DILATOMETRIC STUDY OF THE POLYMORPHISM
OF 1,8-DINITRONAPHTHALENE

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Basing on dilatometric measurements, the existence of Phases III and IV in 1,8-dini-
tronaphthalene, suggested by McCrone, is confirmed. Discussion is given of the stability
conditions and mutual relations between all four phases.

1,8-dinitronaphthalene (henceforth called 1,8-DNN) belongs to the group of aromatic compounds whose molecules possess large-sized substituents placed in neighbouring positions. After Kitaigorodskii [1] such molecules are being termed as "over-crowded". Their properties are interesting from the point of view of the potential energy of interaction of non-bonded atom pairs which sometimes can lead to more than one stable configuration of the molecule. This factor, among others, is considered to be responsible for the existence of polymorphic modifications of the material.

The polymorphism of 1,8-DNN has been studied by McCrone [2] by means of optical methods. Crystals of the phase stable at room temperature (Phase I)[1] are orthorhombic and can be obtained by slow evaporation of benzene- or alcoholic solution.

The morphology of the crystals and refractive indices along the three crystallographic axes are given in McCrone's paper. An X-ray study of the structure of crystals of Phase I has been carried out by Akopian, and Kitaigorodskii and Struchkov [3].

According to observations made by McCrone [2] by means of a heated microscopic stage, the crystals of Phase I on heating undergo an enantiotropic transformation to Phase II at about 110°C. On the other side, if a melt is slowly cooled between two glass plates (m. p. 170-172°C) at least two metastable phases can be observed in the polarizing microscope, and one of them is identical with Phase II. McCrone observes that 1,8-DNN may even have four crystal modifications but the existence of the fourth phase could not be proved.

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[1] The nomenclature of Phases I and II accepted here follows that used by McCrone [2].

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A DTA study of the phase transformation I ↔ II, in the direct and reverse directions has been made by Kozhin [4]. He found that the heat of transition amounts to 1.5 kcal per mole, and the transition temperature is $t_{tr} = 118°C$. Basing on an X-ray study made on supercooled crystals of the high temperature phase Kozhin states [5] that the crystals of Phase II are monoclinic with 8 molecules in the unit cell. However, the undercooled crystals were obtained from the melt and according to McCrone's results they need not necessarily correspond to Phase II but may also represent those of Phase III or IV.

As a result, a certain ambiguity exists concerning the number of polymorphic modifications of 1,8-DNN and their mutual relations. In this situation we undertook a dilatometric study of this compound with hoping to throw more light on that problem.

1. Experimental results

The results of experiments carried out on a number of crystal plates cut in three mutually perpendicular directions are presented in Figs 1–3. Each curve was obtained two or three times on different samples and can be considered to be characteristic for the
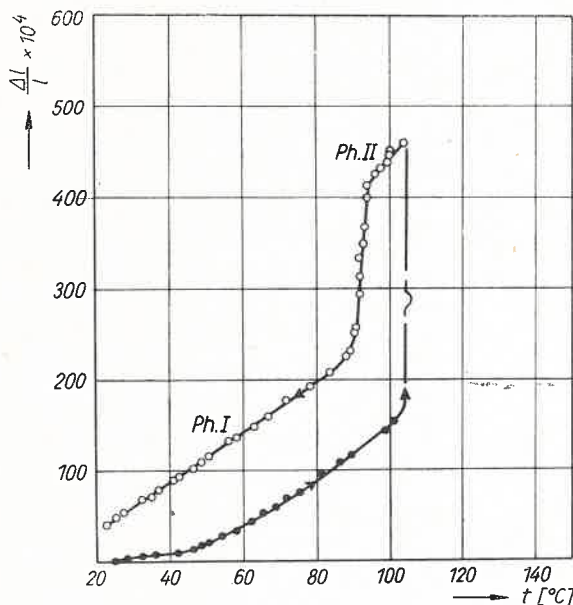

Fig. 1. Temperature dependence of relative increase of length of a 1,8-DNN sample, direction I. Upward arrows indicate heating, downward ones — cooling of the sample

material and crystallographic direction. It can be seen that the thermal expansion coefficient, given by the slope of linear parts of the plots, is an anisotropic property of the crystal. It is also clear that expansion coefficients of Phase I are, is general, different from those of Phase II. Numerical values will be published in a separate paper.

