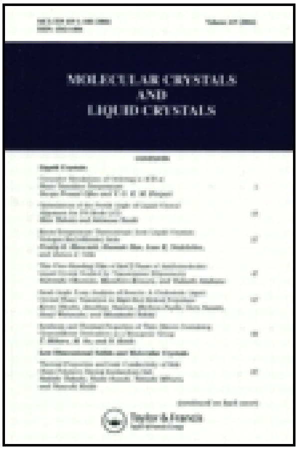

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Isothermal Monomerization of 9-Cyanoanthracene Dimer (9-CNAD)

Donato Donati [a] , Giulio G. T. Guarini [b] [a] & Piero Sarti-fantoni [a]

[a] Centro di studio CNR sulla chimica e la struttura dei composti eterociclici e loro applicazioni. c/o Istituto di Chimica Organica, Università di Firenze, Via Gino Capponi, 9-50121, FIRENZE, Italy

[b] Istituto di Chimica Fisica, Università di Firenze, Via Gino Capponi, 9-50121, FIRENZE, Italy

Version of record first published: 20 Apr 2011.

To cite this article: Donato Donati , Giulio G. T. Guarini & Piero Sarti-fantoni (1981): Isothermal Monomerization of 9-Cyanoanthracene Dimer (9-CNAD), Molecular Crystals and Liquid Crystals, 65:1-2, 147-150

To link to this article: http://dx.doi.org/10.1080/00268948108076136

Mol. Cryst. Liq. Cryst., 1981, Vol. 65, pp. 147–150
0026-8941/81/6502-0147$06.50/0

Printed in the U.S.A.

Isothermal Monomerization of 9-Cyanoanthracene Dimer (9-CNAD)

DONATO DONATI†, GIULIO G. T. GUARINI‡, and
PIERO SARTI-FANTONI†

†*Centro di studio CNR sulla chimica e la struttura dei composti eterociclici e loro applicazioni. c/o Istituto di Chimica Organica, Università di Firenze, Via Gino Capponi, 9 -50121 FIRENZE- (Italy).*
‡*Istituto di Chimica Fisica, Università di Firenze, Via Gino Capponi, 9 -50121 FIRENZE- (Italy).*

(*Received May 19, 1980*)

The monomerization reaction of 9–CNAD crystals, performed by thermal methods under both dynamic and isothermal conditions, has been reconsidered. The dynamic thermal curves confirmed our previous findings while the isothermal ones gave thermal results consistent with the dynamic ones but differing from those recently reported by other authors.

In previous studies we have considered the thermal behaviour of some crystalline anthracene photodimers using a Perkin–Elmer Differential Scanning Calorimeter mod. DSC–1B under dynamic conditions. The calorimetric data[1] and the results of a kinetic investigation on 9-CNAD and 9-CN-10-Acetoxyanthracene dimer monomerization[2] have already been reported.

Recently the kinetics of solid state monomerization of 9-CNAD has been reinvestigated[3] by dynamic and isothermal differential scanning calorimetry and by isothermal spectrophotometric methods. In this article[3] the dynamic exothermal decomposition of 9-CNAD is reported as "followed by sharp melting of the dimer at 480 K" and erroneously referred as in agreement with our previous findings. In addition, from the results reported in Figure 2a of this recent paper,[3] it turns out that the solid state monomerization reaction of 9-CNAD requires ~12, ~6, ~3 minutes at 412, 418.5, 426.5 K respectively when isothermal calorimetric measurements were used.

As the same reaction took ~70 min for completion at a scan speed (SS) of 0.5 $K \cdot min^{-1}$,[2] the freshly reported results prompted us to check our previous findings, i.e. those already obtained at low SS (0.5 and 1 $K \cdot min^{-1}$),

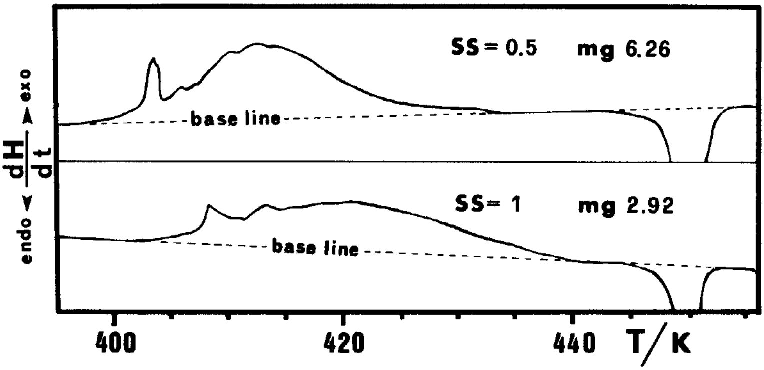

FIGURE 1 Dynamic thermal curves for the monomerization reaction of 9-CNAD microcrystals.

using the same apparatus and experimental conditions previously reported.[2] The samples (3–10 mg of microcrystals having an average size of ~40 μm) were closed in the aluminium volatile sample pans.

