The Thermally Induced Phase Transition of Crystalline 9-Cyanoanthracene Dimer: a Single Crystal Study

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The crystal structure of the title compound is reported, and single crystal *X*-ray techniques are used to show that at temperatures close to the first exothermic peak of the title compound calorigram, a phase transition occurs which results in the formation of a new dimer structure; details of this structure are also reported.

U.v. irradiation of crystalline 9-cyanoanthracene (9-CNA) results in the formation of the *trans* photodimer (9-CNAD); the reaction is believed to occur at crystalline defects.[1] The reverse reaction, monomerisation, may also take place in the crystal, being induced either thermally or photochemically. This reverse reaction is of interest for both theoretical and practical reasons, not least as one of the candidates for the storage of solar energy in chemical bonds.[2]

Detailed differential scanning calorimetric studies of 9-CNAD show two exothermic peaks which are followed by an endothermic peak associated with the melting of the formed monomer.[3] The second exotherm, a broad peak, corresponds to complete monomerisation, but the first (a sharper peak) which occurs at 425 K has been hitherto assigned by different workers to a variety of solid-state processes.[3—6] We embarked upon the determination of the crystal structure of 9-CNAD in the hope of elucidating the processes which are associated with the first exothermic peak.

9-CNAD packs in space group $P\bar{1}$,† with the asymmetric unit containing 3 fragments: 1 whole dimer-molecule whose molecular centre of symmetry does not correspond to a crystallographic one (molecule 1 in Figure 1) and two half dimer molecules (molecules 2 and 3 in Figure 1), each corresponding to a monomer residue. For these last fragments, the molecular centre of symmetry coincides with a crystallographic centre of symmetry, thus giving a total of four molecules in the unit cell. Since previous workers reported 9-CNAD to undergo *X*-ray induced monomerisation (and

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† 9-CNAD: $C_{30}N_2H_{18}$, $M = 406.49$, space group $P\bar{1}$, $a = 10.146(1)$, $b = 17.785(1)$, $c = 11.501(1)$ Å, $\alpha = 92.95(1)$, $\beta = 95.59(1)$, $\gamma = 89.82(1)^\circ$, $U = 2062.7$ Å^3, $F(000) = 848$, $D_c = 1.309$ Mg m^{-3}, $Z = 4$, $\mu = 5.13$ cm^{-1}, crystal size $= 0.15 \times 0.10 \times 0.11$ mm^3, $3 < \theta < 70^\circ$. Data: unique, 7807 reflections; observed $[F_o > 2\sigma(F_o)]$, 2785 reflections. $R = 0.0436$, $R_w = 0.0407$.

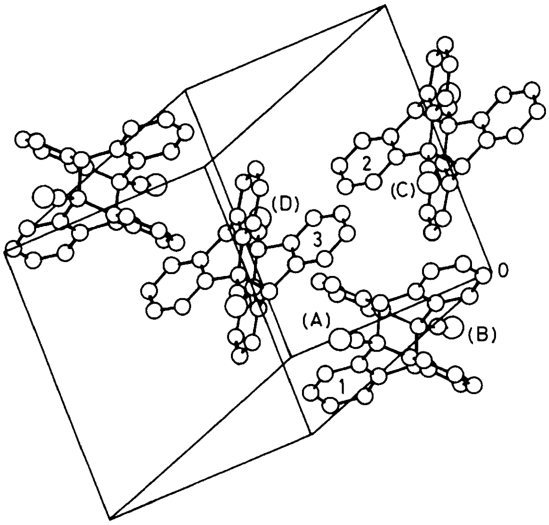

Figure 1. Crystal structure of 9-CNAD. Monomer residues marked (A), (B), (C) and (D) make up the asymmetric unit.

because of the crystal fading to the extent of 20% during data collection) a refinement of occupancy factors was carried out, which yielded values very close to 1.0. Thus, we conclude that monomerisation had not occurred to any significant extent.