On heating, the transition I → II occurs within a temperature interval of 100–150°C, and is accompanied by a marked dilatation of the sample. For the reverse direction, II →I,
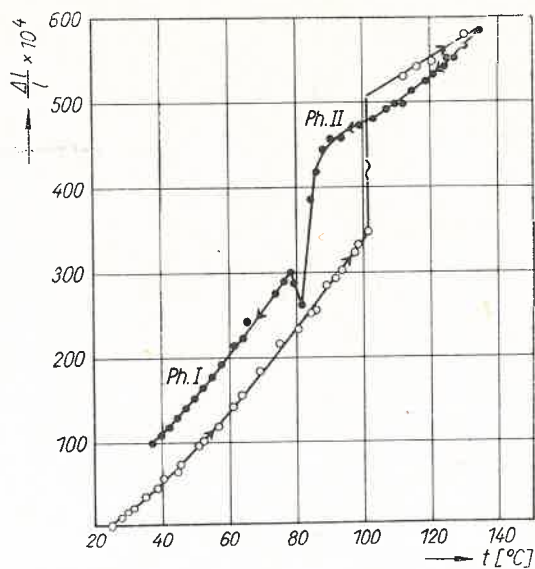
Fig. 2. Temperature dependence of relative increase of length of a 1,8-DNN sample, direction II
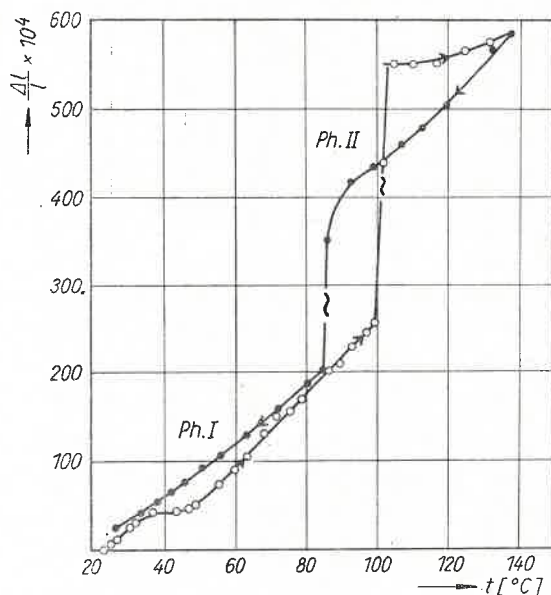

Fig. 3. Temperature dependence of relative increase of length of a 1,8-DNN sample, direction III

the transition is observed at a lower temperature, 85°C, and the change of length is smaller than that for the forward direction. The subsequent cycles carried out with the same sample show that the character of dilatation curves is more or less repeatable within the temperature interval of $100° > t > 50°$. In contrast, the properties of Phase I below 50°C seem to be irreversible in the sense that the anomalous behaviour appearing in the temperature

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interval of 30–45°C can be observed only in the first cycle and only in two of the three directions of measurements (*cf.* Figs 1 and 3 with Fig. 2).

Reversible behaviour of Phase I on cooling is also shown in Fig. 4, curves *1* and *3*, where the heating curves are omitted. However, a II → I phase transformation appears if the maximum temperature of the sample is kept below a temperature t_s corresponding to the softening of the material. If a sample is "overheated" to $t \geqslant t_s$, no decrease of length whatever is observed in the vicinity of 85°C on cooling but instead a small increase of length occurs at about 60°C (curve *2*, Fig. 4). This behaviour may be interpreted as cor-
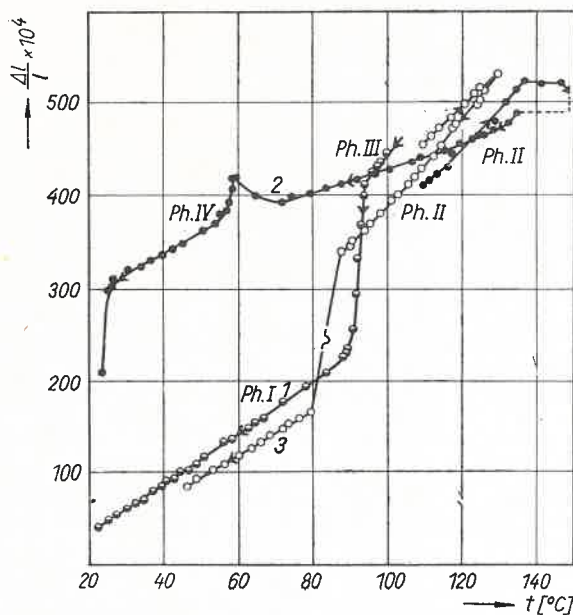

Fig. 4. Cooling curves for 1,8-DNN observed in direction I. Curves *1* and *3* illustrate the behaviour of samples heated to about 120°C, curve *2* was obtained for a sample heated to about 150°C

responding to a formation of Phase III at the softening temperature, t_s. Phase III is stable on cooling down of the sample to about 60°, where a new Phase IV appears. This is supported by the fact that linear parts of dilatation curve above and below 60°C have different slopes, *i. e.* Phases III and IV differ by values of thermal expansion coefficients. After some time of the order of magnitude of several hours, Phase IV spontaneously transforms to Phase I. Indeed, on subsequent heating the sample shows the expansion coefficient corresponding to Phase I.

Samples useful for optical observations can be obtained from the melt by slow crystallization in a quartz cuvette of 0.1 mm thickness. If cautiously cooled, the sheet undergoes a number of phase transitions and finally reaches a state corresponding to Phase I, with a transparency well sufficient for microscopic examinations. Both these, and dilatometric observations indicate that during the I → II transformation the monocrystalline structure of Phase II becomes, at least partially, destroyed. Even a stronger pulverization occurs in the reverse direction, II → I.

