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# The order–disorder transitions in some organic crystals [☆]

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**Abstract**

The order–disorder and glass formation processes occurring in some solid organic compounds with cage structures and in some solid halogen-ethanes have been studied by low-temperature calorimetry. The thermodynamic data have been used together with the results of other physicochemical experiments to interpret the molecular processes which occur during the phase transformation.

*Keywords:* Crystal; Glass; Halogen; Phase transitions

## 1. Introduction

Many organic substances form several crystalline phases which can be distinguished by thermal or other physicochemical methods. Attempts have been made to classify the phase transitions occurring in solid organic substances. The thermodynamic approach of Ehrenfest [1] forms a theoretical basis for the classification, and some transitions have been successfully classified by this method. However, many real solid-state transitions cannot be described by the Ehrenfest theory, especially if they occur over a range of temperatures. Because of difficulties arising in the theoretical classification of solid-state transitions, McCullough proposed a phenomenological approach, according to which seven types of transitions could be distinguished by examination of $C_S$–$T$ curves in the transition region [2]. But even these seven types do not embrace all the range of transformations occurring in organic substances. Furthermore, this empirical classification does not apply to the processes taking place in the substance during the phase transformation.

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[☆] Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

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The variety of solid-state transitions generally depends on the diversity of the molecular and intramolecular motions in a molecular crystal lattice. Therefore, the understanding of the processes occurring during these transformations requires a thorough experimental study of the low- and high-temperature phases, including calorimeteric measurements, investigation of crystal structure, infrared, Raman, and nuclear magnetic resonance spectra, dielectric properties, etc.

Many solid-state transitions in organic crystals have been successfully interpreted in terms of the order–disorder concept [3, 4]. Thermodynamic data are especially valuable in the interpretation of order–disorder transitions, because for such processes the entropy of transition, $\Delta S_{trs}$, will be be nearly equal to $R \ln (N_2/N_1)$, where $N_2$ and $N_1$ are the numbers of states of disorder in the two phases; the problem is mainly to find a reasonable set of states of disorder. This approach has been widely used by Westrum and McCullough [3] in the examination of orientational and conformational disorder in some molecular crystals.

The order–disorder concept has been used in numerous studies of plastic crystals. These crystalline substances are most often composed of almost spherical (so-called "globular") molecules and have very specific properties, e.g. unusually high mobility, one or several transitions in the solid state, etc. [5, 6]. The transitions in plastic crystals are often treated in terms of orientational disordering of globular-shaped molecules at lattice sites, or "rotation", although it is not actually a free rotation but a motion against a potential barrier which causes reorientations, with rather high frequency, from one preferred orientation to another [3]; we shall use the term "rotation" in this sense hereafter. These orientationally disordered crystals have a low entropy of fusion, usually less than 20 J $K^{-1}$ $mol^{-1}$ [6]. Many plastic crystals formed by highly symmetrical cage molecules, such as bicyclo [2, 2, 2]octane, adamantane, and others, have been studied by Westrum and coworkers by means of low-temperature calorimetry [7–9].

Orientational disorder about one of the molecular axes has sometimes been observed instead of isotropic disorder. Compounds with one axis of symmetry, e.g. long-chain compounds, are especially prone to this axial "rotation" [4]. The entropy of fusion of these compounds is significantly higher than $\Delta S_{fus}$ of plastic crystals where isotropic rotation dominates. The ratio $\Delta S_{trs}/\Delta S_{fus}$ varies mostly from 2 to 6 for plastic crystals, whereas for axially disordered crystals it is usually less than 1.

A common feature of many transitions in organic crystals is a slow thermal equilibrium between co-existing phases. If equilibrium is not achieved, it often leads to the formation of metastable phases which can exist in a wide temperature range. The metastable phases are mostly formed on undercooling of liquid or as result of a high-temperature solid modification below the fusion or transition temperature. If the range of existence of the metastable phase stretches to 0 K, it is possible to calculate its residual entropy from heat capacity measurements, and to use this value to characterize this non-equilibrium system.

Studies of metastable phases are numerious, for example, the many papers of Seki, Suga and their co-workers. In particular, Adashi, Suga and Seki studied the freezing process and orientational disorder in cyclohexanol by low-temperature calorimetry and dielectric loss measurements [10, 11]. They found that crystal **I**, being a typical plastic crystal, can easily be undercooled below its normal transition temperature of 265.5 K. The residual entropy of undercooled crystal **I** differed substantially from zero. A heat capacity jump, typical for a glass transition, was observed on the $C_S$–$T$ curve of undercooled crystal **I**. Taking into account these facts, the authors [10, 11] proposed a new term "glassy crystal" for this frozen-in disordered state. The term "glassy crystal" was later extended to stable crystal phases exhibiting glass transitions and frozen disorder, regardless of its nature [11, 12]. It was found recently that, at low temperatures, fullerene $C_{60}$ forms a glassy crystal in which orientational disorder is frozen [13, 14]. A review of the slow relaxation processes in glassy crystals has recently been published by Suga [15].

