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DSC INVESTIGATION ON ANTHRACENE DERIVATIVE PHOTODIMERS

D. Donati, G. G. T. Guarini and P. Sarti-Fantoni*

DIPARTIMENTO DI CHIMICA ORGANICA E CENTRO CNR SULLA CHIMICA E LA STRUTTURA DEI COMPOSTI ETEROCICLICI E LORO APPLICAZIONI, UNIV. DI FIRENZE, VIA G. CAPPONI 9, I-50121 FIRENZE
*DIPARTIMENTO DI CHIMICA, UNIV. DI FIRENZE, VIA G. CAPPONI 9, I-50121 FIRENZE, ITALY

Anthracene derivative dimers reveal a thermal monomerization at temperatures higher than the melting points of the corresponding monomers. Thermograms of these dimers are consisting of a broad endotherm followed by a small exotherm. A detailed investigation on 9–chloroanthracene dimer allowed to explain this peculiar behaviour.

Introduction

Owing to the growing interest on thermal properties of anthracene and anthracene derivative photodimers [1–4], we re-examined some of our previously published [5–7] and unpublished results on this topic. In particular the study of thermal behaviour of such crystalline photodimers allows a division of these compounds into two classes [6]:

a) dimers which monomerize at temperatures lower than those of m.p. of the corresponding monomers (e.g. 9–cyanoanthracene dimer and 9-cyano-10–acetoxyanthracene dimer) for which an exothermal monomerization portion of the curve is followed by the endotherm corresponding to the melting of the formed monomer;

b) dimers which monomerize at temperatures higher than those of m.p. of the corresponding monomers (e.g. 9–chloroanthracene dimer (9–ClAD), 9–anthraldehyde dimer (9–CHOAD), 1-chloroanthracene dimer (1–ClAD). A typical example for dimers of this class is 9–CHOAD [5] which shows a broad endotherm followed by an exothermal portion of limited extent.

The case of anthracene dimer (AD) is interesting because the thermal behaviour is typical for class *a* dimers in isothermal or very low heating rate experiments while, at higher heating rates, the thermal curves become those characteristic for class *b* dimers [7]. It is noteworthy that no conclusive explanation has been reported as yet for the thermal behaviour of class *b* compounds. We notice also that 9–methylanthracene (9–MeAD) has recently been reported to monomerize exothermally [4].

Experimental

The thermograms were obtained by means of a Perkin-Elmer DSC7 Differential Scanning Calorimeter but, for the sake of better comparison with previously recorded data, a Perkin–Elmer DSC1b Differential Scanning Calorimeter and a Mettler TA2000 Thermal Analyzer were also employed. The dimers studied were the same as used in ref. 5 with the addition of 9–MeAD that however had been prepared from solution during the same studies. This shows that these dimers are stable for over twenty years.

Results and discussion

The aim of the present investigation is to contribute to the understanding of the above behaviour associated with the monomerization of the dimers of group *b*. The diagrams reported for 1–ClAD, AD, 9–MeAD, 9–ClAD (Figs 1*a*,*b* 2*a*,*b*), indicate that the overall shape of the thermal curve is similar to that already reported for 9–CHOAD consisting in an initial endothermal portion followed by an exotherm of different extent. The case of 9–ClAD is outstanding; in fact for this compound the final exothermal portion of the thermal monomerization curve is particularly evident both in linearly increasing temperature experiments and in isothermal run at temperatures near 200°.

Because of the peculiar extent of the final exotherm we decided to undertake a detailed study of the thermal behaviour of 9–ClAD. The interruption of an increasing temperature experiment in the neighbourhood of the temperature of the maximum of the endothermal peak (Fig. 3*a*) and the repetition of the run on the same sample, allows the recording of the thermal curve reported in Fig. 3*b*. The partial monomerization of 9–ClAD attained in the experiment reported in Fig. 3*a* is evidenced by the presence in Fig. 3*b* of the melting of the monomer peaked at 106°; in addition, in the same Fig. 3*b* a small broad exotherm ranging between 180° and 200° is present, this was attributed to the thermal homogeneous decomposition of the residual 9–ClAD in the molten 9–ClA. Taking into consideration the ΔH_{fus} of the melting of 9–ClA [5], it was then possible to calculate the amount of 9–ClA formed in the initial decomposition (Fig. 3*a*) and therefore the quantity of the residual dimer assumed dissolved in the molten monomer.

