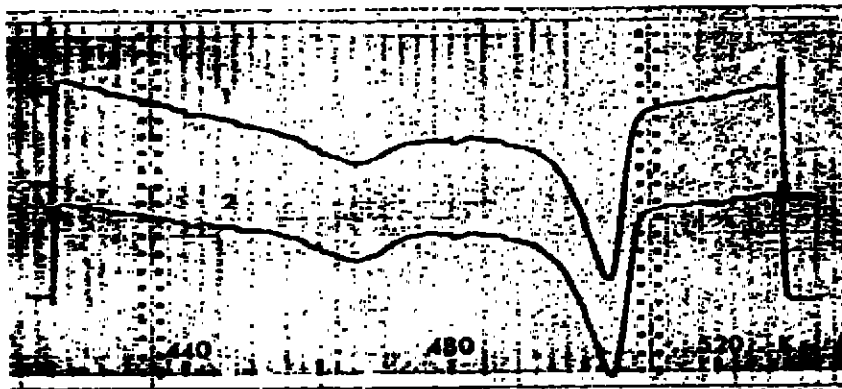


Fig. 4. DSC thermograms of α -H₂Pc (batch No. 1). 1 -- Range: 0.5 mcal sec⁻¹; heating rate: 2.5°C min⁻¹; weight of the sample: 12.76 mg. 2 -- Range: 1.0; heating rate: 2.5°C min⁻¹; weight of the sample: 24.34 mg.

TABLE 2

HEAT OF $\alpha \rightarrow \beta$ POLYMORPHIC PHASE TRANSITION AT DIFFERENT HEATING RATES

Heating rate (°C min ⁻¹)	The heat of the $\alpha \rightarrow \beta$ polymorphic phase transition (cal g ⁻¹)
20	3.6
10	3.8
5	3.8
2.5	3.9
1.5	3.8

form. At subsequent reheating, only the high temperature peak appeared and the sample gave an infrared spectrum characterizing the β form. The heats of the $\alpha \rightarrow \beta$ polymorphic phase transition at different heating rates are summarized in Table 2.



Fig. 5. DSC thermograms of H₂Pc. 1 = Scan of α -H₂Pc (batch No. 2); range: 1 mcal sec⁻¹; heating rate: 2.5°C min⁻¹. 2 = Rescan of the same sample after cooling from 510 to 440 K (1 mcal sec⁻¹; 2.5°C min⁻¹).

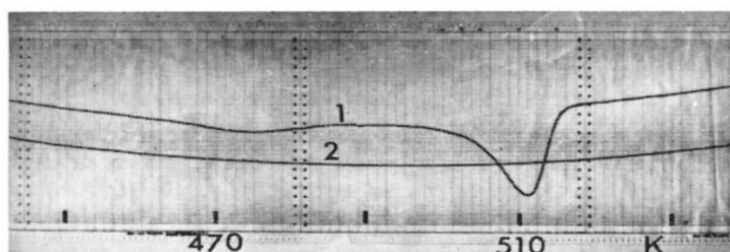


Fig. 6. DSC thermogram of α -H₂Pc (batch No. 3) 1 and baseline 2. Range: 2 mcal sec⁻¹, heating rate: 5°C min⁻¹.

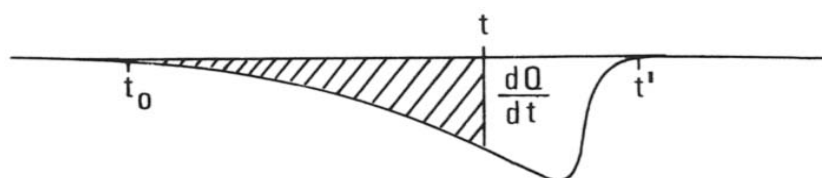


Fig. 7. A typical DSC curve of the thermal $\alpha \rightarrow \beta$ polymorphic conversion of H₂Pc.

The area of peak over the range from 450 to 475 K depends on the preparation of α -H₂Pc and varies from batch to batch (Figs. 4–6). In the framework of the present investigations, the reason for the presence of this exothermic peak was not explained.

On the kinetics of the thermal $\alpha \rightarrow \beta$ polymorphic conversion

The type of curve shown in Fig. 7 is able to supply data concerning kinetic considerations. The initial equation was proposed by Gray⁸ according to the generalized theory for the analysis of dynamic thermal measurements:

$$\frac{dh}{dt} = -\frac{dq}{dt} + (C_s - C_r) \frac{dT_p}{dt} - RC_s \frac{d^2q}{dt^2} \quad (1)$$

Here dh/dt is the heat generated or absorbed by the sample per unit time; $dq/dt = (T_s - T_r)/R$ is the difference of the rates of heat loss between the sample and reference as well as surroundings (sample holders) through the thermal resistance R ; C_s is the heat capacity of the sample plus container; C_r is the total heat capacity of the reference; dT_p/dt is the heating rate and T_s , T_r and T_p are the temperature of sample, reference and surroundings, respectively. The rate of heat generated by the sample is proportional to dx/dt , the rate of polymorphic conversion through the following relationship:

$$\frac{dh}{dt} = S \frac{dx}{dt} \quad (2)$$

where x is the transformed fraction and S (which directly equals to the area under the DSC peak) is the total heat of phase transformation. The rate of reaction of a process can generally be expressed by

$$\frac{dx}{dt} = K(T)f(x) \quad (3)$$

where $K(T)$ is the temperature dependent rate constant and $f(x)$ is a function representing the hypothetical model of the reaction mechanism. The value of K may be given by the Arrhenius equation as

$$K = A \exp [- E/RT] \quad (4)$$

where A , E , R and T are pre-exponential factors, activation energy, universal gas constant and absolute temperature, respectively.

