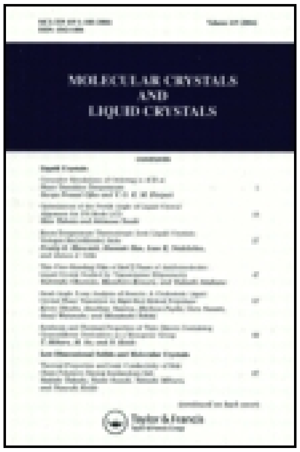

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Calorimetric Study on Some Anthracene Photodimers

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Calorimetric Study on Some Anthracene Photodimers

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Abstract—Calorimetric data referring to dimers of anthracene, 9-CN-anthracene, 9-Cl-anthracene, 1-Cl-anthracene and 9-anthraldehyde are reported. Values for heat of melting for monomers are listed.

Anthracene[1] and anthracene derivative[2] photodimers formed by irradiation from solution have been known for a long time. Luther and Weigert[3] reported the dimerization of anthracene in the solid state. Recently solid state dimerization of anthracene has been confirmed and extended to anthracene derivatives.[4] The dimers have been found to have the same structure as those obtained from the irradiated solutions.

In spite of several researches, discrepancies still persist concerning the behaviour of the dimers under heating. The case of 9-anthraldehyde dimer is outstanding: Mustafa[5] gives m.p. 250°, Calas *et al.*[6] m.p. 270° whereas Green *et al.*[7] report the much lower value m.p. 186–187 °C.

In most cases, depolymerization occurs at a temperature above the monomer melting point,[2] and it is then difficult or impossible to distinguish the thermal properties of the dissociation from those of melting of the dissociation products and dissolution of the unchanged dimer in the molten monomer. For this reason there is a special interest in 9-cyanoanthracene dimer (9-CNAD) which we find to dissociate at a temperature below the monomer melting point. Another case is known.[2]

The behaviour of various dimers on heating has been reinvesti-

Table 1 · Calorimetric data‡ for some anthracene derivative dimers

	m.p. (dec.) reported in the literature (°C)	ΔT found	Scan speed (°C/min)	m.p. monomer (°C)	ΔH melting monomer (cal mole^{-1})
Dianthracene	242–244	215/244	1	217	+6690
	272–274 (2)	218/264	8		
	270–280	244/277	16		
9-Anthraldehyde Dimer	270 (5)	157/163	0.5	104	+4210
	250 (4)	176/192	8		
	187 (7)	157/169	1		
		172/183	4		
1-Cl-Anthracene Dimer	235 (2)	237/270	8	82	+3380
		225/252	4		
9-Cl-Anthracene Dimer	265 (2)	187/193	1	106	+4460
		191/200	2		
		206/217	8		
9-CN-Anthracene Dimer	205 (8)	127/162	0.5	172	+6020
		130/167	1		

‡ All ΔH values are within 5% error. All dimers but 9-CNAD were prepared from irradiated solution; 9-CNAD was prepared from solid state.

gated by using a Differential Scanning Calorimeter Perkin–Elmer DSC-1B in order to study stability in a reproducible way. The examples studied are reported in Table 1; ΔT is the temperature range between the first deflection from the base line and the peak temperature. In the case of 9-CNAD ΔT refers to the complete decomposition range. Small quantities ($\simeq$10 mg) of sample sealed in the usual volatile sample pan were scanned at different speed as reported in Table 1. ΔT values are of course dependent on the heating rate.

The area corresponding to the endothermic fusion of the monomer is also measured and the ΔH values calculated are reported in the table. The melting points found for monomers are in good agreement with those reported in the literature.

The important result is that 9-CNAD, which depolymerizes in a temperature range where monomer melting does not interfere, does so exothermically; $\Delta H \simeq -20$ kcal mole^{-1}. The endothermic effect observed for the other dimers is found because of the dominating endothermic melting process. An attempt to determine the ΔH for decomposition of the other dimers is now in progress. The scanning diagrams of 9-CNAD and 9-anthral-

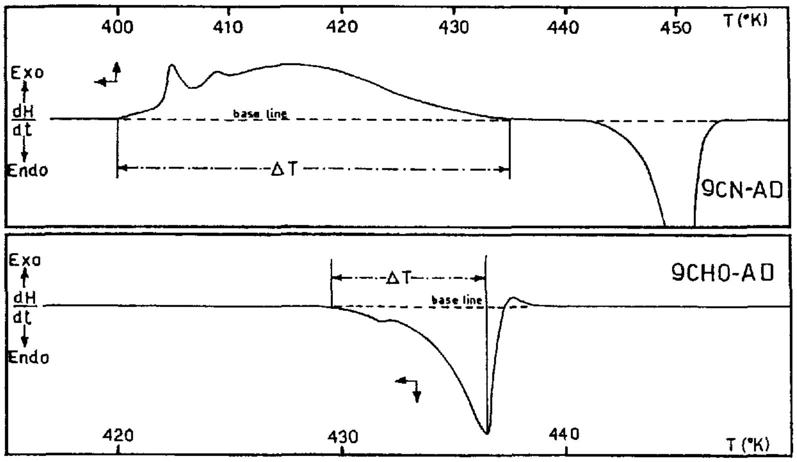

FIGURE 1

dehyde dimer are reported in Fig. 1. Our results are in good agreement with those reported in the literature for dianthracene and 1-chloroanthracene dimer only if high scan speeds are considered.

REFERENCES

1. Linebarger, C. E., *Ann. Chem. J.* **14**, 599 (1892).
2. Calas, R. and Lalande, R., *Bull. Soc. Chim. France*, 763 (1959).
3. Luther, R. and Weigert, F., *Z. Phys. Chem.* **51**, 297 (1905).
4. Craig, D. P. and Sarti-Fantoni, P., *Chem. Comm.*, 742 (1966).
5. Mustafa, H., *J. Chem. Soc.*, 1034 (1951).
6. Calas, R., Lalande, R., Moulines, F., and Faugère, J. G., *Bull. Soc. Chim. France*, 121 (1965).
7. Green, F. D., Misrock, S. L., and Wolfe, J. R., *J. Amer. Chem. Soc.* **77**, 3852 (1955).
8. Lalande, R. and Calas, R., *Bull. Soc. Chim. France*, 766 (1959).