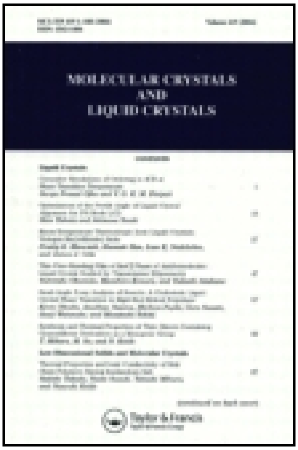

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Thermal Behaviour and Monomerization Kinetics of 9-CN Anthracene and 9-CN, 10-Acetoxy Anthracene Dimers in the Solid State

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Abstract—The thermal stability of 9-CN-anthracene dimer (9-CNAD) and 9-CN, 10-Acetoxy anthracene dimer (9-CN, 10-Ac AD) was studied by differential scanning calorimetry and by direct microscopic examination. Both compounds monomerize below the melting point of the corresponding monomer. From thermograms, first order kinetics are found for both. 9-CN, 10-Ac AD monomerizes, even at room temperature, to an amorphous phase which then crystallizes. Thermal data and activation energies are reported.

1. Introduction

Recently the thermal stability of photodimers of anthracene and some anthracene derivatives have been investigated by means of differential scanning calorimetry (DSC)⁽¹⁾ in order to determine in a reproducible way the temperature ranges of monomerization. We found that the compounds studied could be divided into two classes; the one including anthracene dimer, 9-anthraldehyde dimer, 1-Cl, anthracene dimer, and 9-Cl, anthracene dimer for which the monomerization occurs at higher temperature than that of the m.p. of the corresponding monomer, and the other of 9-CN anthracene dimer (9-CNAD) for which the monomerization is found in a range of temperatures lower than the m.p. of the monomer (9-CNA).

9-CN, 10-acetoxy anthracene dimer (9-CN, 10-Ac AD) has also been reported(2) to dissociate at 150 °C to give the corresponding monomer (9-CN, 10-Ac A) having m.p. 199–200 °C.

For the dimers of the first class we gave only the temperature range (ΔT) of monomerization(1) because the corresponding heat change (ΔH) was not easily obtained owing to a number of thermal effects being superimposed, namely: (i) the heat of monomerization; (ii) the heat of melting of monomer and (iii) the heat of dissolution of dimer in the molten monomer. For 9-CNAD we reported both $\Delta T'$ and ΔH for the reaction.

In this paper we report on the kinetics of monomerization of 9-CNAD and 9-CN, 10-Ac AD in the solid state as determined by DSC.

2. Thermal Analysis of 9-CNAD and 9-CN, 10-Ac AD

In Fig. 1 the characteristic thermograms of 9-CNAD and 9-CN, 10-Ac AD are reported. The $\Delta T'$ (decomposition range) for 9-CN, 10-Ac AD is 310–338 °K and ΔH for the reaction is 19.7 ± 0.5 kcal/mole. Both thermograms show peaks superimposed on a broad exotherm associated with the dimer→monomer reaction. The ΔH of melting for 9-CN, 10-Ac A was found to be 7.2 ± 0.8 kcal/mole.

9-CNAD crystals were examined and photographed on the hot stage of a microscope between crossed Nicols. Temperatures of the crystals were monitored by means of a copper-constantan thermocouple and also by placing, near the sample, crystals of two compounds having m.p. 130–131 °C and 136–137 °C respectively: that is covering the range of the first peak.