In the present article, the results of studies of some order–disorder transitions in solid organic substances are described, mainly reviewing the research carried out in the Thermochemistry Laboratory of the Moscow State University. Most attention has been paid to studies of orientational and conformational disorder. Substances with globular-shaped or other highly symmetrical molecules were used for the study of orientational disordering. Conformational transitions have been studied using substances with $CX_2Y$–$CX_2Y$ or related formulae. These two groups are discussed separately, although transformations of both types have often been observed in real materials.

## 2. Results and discussion

### 2.1. *Phase transitions in molecular crystals composed of highly symmetrical molecules*

The following groups of organic compounds are considered below: (a) derivatives of bicyclo [2, 2, 1]heptane (norbornane); (b) perfluorinated tertiary amines; and (c) bicyclic perfluorocarbons. All of them are inclined to solid–solid transitions accompanied by orientational disordering.

### 2.1.1. *Derivatives of bicyclo[2, 2, 1]heptane*

The heat capacities of four norbornane derivatives: *exo*-2-cyanobicyclo[2, 2, 1]heptane [**I**], *endo*-2-cyanobicyclo[2, 2, 1]heptane [**II**], *exo*-2-methylbicyclo[2, 2, 1]heptane [**III**] and *endo*-2-methylbicyclo[2, 2, 1]heptane [**IV**] were measured in the range 12–350 K in a vacuum adiabatic calorimeter [16–18]. The heat capacity of unsubstituted bicyclo[2, 2, 1]heptane was previously measured by Guthrie and McCullough [19]. They discovered two non-isothermal transitions at 131.5 and 305.8 K, with entropies of transitions of 31.5 and 0.25 J K$^{-1}$ mol$^{-1}$, respectively. In the range from 131.5 K to the melting temperature (359 K), bicyclo[2, 2, 1]heptane formed a plastic crystalline phase.

A study of the two steric forms of each derivative of bicyclo[2, 2, 1]heptane made it possible to trace the influence of their structure and chemical nature on the ability to form plastic crystals and on the thermodynamic properties of the solids. Metastable glassy phases were formed by both exo-isomers (**I** and **III**) on rapid cooling of the liquids. Their transformations to stable crystalline phases occurred at about 177 K (**I**) and 127 K (**III**) and were accompanied by considerable heat evolution. Below these crystallization temperatures, the heat capacity of the metastable phases was measured up to 0 K, and over the whole range of their existence it was substantially higher than heat capacity of the stable phases.

Enantiotropic phase transitions were found in the stable phases **I**, **II** and **IV**. The enthalpies and entropies of the transitions are presented in Table 1. Very small fusion entropies indicate that the high-temperature phases of these three substances (crystal **I**) have a plastic crystalline character.

Unlike these substances, *exo*-2-methylbicyclo[2, 2, 1]heptane [**III**] did not reveal any peaks typical of transitions on the $C_S$–$T$ curve up to the melting point, 164.1 ± 0.1 K. However, taking into account the extremely slow thermal equilibrium near $T_m$, it is expected that this substance also undergoes a solid-phase transition at a temperature very close to $T_m$. Parsonage and Stavely mentioned that the transition to plastic crystal in ethane was only 0.5 K below the triple point [4]. They also stated that ethane almost certainly has the plastic crystalline phase with the shortest known range of existence at ordinary pressures. Perhaps the transition and melting processes in **III** were not separated because of the proximity of $T_{trs}$ to $T_m$. If so, *exo*-2-methylbicyclo[2, 2, 1]heptane apparently has an even shorter range of existence in the plastic crystalline phase than ethane.

It is obvious that the substituents in the bicyclic compound influence the symmetry of the molecules and increase the potential barriers of their motion. This influence also depends on the steric disposition of the substituents. Qualitatively, it is displayed in the increasing temperatures of the disordering transitions in **I**–**IV** ($T_{trs}$ in Table 1) compared to $T_{trs}$ of unsubstituted bicyclo[2, 2, 1]heptane (131.5 K). It can also be seen that the $T_{trs}$ of the exo-isomers are higher than those of the corresponding endo-isomers; in other words, the potential barriers of rotation for exo-isomers are higher than for endo-isomers. Therefore, considering rotational transition as a co-operative phenomenon, co-operation between molecules of exo-isomers should be greater than co-operation between molecules of the corresponding endo-isomers. This co-operative character of rotation should obviously stimulate destruction of the crystal lattice.

