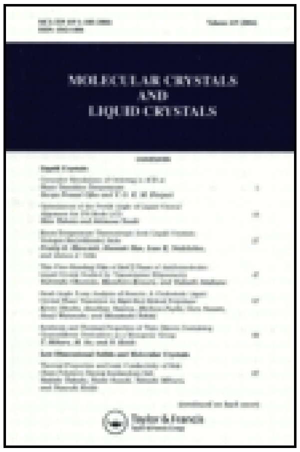

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: Jerome M. Rosen , James R. Holden & Herbert T. Simmons Sr. (1969): Heats of Transition and Fusion of Nitroalkane Alcohols and Related Nitroalkanes, Molecular Crystals, 6:2, 205-210

To link to this article: http://dx.doi.org/10.1080/15421406908082959

Molecular Crystals and Liquid Crystals, 1969, Vol. 6, pp. 205–210

Printed in Great Britain

Heats of Transition and Fusion of Nitroalkane Alcohols and Related Nitroalkanes

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Received April 18, 1969; *in revised form May* 23, 1969

Abstract—2,2,2-Trinitroethanol, 2,2-dinitropropanol and 2,2-dinitropropanediol-1,3 undergo enantiotropic transitions at 39.3°C, 9.1°C and 68.0°C, respectively. All of the high temperature forms (II) are cubic and possess properties of the plastic crystalline state. A differential scanning calorimeter was used to measure the heats of transition: 2,2,2-trinitroethanol, 4.3 kcal/mole; 2,2-dinitropropanol, 3.6 kcal/mole; and 2,2-dinitropropanediol-1,3, 5.1 kcal/mole. The difference between the heat of transition of each nitroalcohol and its corresponding nitroalkane has been interpreted as a measure of hydrogen bonding energy in the low temperature form (I) of the alcohol. Hydrogen bonding energies (kcal/mole) of 2,2,2-trinitroethanol-I, 2,2-dinitropropanol-I and 2,2-dinitropropanediol-1,3-I are 3.2, 0.8 and 2.3, respectively. The heats of fusion of 2,2,2-trinitroethanol and 2,2-dinitropropanol also were obtained.

Introduction

In a previous study, some of the crystalline properties of 1,1,1-trinitroethane and hexanitroethane were reported.[1] Both undergo enantiotropic transitions, and both high temperature forms possess properties which indicate molecular rotation in the crystal lattice. Because of their similarity to 1,1,1-trinitroethane in molecular structure and symmetry, we chose to investigate the related solids, 2,2,2-trinitroethanol, 2,2-dinitropropanol and 2,2-dinitropropanediol-1,3. Comparisons of the characteristics of solid nitroalkane alcohols with the corresponding nitroalkanes appeared worthwhile, because of the possibility of obtaining a measure of hydrogen bonding energies.

Results and Discussion

As had been suspected, 2,2,2-trinitroethanol, 2,2-dinitropropanol and 2,2-dinitropropanediol-1,3 also undergo enantiotropic transitions, i.e., they are characterized by a reversible solid–solid change at a fixed temperature. The high temperature forms (II) are cubic while the low temperature forms (I) are anisotropic. Observations were made with a polarizing microscope[2] using a hot-stage or a cold-stage. Transition temperatures and melting points are given in Table 1.

Table 1 Transition Temperatures

Compound	Melting Point, °C	Transition Temperature, °C	Form II
2,2,2-Trinitroethanol	71.5–72.0	I→II, 39.3	Cubic
2,2-Dinitropropanol	93.0–94.0	I→II, 9.1 II→I, 7.9	Cubic
2,2-Dinitropropanediol-1,3	decomp. before melting ~142	I→II, 68.0	Cubic
1,1,1-Trinitroethane[1]	54.2	I→II, 38.5	Anisotropic
2,2-Dinitropropane	54.2	I→II, −3.9 II→I, −4.8	Cubic

When 2,2,2-trinitroethanol is heated above its solid–solid transition temperature and then cooled to room temperature, it remains as metastable form II for at least 24 hours. However, the 2,2-dinitropropanol solid–solid transition is reversible with relatively little temperature lag, (see Table 1). The 2,2-dinitropropanediol-1,3 solid–solid transition is also reversible. On cooling, there is about a 2°C lag before the II → I change begins, but there is no real tendency for form II to presist in the metastable temperature range. Our measurement of the 2,2-dinitropropane solid–solid transition temperature is in good agreement with the literature value: I → II, $-5.0°C$; II → I, $-7.0°C$.[3]

A differential scanning calorimeter was used to measure heats of transition and fusion. These data are assembled in Table II along with the calculated entropies of transition and fusion. The small entropies of fusion of 2,2,2-trinitroethanol and 2,2-dinitropropanol as well as the large heats of transition of these compounds and 2,2-dinitropropanediol-1,3 are evidence of the plastic crystalline nature of the high temperature forms.[4] The abrupt change in the crystal lattice at the I → II transition is entirely consistent with previously observed relationships between molecular symmetry and polymorphism.[3,5]

A low entropy of fusion indicates molecular freedom within the crystal lattice, and a crystal structure study of cubic 2,2-dinitropropane did indicate a high degree of orientational disorder.[6] Thus the results of the crystal structure study are consistent with its low entropy of fusion, 1.98 e.u. We would expect 2,2,2-trinitroethanol-II and 2,2-dinitropropanol-II to exhibit the same degree of orientational disorder as 2,2-dinitropropane-II because of their low entropies of fusion, Table 2. 2,2-Dinitropropanediol-1,3 is too unstable at the melting point to measure its heat of fusion. However, other similarities lead us to believe that its Form II lattice is equivalent to those of 2,2,2-trinitroethanol-II and 2,2-dinitropropanol-II.