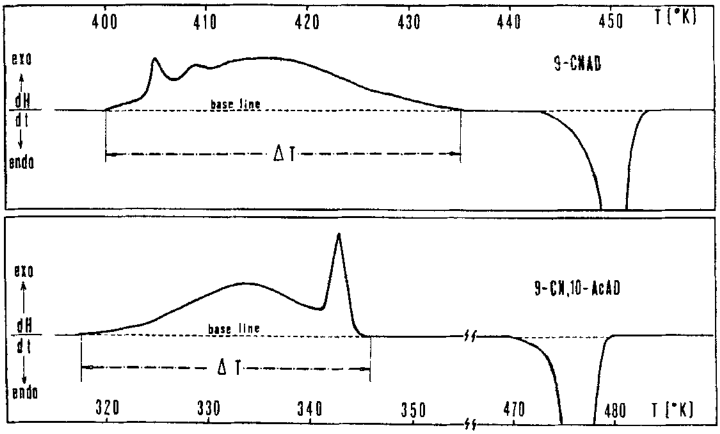

Figure 1. Thermograms of 9-CNAD and 9-CN, 10-Ac AD.

Between the melting points of the first and second internal standards a progressive darkening of the crystals examined is observed. We interpret this behaviour as a spreading of nuclei on a number of crystal planes with subsequent collapse of the crystal. This effect is then related to the first peak of the thermogram reported in Fig. 1. This point of view is also confirmed by observing under the microscope, a number of 9-CNAD crystals previously heated on the calorimeter till the onset of the first peak and then suddenly cooled down in order to stop the progress of spreading. The crystals so treated show the same features already described. It is noteworthy that crystals heated by DSC to few degrees before the beginning of the first peak appeared yellowish while remaining transparent.

9-CNAD crystals are stable at room temperature over long periods. In order to investigate the nature of the sharp peak in the thermogram of 9-CN, 10-Ac AD we followed, under the microscope between crossed Nicols the effect of increasing temperature on the crystals. Bright crystals changed progressively to a full darkness but at slightly higher temperature become light again. The observed dark→light change is in the right temperature range for the sharp peak. This behaviour together with the sharpness of the peak observed in the thermogram is in good agreement for an amorphous→crystalline transition. That is 9-CN, 10-Ac AD monomerizes to give an amorphous phase of 9-CN, 10-Ac A which subsequently takes on his crystalline structure (m.p. 199–200 ° C).

3. Kinetics of Thermal Monomerization of 9-CNAD and 9-CN, 10-Ac AD

Following Dufraisse and Mathieu(2) we assume that 9-CN, 10-Ac A photodimerizes in solution; also it is known(3,4) that 9-CNA gives trans-dimer under irradiation both in solution and in the solid state. Therefore for both compounds we believe that the main reaction investigated kinetically is:

$$\text{Dimer} \rightarrow 2\ \text{Monomer}$$

No data on the structure of 9-CN, 10-Ac AD are available.

Data obtained for 9-CNAD by careful determination of partial areas and heights from DSC thermograms were tested with the usual equations(5) for the kinetics of decomposition of solids making use of the equation:

$$\frac{d\alpha}{dt} = \frac{1}{A} \cdot \frac{dH}{dt}$$

used by Thomas for DSC.(6,7,8)

In Fig. 2 the ln k (k = first order rate constant) is plotted against the reciprocal temperature (°K^{-1}) for samples prepared from benzene solution (▲ small crystals ≃ 3 μ, ■ large crystals ≃ 0.3 mm).

Both kinds of crystals show the same kinetic behaviour characterized by two different activation energies (least square method). The low temperature portion has an activation energy of about the

