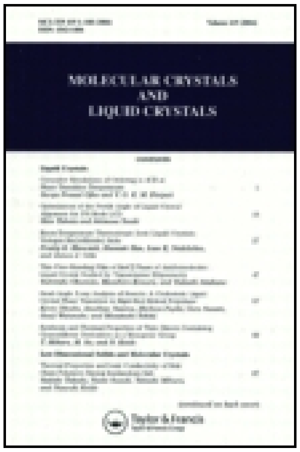

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The Polymorphism of 2,2-Dinitropropyl 4,4,4-Trinitrobutyrate

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Abstract—Properties of three crystallographic modifications of 2,2-dinitropropyl 4,4,4-trinitrobutyrate are reported. The polymorphic system is represented by a phase diagram which includes two enantiotropic transitions: I → II at 11 °C; and II → III at 62.5 °C. The high temperature polymorph, stable between 62.5 °C and the melting point, 95.0 °C, possesses most of the properties of the plastic crystalline state including a low entropy of fusion, 4.5 e.u. Although the 2,2-dinitropropyl 4,4,4-trinitrobutyrate molecule does not have spherical symmetry, the low entropy of fusion is evidence of considerable orientational disorder in the lattice of the high temperature form. A differential scanning calorimeter was used to determine heats of transition: I → III = 6.2 kcal/mole; II → III = 5.0 kcal/mole.

Several new organic compounds containing the trinitromethyl group have been prepared and studied at this Laboratory. During a study of one of these, 2,2-dinitropropyl 4,4,4-trinitrobutyrate, DNPTB, three different crystalline forms were identified. Interrelationships and properties of these polymorphs are reported herein.

Results and Discussion

Three distinct crystallographic modifications of DNPTB have been observed. These polymorphs have been characterized by X-ray diffraction and microscopic observation. The polymorphic system may be represented by the phase diagram, Fig. 1, in which

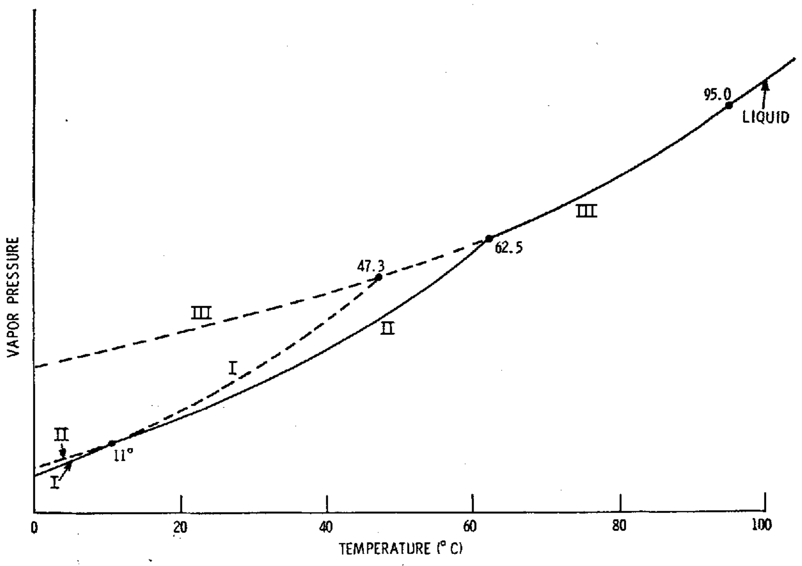

Figure 1. Phase diagram of 2,2-dinitropropyl 4,4,4-trinitrobutyrate, DNPTB

broken lines represent metastable states which persist for a significant length of time.

DNPTB-III melts sharply at 95.0 °C. The liquid solidifies without supercooling to a transparent tacky solid with a glassy appearance. The high temperature polymorph is anisotropic with a birefringence of 0.001. This very low birefringence would indicate a high degree of lattice symmetry.

When DNPTB-III is supercooled to room temperature it always transforms to I and not to II, even though II is the stable polymorph at this temperature. At room temperature in the absence of seeding, several days are required before nuclei of I appear in III. These nuclei then grow at a linear rate of about 3 mm. in 24 hours. When DNPTB-III is supercooled below 11 °C, it still transforms to I.