Using the method of Borchardt and Daniels⁹ for differential scanning calorimetry¹⁰, the rate constants can be calculated:

$$K = \frac{dQ/dt}{S f(x)} \quad (5)$$

where dQ/dt is the ordinate displacement of the DSC curve (Fig. 7). This value is equivalent to the right-hand side of eqn (1) when its third term is neglected. If the function $f(x)$ describes the process of phase transformation correctly, the Arrhenius plot of $\ln K$ against $1/T$ should yield a straight line from which the activation energy E and preexponential factor A can be obtained.

After having studied the polymorphic change $\alpha \rightarrow \beta$ of H_2Pc , we investigated the following forms of the differential eqn (3):

$$\frac{dx}{dt} = K_1 (1 - x)^n \quad (6)$$

$$\frac{dx}{dt} = K_2 (1 - x) [- \ln (1 - x)]^{(n-1)/n} \quad (7)$$

$$\frac{dx}{dt} = K_3 x^n \quad (8)$$

Equation (6) describes the phase-boundary controlled processes: surface nucleation takes place extremely rapidly and the total process is governed by movement of the resulting interface. Equation (8) represents reactions controlled by nucleation according to the power law. The exponential growth law summarised in Avrami's equation: (7) is valid for linear growth under most circumstances and approximately valid for the early stages of diffusion-controlled growth^{11, 12}.

Several values for n were tried in an endeavour to get the rate constants K_1 , K_2 and K_3 . The calculations were carried out by computer program based on eqns (6), (7) and (8) and tested by eq. (4).

According to eqn (2) the transformed fraction x equals the ratio of s/S , where s is the area enclosed by the DSC curve between the points t_0 and t (the shaded area in Fig. 7). The values of s , S and dQ/dt determined from each DSC curve depend on the shape of the baseline drawn during the polymorphic conversion. As mentioned above the specific heats of the α and β forms differ very little from each other in the

TABLE 3

Sample weight (mg)	Heating rate ($^{\circ}\text{C min}^{-1}$)	n	E (kcal mol $^{-1}$)	Standard deviation	Correlation coefficient	E^{**} (kcal mol $^{-1}$)	Batch
12.76	2.5	0.4	120	0.0084	0.9993		
18.74	2.5	0.5	120	0.0095	0.9994	118	
24.34	2.5	0.5	125	0.0031	0.9999		
24.75	5	0.4	119	0.0047	0.9997	144	No. 2
17.07	2.5	0.4	87	0.0038	0.9998		No. 3
32.32	1.25	0.4	88	0.0033	0.9998		No. 3

E^{**} is calculated by the initial-rates method.

programmed temperature range and increase with increasing temperature. Therefore, the baseline has been approximated by a straight line drawn between the assumed initial (t_0) and final (t') points of the phase transformation (Fig. 7).

During the kinetic investigations of solid-state reactions by DSC, the most important task is to ensure a uniform temperature in the sample holders. To reduce the temperature gradient in the samples to a minimum, our measurements were made with small samples at low scanning rate.

According to our calculations the rate equation which gives the best linear plot of $\ln K$ against $1/T$ is the following:

$$\frac{dx}{dt} = K_1 (1 - x)^{0.5 \pm 0.1} \quad (9)$$

As the results in Table 3 show, the values of n and the calculated activation energy E did not change at different scanning rates and sample weights in the same batch of $\alpha\text{-H}_2\text{Pc}$.

To estimate the magnitude of activation energy E , the initial-rates method of Borchardt¹³ can be applied. This approach starts from eqn (5). At any one of rate eqns (6), (7) and (8), $f(x) \rightarrow 1$, when $x \rightarrow 0$, i.e., x is negligible to 1. In this case the rate constants can be determined by a simple form as

$$K = \frac{dQ/dt}{S} \quad (10)$$

If the ratio of

$$\left(\frac{dQ}{dt} \right) / \left(\frac{dQ}{dt} \right)_{\max}$$

does not exceed 0.1, this method should yield the value of E within an error¹³ of $\pm 20\%$. In Table 3, we have denoted the values of activation energy determined by the initial-rates methods with E^{**} .

CONCLUSIONS

(1) The specific heats of the α and β forms of H_2Pc were measured in different temperature ranges and are summarized in Table 1.

(2) The shape of thermograms obtained in the temperature range 250–340 K depended on the thermal history of the sample and it can be assumed that a slow, first-order phase transition appears in this temperature range.

(3) The capacitance measurements suggest the presence of a low-temperature ferroelectric phase.

(4) The heat of the $\alpha \rightarrow \beta$ polymorphic transition is $3.9 \pm 0.1 \text{ cal g}^{-1}$.

(5) Having studied the polymorphic change $\alpha \rightarrow \beta$ of H_2Pc , we found that the differential Eqn (9) describes the transformation, and the activation energy of the process is 90–120 kcal mol⁻¹ depending on the preparation of α - H_2Pc .

(6) It can be assumed that the $\alpha \rightarrow \beta$ polymorphic transition, according to eqn (9), is a conversion controlled by phase boundary.

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