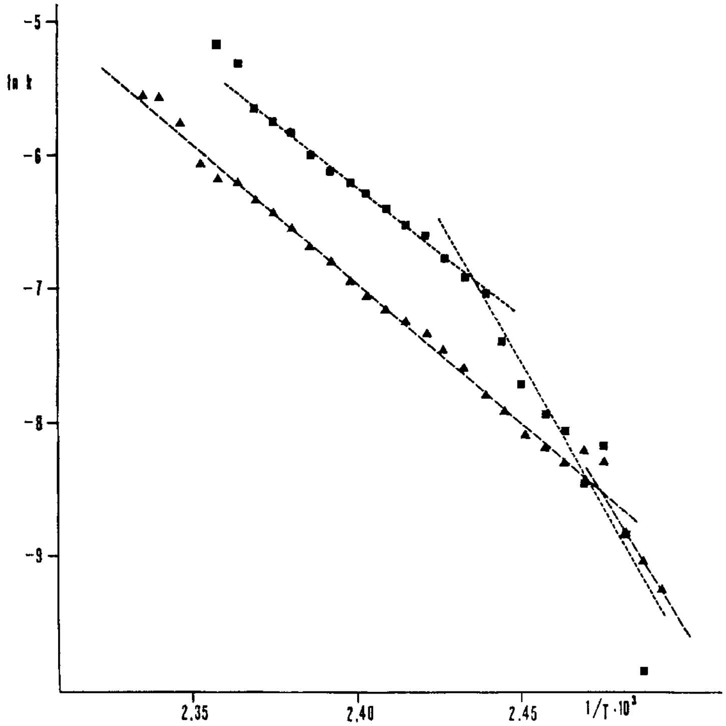

Figure 2. Arrhenius plot of first order rate constants for 9-CNAD monomerization. ■ Large crystals; ▲ thin powders both prepared from benzene solution.

same value ($E_a \simeq 86$ kcal/mole) and the high temperature portion shows an activation energy of $\simeq 42$ kcal/mole and 39 kcal/mole for small and large crystals respectively. The relative extent of the high activation energy portion with respect to the low activation portion is the main difference between small and large crystals.

The procedure reported for 9-CNAD has been also used to investigate the kinetics of monomerization of 9-CN, 10-Ac AD. Again, for freshly prepared samples, the Arrhenius plot shows (Fig. 3, ageing = 0) good agreement with first order kinetics with a change in slope. The activation energies are $\simeq 56$ kcal/mole for the low temperature portion and $\simeq 39$ kcal/mole for the high temperature region.

Dufraisse and Mathieu[2] observed that the colourless crystals of 9-CN, 10-Ac AD turn yellow after a certain period even kept in the

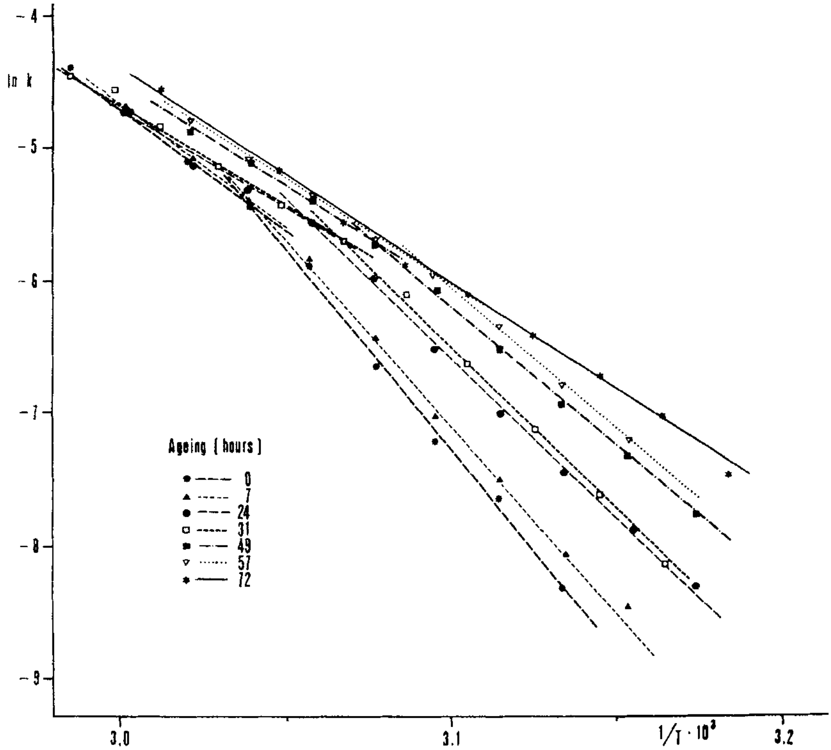

Figure 3. Arrhenius plot of first order rate constants for 9-CN, 10-Ac AD showing the effect of ageing.

dark. Because the original colour was restored under irradiation, this behaviour was interpreted as a case of negative phototropy.