DNPTB-I crystallizes from solution at room temperature producing highly birefringent, well formed crystals. This is the case for the following solvents and solvent pairs: carbon tetrachloride, chloroform, acetone, chloroform-hexane, acetone-water and methanol-water. A solution of DNPTB in chloroform cooled to 2 °C produces form I upon the addition of hexane at the same temperature. Prolonged standing of form I at room temperature under the mother liquor promotes a solution phase transition to form II. In the case of chloroform-hexane, four to six days are required for completion of this I → II transition.

Although DNPTB-I is metastable at room temperature, it is obtained preferentially both by crystallization from a solvent and by the form III solid-solid transition. Probably this means that the rate of crystallization of I is greater than that of II. DNPTB-I shows a strong tendency to persist at room temperature. Dry samples have been stored for several months with no sign of a transformation.

When form I is heated to 47.3 °C it transforms slowly to III. About three to five minutes are required for the I → III transition in a small single crystal observed on the microscope hot stage.

A determination of the I → II transition temperature was made by noting the temperature at which a solution phase transition took place using solid DNPTB in contact with equal volumes of chloroform and hexane. The I → II and II → I solution phase transitions required several weeks at temperatures near the transition point. The following solution phase transitions were observed: II → I at 10.3 °C and I → II at 11.3 °C.

DNPTB-II crystals are anisotropic. They undergo a slow transition to form III at 62.5 °C. The transition temperature was determined on a microscope hot stage; the transition was also followed on the heated sample mount of an X-ray diffractometer.

The following heat of fusion and heats of transition of DNPTB were determined with a differential scanning calorimeter: $\Delta Hf = 1.6$ kcal/mole; ΔHt I → III = 6.2 kcal/mole; ΔHt II → III = 5.0 kcal/mole. A highly purified sample of 2,2-dinitropropane with a heat of fusion of 647 cal/mole was used as a reference.

DNPTB-III possesses most of the properties of plastic crystals[1,2] including a low entropy of fusion, 4.5 e.u. This low entropy of fusion indicates a considerable degree of orientational disorder within the crystal lattice. What might be considered as the " missing heat of fusion " shows up at a lower temperature as an energetic solid-solid transition. There is some temptation to classify DNPTB-III as a highly viscous liquid or glass. However, this is not correct because it has a very sharp melting point and crystallizes rapidly, even when the temperature is only about 0.2 °C below the melting point.

DNPTB is particularly interesting because its molecular shape is very different from nearly all of the other substances which produce plastic crystals. These substances have a high degree of spherical symmetry which allows for some degree of molecular " rotation ", within the crystal lattice. As far as we have been able to determine, DNPTB-III is the most unusual plastic crystalline substance reported to date by virtue of its non-spherical symmetry and high molecular weight. Preliminary studies of several other compounds closely related to DNPTB indicate that some of them have crystalline properties similar to those of DNPTB.

Experimental Details

DNPTB was purified by crystallization from chloroform-hexane. A high degree of purity was indicated by its very sharp melting point and chemical analyses by the method developed by Glover[3] for trinitromethyl compounds. The synthesis of DNPTB has been described by Hill.[4]

DNPTB-II was prepared by allowing the material to remain in contact with 1 : 1 chloroform-hexane for at least one week at room temperature. After removal of the solvent, the solid was air dried at room temperature. Form I was prepared by an analogous procedure using 1 : 1 chloroform-hexane at 0 °C.

The polymorphs are identified easily by their X-ray powder diffraction patterns. The form III pattern contains only three lines with interplanar spacings of 5.58 Å, 5.25 Å and 4.95 Å. A quick identification can be carried out with a Geiger counter spectrometer using copper radiation by scanning slowly from 16° to 17°. Form II produces a strong line at 16.3°, form I at 16.6° and form III at 16.9°.

Temperature measurements on the microscope hot stage were made with a # 30 iron–constantan thermocouple along with an ice point reference junction. Equilibrium temperatures were obtained at a heating rate below 0.2 °C per minute. Purified reference compounds melted within about 0.1 °C of reported values.

The differential scanning calorimeter was operated at a heating rate of 2.5 °C per minute.

DNPTB is a high energy compound and should be handled with care. It shows excellent thermal stability and can be held in the liquid state near its melting point for two or three days without significant decomposition.

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