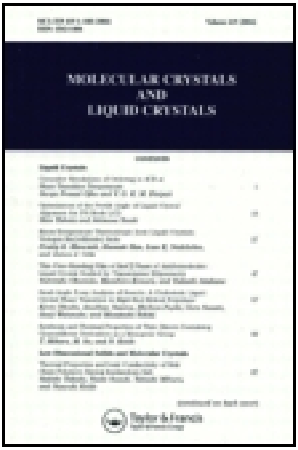

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Evaluation of the Enthalpic Change During the Monomerization Reaction of Crystalline Anthracene Photodimer (AD)

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To cite this article: Donato Donati , Giulio G. T. Guarini & Piero Sarti-fantoni (1981): Evaluation of the Enthalpic Change During the Monomerization Reaction of Crystalline Anthracene Photodimer (AD), Molecular Crystals and Liquid Crystals, 69:3-4, 241-243

To link to this article: http://dx.doi.org/10.1080/00268948108072704

Mol. Cryst. Liq. Cryst., 1981, Vol. 69, pp. 241-243
0026-8941/81/6903-0241/$06.50/0

Printed in the United States of America

Evaluation of the Enthalpic Change During the Monomerization Reaction of Crystalline Anthracene Photodimer (AD)

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(*Received September 25, 1980*)

The isothermal determination of the heat change during the monomerization reaction of crystalline anthracene photodimer (AD) was performed by quantitative differential enthalpic analysis at temperatures lower than the melting point of the formed monomer.

During a series of studies[1-4] on anthracene derivative photodimers some interest emerged on defining their thermal properties. These dimers do not show a well defined melting point as during the heating monomerization occurs.[1,2] In addition it has been found that anthracene derivative photodimers can be divided into two classes, namely those having a depolymerization temperature lower than the m.p. of the corresponding monomer and those having a depolymerization temperature above or very close to the m.p. of the corresponding monomer.[2] In particular 9-Cyanoanthracene dimer and 9-CN-10-Acetoxyanthracene dimer (9CN10AcAD) were found to belong to the first class.[3] This behaviour allowed us to study in some detail the thermal monomerization reactions of 9-Cyanoanthracene dimer and 9CN10AcAD by dynamic differential scanning calorimetry.[3] For the dimers of the second class, including AD, 9-Anthraldehyde dimer, 1-Chloroanthracene dimer, 9-Chloroanthracene dimer, only a ΔT was reported i.e. "the temperature range between the first deflection from the base-line and the peak temperature".[2]

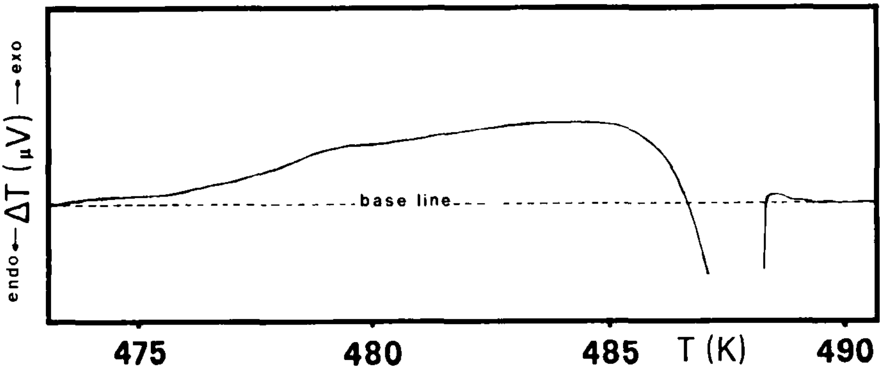

FIGURE 1 Thermal curve for the monomerization of AD recorded at SS = 0.1 K.min^{-1} for a 12.54 mg sample. No thermal data have been deduced from curves of this type because of the evident superposition of exothermic monomerization and endothermic melting.

During a recent reinvestigation of the monomerization reaction of 9-Cyanoanthracene dimer[5] special care was devoted to the study of the above reaction at very low scan speed (SS). For this purpose a Mettler TA 2000 system was employed. The results obtained for 9-Cyanoanthracene dimer stimulated us to extend this type of studies to those dimers whose monomerization temperature was close to the m.p. of the corresponding monomer. From data already reported,[2] AD was then chosen for this type of reinvestigation.

In Figure 1 the thermal curve recorded at SS = 0.1 K.min^{-1} shows that an exothermal portion precedes the endothermic melting of the monomer. This result had not been achieved by Differential Scanning Calorimetry at SS = 1 K.min^{-1} [2] or as SS = 0.5 K.min^{-1};[5] in fact in these cases only an endothermic behaviour was recorded. The above finding prompted us to study the monomerization reaction of AD by isothermal differential enthalpic analysis. For this purpose a temperature range between 475 and 485 K was chosen. In Figure 2 a typical curve, recorded at 479 K, is reported. The planimetric

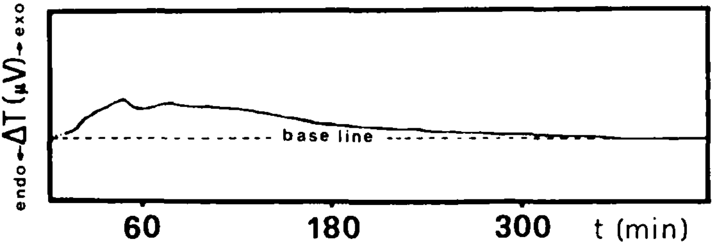

FIGURE 2 Typical isothermal curve for the monomerization of AD recorded at 479 K for a 16.84 mg sample.

measurement of the area under the broad exotherm allowed an evaluation of the heat involved. From a number of isothermal determinations in the above temperature range a mean value 81 ± 17 joules.g^{-1} was deduced. This experimental value compares with the previously estimated one[6] and is lower than the corresponding heat of monomerization evaluated for 9-Cyanoanthracene dimer.[2]

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