2. Discussion

Summarizing the results presented in the preceding paragraph we may conclude that on heating above the room temperature 1,8,-DNN undergoes at 100–105°C a dilatometrically reversible phase transformation, I → II, which is accompanied by a sudden increase of the length of the crystal and a change of thermal expansion coefficient. Starting with a sample in the form of a single crystal (c) we arrive after transformation at polycrystalline material (pc) and, therefore, the transformation is of the type c → pc. On cooling, the transformation in the reverse direction is initiated at a lower temperature, about 85°C, and is accompanied by a decrease of length of the sample and by a reversible change of thermal expansion coefficient. As a whole, both transformations form a "hysteresis loop" with a width of $\Delta t = 15$–20°C, which is characteristic for a c → c transformation. A case with $\Delta t \neq 0$ means that the transformation is a crystallization process which is preceded by a formation of crystallization seeds of a new phase within a metastable medium. Thermodynamic conditions which require that Δt must differ from zero in order for crystallization centres to be formed in liquid or gaseous phases must, of course, also be valid in the case of a solid-solid transformation. The only difference between fluid and solid media is that in the latter case Δt can be either positive or negative depending on the actual direction of the transformation. Non-zero difference of temperature is also required for a further growth of crystallization centres.

Any transformation proceeds with a change of free energy, $\Delta \Phi$. In the case $\Delta \Phi < 0$ the transformation is spontaneous in a c → c case, or in a c → pc case, if the new phase consists of crystal grains of comparatively large size. Otherwise, as is in the case of microcrystalline phases, $\Delta \Phi$ should be extended by an additional term, $\gamma l^2 \sigma$, corresponding to the contribution of surface energy.

Therefore, for the latter case we have:

$$\Phi = N_1 \varphi_1 + N_2 \varphi_2 + \gamma l^2 \sigma,$$

where N_1 and N_2 are numbers of molecules constituting Phase I or II where their chemical potentials are φ_1 or φ_2, respectively, γ is a shape parameter of the micro-crystal which has a linear dimension l, and σ is the surface free energy per unit area.

The actual difference in free energy, $\Delta \Phi$, can therefore be considered to be composed of two contributions, the former corresponding to the volume of a new phase and the latter

$$\Delta \Phi = \Delta \Phi_v + \Delta \Phi_s$$

to its surface. The phase transformation in 1,8-DNN is of c → pc type in the direction I → II, and both contributions have equal signs giving a large increase in Φ. However, for the reverse direction, II → I, the transformation is of the type pc → pc, and sings of both contributions are different. This explains why a much lower peak is observed on a DTA curve for a II → I transformation in comparison to that observed in the reverse direction [4].

If a sample is over-heated to a softening temperature, about 150°C, it shows an anomalous behaviour as already has been stated in the preceding paragraph. Phase III spontaneously transforms to Phase IV at about 60°C, but the process is gentle enough and takes

place without any marked destruction of crystal lattice. However, the transformation IV → I is a slow process at room temperature, and Phase IV shows a comparatively long "life-time" and quite a good transparency. Basing on these properties derived from microscopic observations, we may suppose that Kozhin's "Phase II" used in his *X*-ray study [5] corresponded, as a matter of fact, to Phase IV.

The relations between Phases I to IV so far discussed are summarized in the following Table:
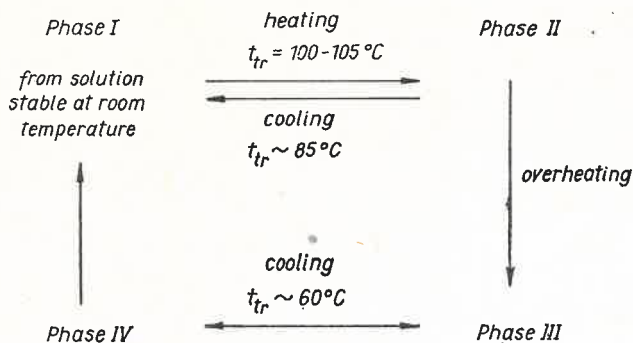
Experimental procedure

1,8-dinitronaphthalene used in this study was synthetized in the Department of Organic Chemistry of the Wrocław University. The crude material was very carefully purified because even small amounts of impurities can affect the parameters of the phase transformation or even inhibit its appearance [6]. The compound was crystallized several times from c. p. benzene and subsequently distilled in vacuum. After this procedure the material was zone-melted with 60 passages of the zone. From the purified compound, crystals were grown by evaporation of the solvent (90 % toluene, 10 % acetone) at room temperature. Crystals obtained had the form of paralellopipeds with largest dimensions of $10 \times 5 \times 4$ mm and an excellent transparency.

Microscopic observations were carried out on a Boetius' microscopic hot-stage, and dilatometric measurements were made by means of a microscopic method using an apparatus constructed in our laboratory [7].

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