TABLE 2 Heats and Entropies of Transition and Fusion

Compound	Heat of Transition, kcal/mole	Entropy of Transition, e.u.	Heat of Fusion, kcal/mole	Entropy of Fusion, e.u.
2,2,2-Trinitroethanol	4.3	13.8	0.65	1.88
2,2-Dinitropropanol	3.6	12.8	0.68	1.86
2,2-Dinitropropanediol-1,3	5.1	15.0	—	—
1,1,1-Trinitroethane[1]	1.1	3.5	2.8	8.5
2,2-Dinitropropane	2.8	10.4	0.647[1]	1.98

2,2,2-Trinitroethanol has a larger heat of transition than 1,1,1-trinitroethane. The difference between these two values, 3.2 kcal/mole, is a measure of hydrogen bonding. If indeed there is hydrogen bonding in 2,2,2-trinitroethanol-I, we would expect none in 2,2,2-trinitroethanol-II by virtue of its low entropy of fusion. Whatever structural change takes place in 1,1,1-trinitroethane at the solid–solid transition point, hydrogen bonding is not involved. It thus seems reasonable to consider the difference between the heats of transition of 2,2,2-trinitroethanol and 1,1,1-trinitroethane as a measure of hydrogen bonding energy in 2,2,2-trinitroethanol-I.

The heat of transition of 2,2-dinitropropane is 0.8 kcal less than that of 2,2-dinitropropanol. As in 2,2,2-trinitroethanol, this difference in heats of transition is interpreted as the hydrogen bonding energy in 2,2-dinitropropanol-I. The heat of transition of 2,2-dinitropropanediol-1,3 is 2.3 kcal/mole greater than that of 2,2-dinitropropane. In this latter example, there are two OH groups available for hydrogen bonding.

In a study of nitroalcohols, Ungnade and Kissinger[7] have presented evidence for hydrogen bonding in solid 2,2-dinitropropanediol-1,3, based on infrared spectral measurements. They did not observe hydrogen bonding in 2,2-dinitropropanol but this now can be explained. Their measurements were made on the high temperature polymorph. Had they examined solid 2,2-dinitropropanol below the solid–solid transition temperature, 9°C, they probably would have found evidence of hydrogen bonding.

Ungnade and Kissinger also did not find hydrogen bonding in 2,2,2-trinitroethanol. This is somewhat surprising as the low temperature form is stable at room temperature. It is quite likely that the KBr pellet containing the sample reached a temperature above the transition point (39.3°C). Thus, they would have been measuring the spectrum of form II.

Molecules containing the OH group are well recognized as forming hydrogen bonds.[8] The hydrogen atom is strongly bonded to the oxygen atom and to a lesser extent an adjacent oxygen atom of another molecule. Schematically, this is represented as:

$$\overset{-}{\mathrm{O}}—\overset{+}{\mathrm{H}}\,-\,-\,-\,\overset{-}{\mathrm{O}},$$

where oxygen is slightly electronegative and hydrogen electropositive. The electropositive hydrogen is capable of interacting with electronegative oxygen of an adjacent molecule. In solid nitroalcohols, one would expect a three-dimensional intermolecular network of hydrogen bonds. In the nitroalkanes, the carbon atom is a rather poor donor so that hydrogen atoms are not available to interact with any atom of an adjacent molecule. The subject of hydrogen bonding in solids is very well covered in a recent book by Hamilton and Ibers.[8]

We feel that infrared absorption spectra of these solid nitroalcohols recorded just below and just above the transition temperature would reveal OH band shifts. This would substantiate our premise that hydrogen bonding is present in the low but not in the high temperature forms.

Experimental Details

All of the compounds were purified in the final stage by sublimation under reduced pressure of about 0.5 torr. The products were collected on a cold finger cooled with tap water. During the sublimation process, 2,2,2-trinitroethanol was heated at about 40°C while 2,2-dinitropropanol and 2,2-dinitropropanediol-1,3 were both heated at about 60°C. Because 2,2-dinitropropanol proved difficult to purify, it was sublimed three times. Products obtained from the sublimation process were believed equal or better in purity than the best corresponding compounds reported in the literature.[7,9,10].

The microscope-hot-stage was used as previously described.[1] A Thomas–McCrone micro-cold-stage was used[11,12] along with a #30 iron–constantan thermocouple. The thermocouple junction rested on the sample which was placed between two #1 cover glasses. The measured melting points of purified benzene and *n*-dodecane were within 0.2°C of their reported values. Equilibrium temperatures on the cold-stage were measured at heating and cooling rates of about 0.2°C per minute.

The differential scanning calorimeter was operated at a heating rate of 2.5°C per minute. All of the samples were hermetically sealed to prevent sublimation. When this instrument was used in the low temperature range, the sample was cooled at least 30 minutes to allow complete conversion to the low temperature form. Purified indium, *n*-dotriacontane and 2,2-dinitropropane were used for calibration purposes. Calibration values obtained from the known heats of fusion of the three substances varied less than 1%.

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