In order to ascertain whether this could affect the kinetics of monomerization, we have prepared a batch of crystals by irradiation of 9-CN, 10-Ac A in ether solution. Crystals were filtered, washed with little ether and kept in the dark at room temperature (17 ± 1 °C).

The thermograms obtained using samples of about the same weight ($\simeq 3.5$ mgr) having increasing ageing at room temperature are reported in Fig. 4. The area corresponding to the broad monomerization exotherm decreases with time whereas that under the sharp peak (for which a ΔH of $\simeq 2$ kcal/mole and a corresponding ΔS of $\simeq 6$ EU has been computed) remains about the same till the monomerization is no more detectable. After this time, also the sharp peak is affected by ageing and decreases in area toward zero in 14

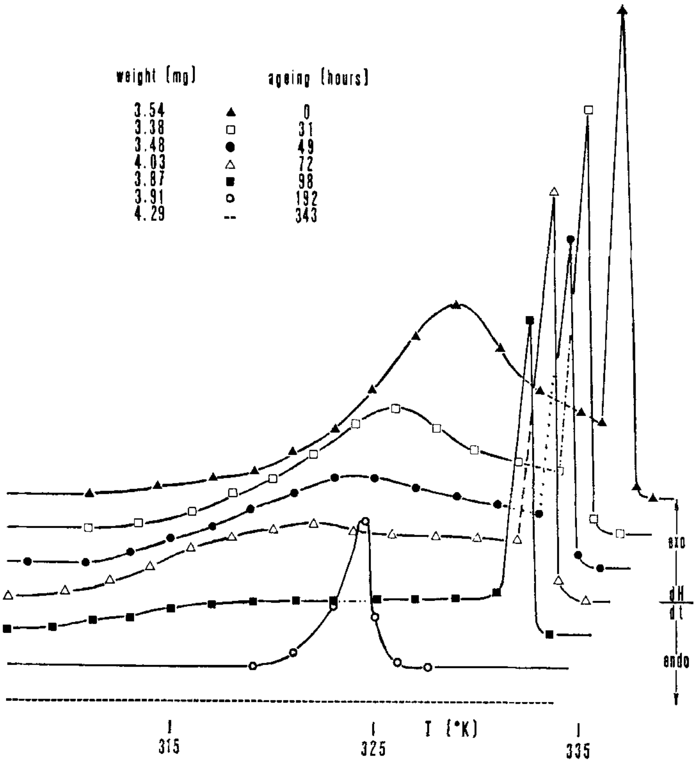

Figure 4. Thermograms of 9-CN, 10-Ac AD showing the ageing effect.

days. This behaviour is in good agreement with a monomerization reaction going on at room temperature to an amorphous phase followed by crystallization. In addition the UV spectrum of the 9-CN, 10-Ac A in methanol solution (Fig. 5) was found to be the same as that obtained from 9-CN, 10-Ac AD (of the same batch used for the thermograms) after being kept in the dark for 8 days.

The plot in the Arrhenius diagram of the first order rate constants evaluated till the onset of the crystallization sharp peak gives (Fig. 3), also in this case a change in slope, which is found to vary toward lower temperatures with increased ageing. Computing at the intersection points the values for the total decomposed fraction of dimer (i.e., the fraction reacted at room temperature plus that decomposed during the calorimetric scanning) gives $\alpha = 0.60$–0.70.