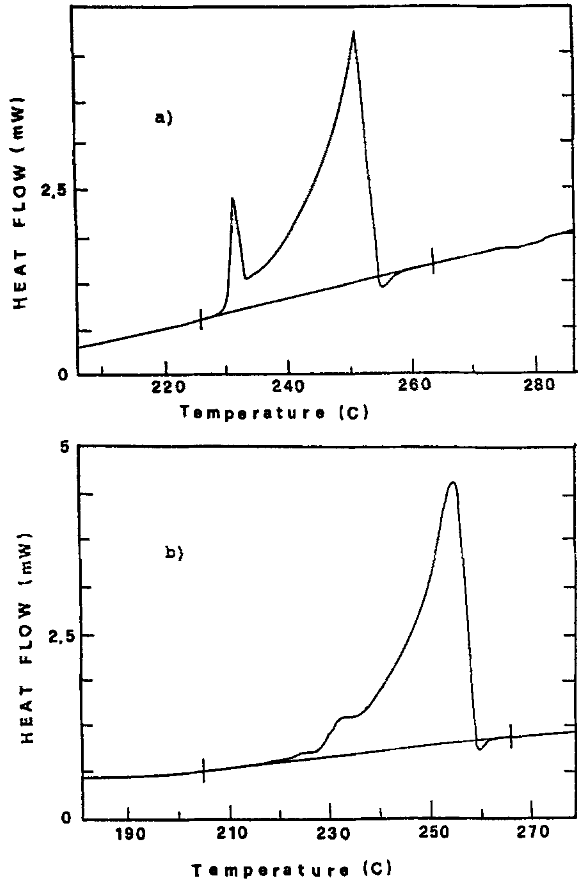

Fig. 1 *a*) DSC curve of 1–ClAD, *b*) DSC curve of AD

The determination of the temperature where to interrupt the first run is critical and depends on the amount of sample and on scan speed. In fact, by interrupting the run too early, i.e. before the maximum of the decomposition endotherm (e.g. 208°), a residual monomerization endotherm still precedes the small final exotherm in the second run. On the contrary, by interrupting the experiment too late, i.e. after the maximum of the decomposition endotherm (e.g. 211°), the final exotherm is no longer detectable in the second

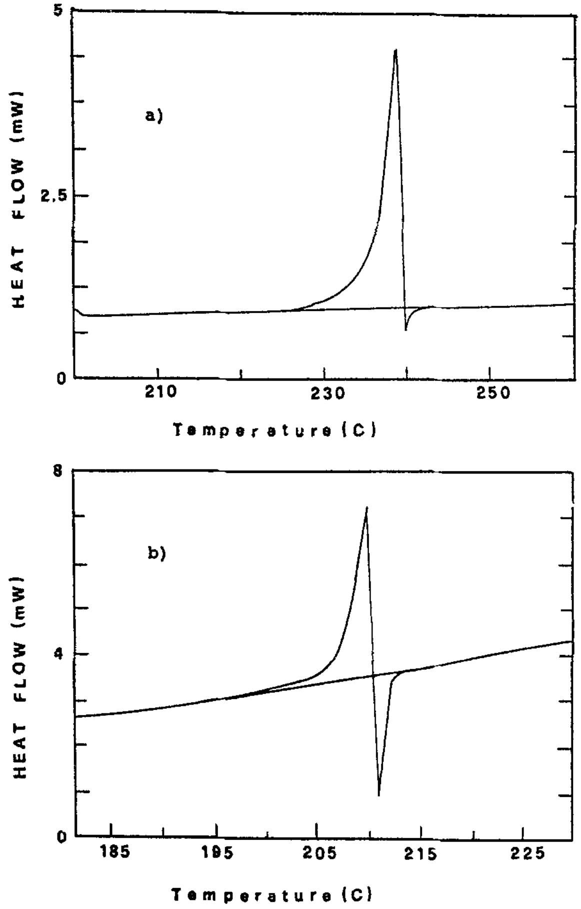

Fig. 2 a) DSC curve of 9–MeAD, b) DSC curve of 9–ClAD

run. In our experiments the best results (as reported in Fig. 3*a*,*b*) were achieved by using a 5.04 mg sample scanned at 5 deg/min and by interrupting the run at 210°. In this experiment the amount of monomer formed during the first run corresponded to ca. 67% of the weighed dimer. Relying on these findings, we prepared a mixture of 9–ClA and 9–ClAD in the same ratio as described above. The thermal curve corresponding to this mixture is reported in Fig. 4 showing the same shape as that reported in Fig. 3*b*. The results obtained by this procedure were in agreement with a homogeneous monomerization of 9–ClAD and allowed an additional evaluation of the heat of the exothermal monomerization of dissolved 9–ClAD in molten 9–ClA ($\Delta_r H = -17.5 + 4$ J/g). As already noted, all the anthracene dimers of class *b* show the same thermal behaviour and in particular the decomposition endotherms are followed by final exotherms usually of extent smaller than the one found for 9–ClAD. This analogy prompts us to suggest that they all behave like 9–ClAD i.e. the solid dimer decompose giving molten monomer which then dissolves some of the residual dimer whose subsequent homogeneous monomerization causes the final exotherm.