The thermal curves for solid state monomerization of crystalline 9-CNAD (SS = 0.5 and 1 $K \cdot min^{-1}$, initial scan temperature ~390 K) shown in Figure 1 are in agreement with those already reported.[1,2] Figure 2 refers to some typical isothermal runs recorded at 402, 406, 412, 418 K. In the isothermal runs the selected temperature was reached by rapid manual operation of the temperature control knob, then the sensitivity was increased to the maximum (1 $mcal \cdot sec^{-1}$) and finally the signal was allowed to stabilize;

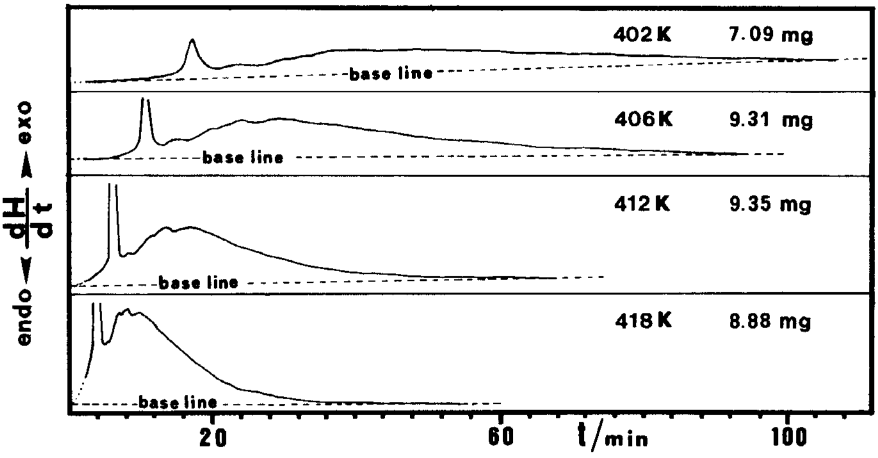

FIGURE 2 Thermal curves for the isothermal monomerization of 9-CNAD microcrystals. The dotted portion of the curves refers to the extrapolation needed to reach $t = 0$ at the middle of the stabilization period.

the whole operation took ~2 minutes. The $t = 0$ was assumed to be at the middle of the stabilization period. Area measurements were performed by polar planimetry.

As it could be expected on the grounds of the runs at SS = 0.5 $K \cdot min^{-1}$, the exothermal signal for the isothermal monomerization reaction lasted for longer (i.e. approximately 106, 93, 67, 53 min at 402, 406, 412, 418 K respectively) than expected on the grounds of recent evidence[3] (cf. Figure 2 in this report with Figure 2a in Ref. 3). A mean value of 75.5 ± 6.3 $kjoules \cdot mole^{-1}$ was deduced for the exothermal heat of transformation in agreement with the value deduced from dynamic runs;[1] this ensured us that, at least in the temperature range investigated, thermal methods give good results for the studied reaction also in isothermal runs. The heat of melting of the formed monomer was also determined (dynamically: SS = 4 $K \cdot min^{-1}$, sensitivity = 8 $mcal \cdot sec^{-1}$) after the end of each exothermal reaction and a mean value of 26.8 ± 0.4 $kjoules \cdot mole^{-1}$ was found in good agreement with previous results[1] thus ensuring us that the monomerization reaction had reached completion; from these experiments the m.p. of the monomer was found higher (451 K instead of 445 K) than previously reported.[1]

The durations of the isothermal monomerization reactions of crystalline 9-CNAD found in the present study compare with those reported in Ref. 3 when the decomposition of dimer films was investigated by a spectroscopic technique.

If we now consider our dynamic thermal curves reported in Figure 1 (see also Refs. 1, 2) together with those reported in Ref. 3, Figure 1, we find a typical exothermic peak at the beginnings of the reaction which has been interpreted in two different manners.[2,3] Also in our isothermal curves (Figure 2) an initial peak is always present; in addition other smaller exothermic effects, superimposed to the broad exothermic curve, are present. Thus we may now suppose that the "isothermal calorimetric profiles for decomposition of 9CNAD" reported in Ref. 3, Figure 2a, refer only to the initial peak and not to the whole reaction. This point of view is confirmed by the short time needed to sweep the area under the above peak (~4 min in Ref. 3, Figure 2a, profile (i), 412 K- and ~3 min in the experiment at 412 K reported in Figure 2, this paper). If this is so, the kinetic analysis, based on isothermal calorimetric data and reported in Ref. 3, is to be considered as referred only to the above initial peak (i.e. to about the initial 8% of the whole reaction).

Acknowledgements

The authors wish to thank Dr. J. O. Williams for having sent them a copy of the manuscript entitled "Calorimetric, Spectroscopic and Structural Studies of the Monomerization of Crystalline 9-Cyanoanthracene Photodimer (9CNAD)," accepted for publication on J.C.S. Faraday I.

References

1. G. Guarini and P. Sarti-Fantoni, *Mol. Cryst. Liq. Cryst.*, **6**, 423 (1970).
2. D. Donati, G. Guarini, and P. Sarti-Fantoni, *Mol. Cryst. Liq. Cryst.*, **17**, 187 (1972).
3. E. M. Ebeid, S. E. Morsi, and J. O. Williams, *J.C.S. Faraday I*, **75**, 1111 (1979).