When 9-CNAD single crystals are heated in an optical microscope to 420 K, a change in colour from colourless to yellow occurs. Oscillation and Weissenberg photographs indicate that such yellow crystals (designated as 9-CNADY) retain single crystal character, and are therefore suitable for full data collection. (No fading was observed.) Successful structure solution and refinement yielded the structure shown in Figure 2. The crystal is still dimeric, but a phase transition has occurred, 9-CNADY packing in $P1$,[‡] with two dimeric molecules in the asymmetric unit. This phase transition is of the single-crystal → single-crystal type, with oscillation and Weissenberg photographs showing the reaction to be topotactic. The a and c axes for the two structures remain parallel and almost equal in length, while b in 9-CNAD corresponds to [110] in 9-CNADY in direction and is twice its length. 9-CNADY shows the characteristic blue fluorescence of 9-CNA indicating that some monomerisation has occurred during heating. The absence of fading during data collection may indicate that X-rays do not induce monomerisation, and any monomer present is due to the thermal treatment. Occupancy factor refinement for 9-CNADY indicates that monomerisation has occurred to the extent of 8%, and probably provides the driving force for this phase transition. The positions of the monomer molecules have not been located, because of their low concentration, and because they lie very close to the dimeric fragments. The presence of monomer explains the rather poor R value, and also the poor bond lengths and bond angles.

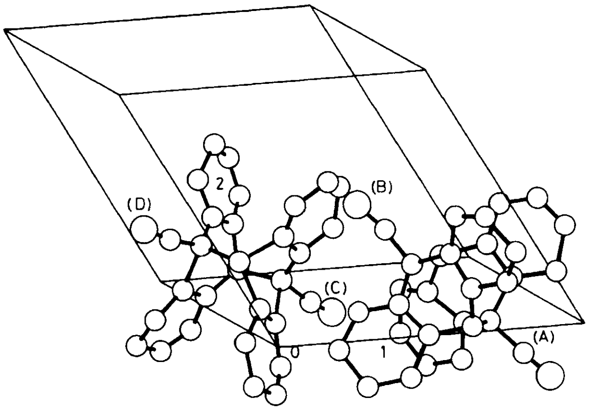

Figure 2. Crystal structure of 9-CNADY. The two molecules shown form the asymmetric unit.

Data collection was carried out using an Enraf-Nonius CAD-4 four-circle diffractometer with Cu-K_α ($\lambda = 1.54178$ Å) radiation, in the manner previously described.[7] The structures were solved by direct methods and refined by block cascaded full least squares techniques. All calculations were carried out using SHELX-76 (G. M. Sheldrick), SHELXS-84 (G. M. Sheldrick), PLUTO-78 (W. D. S. Motherwell), and private programs on an IBM-3081 computer (University of Cambridge).[§][¶]

It has therefore been shown that the first step in the solid-state thermal monomerisation of 9-CNAD is a topotactic single-crystal → single-crystal phase transition to a second dimer phase accompanied by limited (8%) homogeneous monomerisation. This latter phase then proceeds to complete monomerisation to give crystals whose structure is that of the pure monomer.[8] This second step proceeds heterogeneously and may also be rationalised in terms of the 9-CNADY crystal structure.[9]

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References

1 M. D. Cohen, Z. Ludmer, J. M. Thomas, and J. O. Williams, *Proc. R. Soc. London, Ser. A*, 1971, **324**, 459.

2 W. R. Bergmark, G. Jones II, T. E. Reinhardt, and A. M. Halpern, *J. Am. Chem. Soc.*, 1978, **100**, 6665.

3 E-Z. M. Ebeid, S. E. Morsi, and J. O. Williams, *J. Chem. Soc., Faraday Trans.* 1, 1980, **76**, 2170.

4 E-Z. M. Ebeid, A. F. M. Habib, S. A. Azim, and N. J. Bridge, *J. Chem. Soc., Faraday Trans.* 1, 1983, **79**, 2133.

5 D. Donati, G. G. T. Guarini, and P. Sarti-Fantoni, *Mol. Cryst. Liq. Cryst.*, 1972, **17**, 187.

6 D. Donati, P. Sarti-Fantoni, and G. G. T. Guarini, *J. Chem. Soc., Faraday Trans.* 1, 1982, **78**, 771.

7 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

8 H. Rabaud and J. Clastre, *Acta Crystallogr.*, 1959, **12**, 911.

9 C. R. Theocharis and W. Jones, manuscript in preparation.

[‡] 9-CNADY: ($C_{30}N_2H_{18}$), M = (406.49), space-group $P1$, a = 10.217(2), b = 10.235(2), c = 11.594(2) Å, α = 95.20(2), β = 90.37(2), γ = 120.13(1)°, U = 1042.4 Å^3, $F(000)$ = 424, D_c = 1.295 Mg m^{-3}, Z = 2, μ = 5.08 cm^{-1}, crystal size = 0.35 × 0.10 × 0.05 mm^3, $3 < \theta < 70°$. Data: unique, 3465 reflections, observed [$F_o > 2.5\sigma(F_o)$], 1172 reflections. R = 0.1015, R_w = 0.1044.

[§] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[¶] Further experimental and structural details will be given elsewhere.