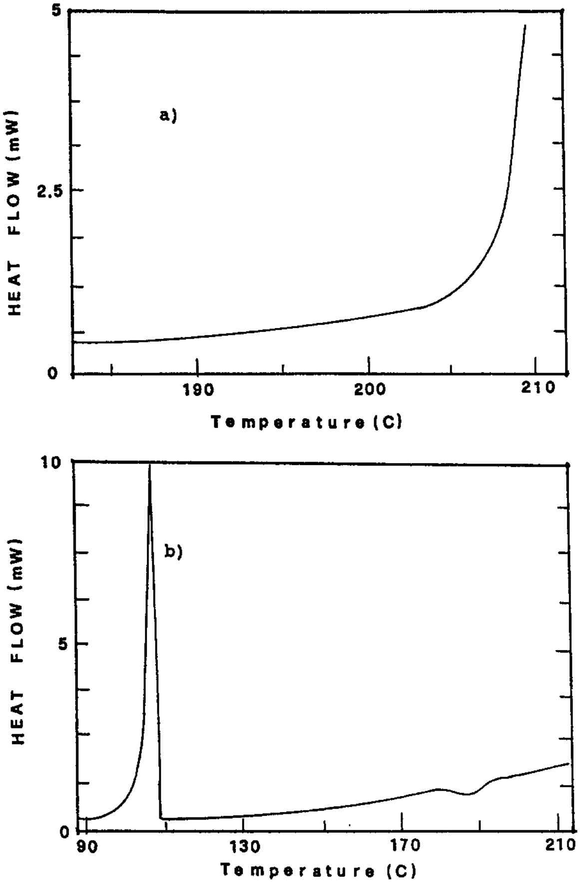

Fig. 3 *a*) DSC curve of 9–ClAD interrupted at 210 °C, *b*) DSC curve of the 9–ClAD sample partially decomposed as reported in Fig. 3*a*

Additional work is required to evaluate the $\Delta_r H$ of the small exotherm of 9–CHOAD, 1–ClAD, 9–MeAD by repeating the procedure above described for 9–ClAD.

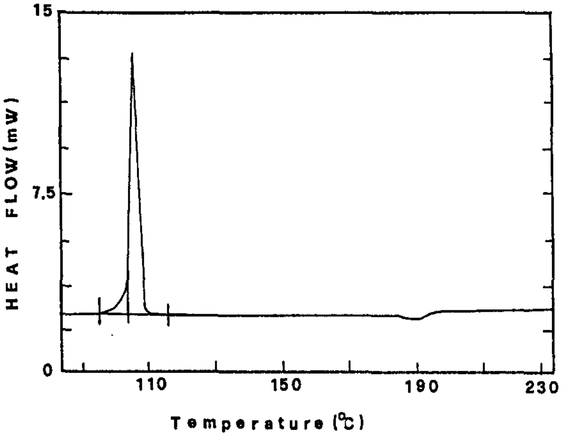

Fig. 4 DSC curve of a mixture of 9–ClA and 9–ClAD in the ratio 2:1

References

1 T. Laird, Chem. Ind., (1978) 186.
2 W. R. Bergmark, G. Jones II, T. E. Reinhardt and A. M. Halpern, J. Am. Chem. Soc., 100 (1978) 6665.
3 A. Albini, E. Fasani and D. Faiardi, J. Org. Chem., 52 (1987) 155.
4 E-Z. M. Ebeid, A-F. M. Habib and S. A. Azim, React. Solids, 6 (1988) 39.
5 G. Guarini and P. Sarti-Fantoni, Mol. Cryst. Liq. Cryst., 6 (1970) 423.
6 D. Donati, G. Guarini and P. Sarti-Fantoni, Mol. Cryst. Liq. Cryst., 17 (1972) 187.
7 D. Donati, G. G. T. Guarini and P. Sarti-Fantoni, Mol. Cryst. Liq. Cryst., 69 (1981) 241.

Zusammenfassung — Dimere Anthracenderivate zeigen für Temperaturen, die höher als die Schmelzpunkte der entsprechenden Monomeren liegen, eine thermische Monomerisierung. Die beobachteten Thermogramme dieser Dimeren bestehen aus einem breiten endothermen Vorgang mit partieller Überlappung eines anschliessenden schwach exothermen Vorgangs. Für 9–Chloroanthracen konnte sowohl mittels geeignet ausgeführter konsekutiver Scans als auch mit einer Modellmischung dieses eigenartige Verhalten erklärt werden.