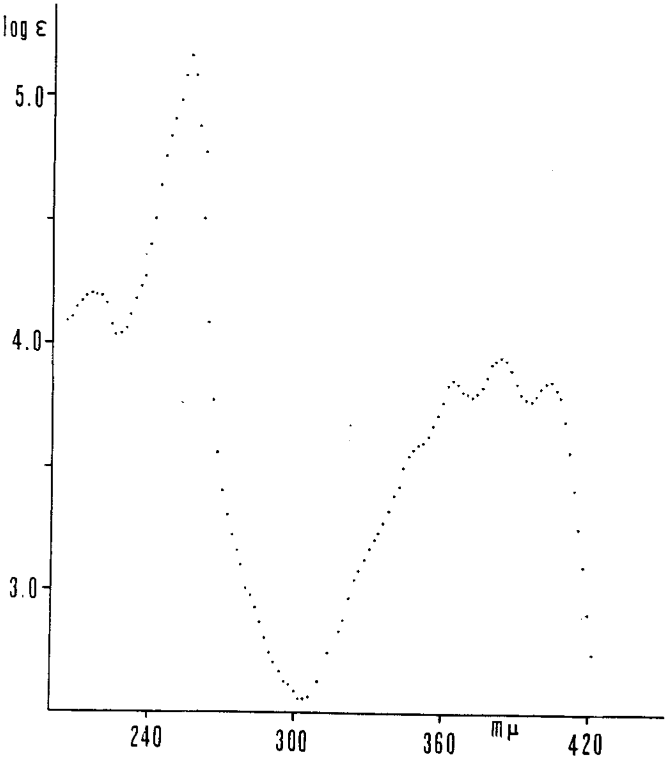

Figure 5. UV absorption spectrum of 9-CN, 10-Ac A in methanol solution.

The monomerization process appears to be first order with two different activation energies. The high temperature activation energy is the same, within experimental errors, for all plots; while the low temperature one is decreasing, with increasing ageing, approaching the high temperature value for long ageing.

In order to explain the kinetic behaviour found for 9-CNAD and 9-CN, 10-Ac AD, with particular reference to the change of the E_a in the diagrams reported in Figs. 2–3 a number of observations may be taken into account: (i) The low temperature process has the higher E_a both for 9-CNAD and 9-CN, 10-Ac AD indicating that this process is preparatory to the one with lower E_a. (ii) The low temperature portion seems to be related to the dimensions of crystals; in fact the temperature range is larger for large crystals (Fig. 2). (iii) Figure 3 shows a progressive decreasing of the high E_a toward the low value with ageing.

The above remarks indicate that there is an extra energy (strain, . . .) to be added to the value of E_a necessary for the dimer→ monomer reaction. We suggest that the proceeding of reaction causes the collapse of the original crystals. When the reaction reaches a certain extent (e.g., 60–70% for 9-CN, 10-Ac AD) the dimer left is embedded in the monomer matrix (amorphous for 9-CN, 10-Ac AD) and behaves as separated dimer molecules which require only the energy necessary for the monomerization reaction.

Both dimers show almost the same value for the E_a in the high temperature region, indicating that a similar process is involved whereas the E_a for the low temperature portion is quite different. Indeed the 9-CNAD is room temperature stable while 9-CN, 10-Ac AD depolymerizes in a relatively short time.

4. Experimental

Thermograms of studied compounds have been obtained by means of a Perkin–Elmer Differential Scanning Calorimeter Mod. DSC-1B connected to a Leeds & Northrup Mod. W recorder. Samples were sealed in the usual aluminium volatile sample pans; an empty pan was used as reference. Both sample holder and reference holder were covered with aluminium holder covers. For 9-CNAD the condition used were: Range (*R*) 1 millical/sec full scale and scan speed (*SS*)

0.5 °K/min, and for 9-CN, 10-Ac AD, $R = 1$ millical/sec and $SS = 1$ °K/min. Areas were measured by means of a polar planimeter.

A Leitz Panphot microscope equipped with Nikon camera was used for studies both in transmitted and reflected light.

UV spectra were recorded with an Uvispek (Hilger & Watts) spectrophotometer.

9-CN, 10-Ac A was prepared following the literature method.(2) The dimer was obtained by irradiating the monomer in ether solution in a glass vessel with a Mazda mercury lamp (250 W). The dimer formed was filtered and washed with little ether. 9-CNAD was prepared by irradiating a benzene solution of the corresponding monomer.

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