Table 1
Thermodynamics of solid-phase transitions and fusion of exo- and endo-isomers of 2-cyanobicyclo[2,2,1]-heptane and of 2-methylbicyclo[2,2,1]heptane (**I**–**IV**)

| Thermodynamic functions | **I** | **II** | **III** | **IV** |
|---|---|---|---|---|
| $T_{trs}$/K | 237.7 ± 0.1 | 177.3 ± 0.1 | (164.1 ± 0.1) | 152.4 ± 0.1 |
| $\Delta H_{trs}$/J mol$^{-1}$ | 7845 ± 46 | 2251.8 ± 2.9 | – | 4707 ± 3 |
| $\Delta S_{trs}$/J K mol$^{-1}$ | 33.3 | 12.7 | – | 30.9 |
| $T_m$/K | 300.27 ± 0.04 | 331.67 ± 0.02 | 164.1 ± 0.1 | 278.25 ± 0.09 |
| $\Delta H_{fus}$/J mol$^{-1}$ | 2943.0 ± 7.5 | 2961.0 ± 13.4 | 8380 ± 150[a] | 1559.1 ± 14.2 |
| $\Delta S_{fus}$/J K$^{-1}$ mol$^{-1}$ | 9.8 | 8.9 | – | 5.8 |
| $\Sigma(\Delta S_{trs} + \Delta S_{fus})$ J K$^{-1}$ mol$^{-1}$ | 43.1 | 21.6 | 51.1 | 36.7 |

[a] Sum of the transition and fusion enthalpies.

Indeed, one can see from a comparison of the melting temperatures (Table 1) that the $T_m$ values of both exo-isomers are lower than those of the endo-isomers of the same substances. The melting temperature of bicyclo[2, 2, 1]heptane (359 K) is substantially higher than the $T_m$ of its derivatives. Thus, the range of existence of a plastic crystalline phase is about 220 K in bicyclo[2, 2, 1]heptane, about 130–150 K in its endo-positioned cyano- and methyl-derivatives, and 60 K in *exo*-2-cyanobicyclo[2, 2, 1]heptane. For *exo*-2-methylbicyclo[2, 2, 1]heptane, the range of existence of the plastic crystals was not determined because of the proximity of the transition and melting temperatures. Perhaps the same steric factors are also responsible for the formation of metastable glassy phases on rapid cooling of **I** and **III**.

The entropies of fusion of the exo- and endo-cyanoderivatives of bicyclo[2, 2, 1]heptane are close to $R$ (Table 1). These values are rather small and suggest a high degree of orientational disorder, when the molecule has a rotational entropy in the plastic crystal that is almost as large as in the liquid, and the entropy of melting is close to the communal entropy [20]. The $\Delta S^0_{fus}$ value of *endo*-2-methyl[2, 2, 1]bicycloheptane is even smaller than $R$. This may indicate that, in addition to the orientational disorder, there is some positional disorder of the centres of gravity of its molecules below the melting point.

### 2.1.2. *Perfluorinated tertiary amines*

The heat capacities of two tertiary aliphatic amines: perfluorotriethylamine (**V**) and perfluoromethyldiethylamine (**VI**) have been measured in the range 6–300 K [21, 22]. On rapid cooling of the liquids, both formed metastable phases which spontaneously became stable at the same temperature of 126.0 ± 0.5 K, with heat evolution. Enantiotropic transition occurred in the stable phase of **V** at 146.4 ± 0.2 K, $\Delta S_{trs} = 10.7 \pm 0.7$ J K$^{-1}$ mol$^{-1}$. The melting point of the high-temperature modification was equal to 156.38 ± 0.03 K, so that its range of existence was only 10 K and for this reason its heat capacity was obviously influenced by pre-transition effects (Fig. 1). No heat capacity anomalies were detected in the stable phase of **VI**.

The heat capacity of both metastable phases was utterly reproducible and independent of cooling rate; typical glass transitions were found at $T_g = 108.5 \pm 0.5$ K (**V**) and 102.4 ± 0.2 K (**VI**). Above $T_g$, the heat capacity lies on the extension of $C_S$–$T$ curves of liquids up to 126.0 K, see, for example Fig. 1. Obviously, the metastable phases of **V** and **VI** are glassy liquids which crystallize at 126.0 ± 0.5 K. This is also confirmed by study of the dielectric constants below $T_m$. Typically for glasses [23], only minor and continuous changes were revealed in $C/C_0$ values obtained with falling temperatures in the metastable phases of **V** and **VI** up to $T_g$, see, for example, Fig. 2.

Studies of thermodynamic and dielectric properties as well as IR and Raman spectra were used to describe the enantiotropic phase transition in **V**. The spectroscopic studies lead to the conclusion that one highly symmetrical conformation prevails in liquid perfluorotriethylamine, although the presence of a non-symmetrical conformation was also detected. Thus, the liquid **V** is obviously an equilibrium mixture of two conformations with a symmetrical form predominating [21].

The bands of the non-symmetrical conformation disappeared during crystallization, and then the IR spectra changed neither on cooling nor at the transition of crystal **I** to crystal **II**. Thus this transition is not associated with the transformation of conformers.

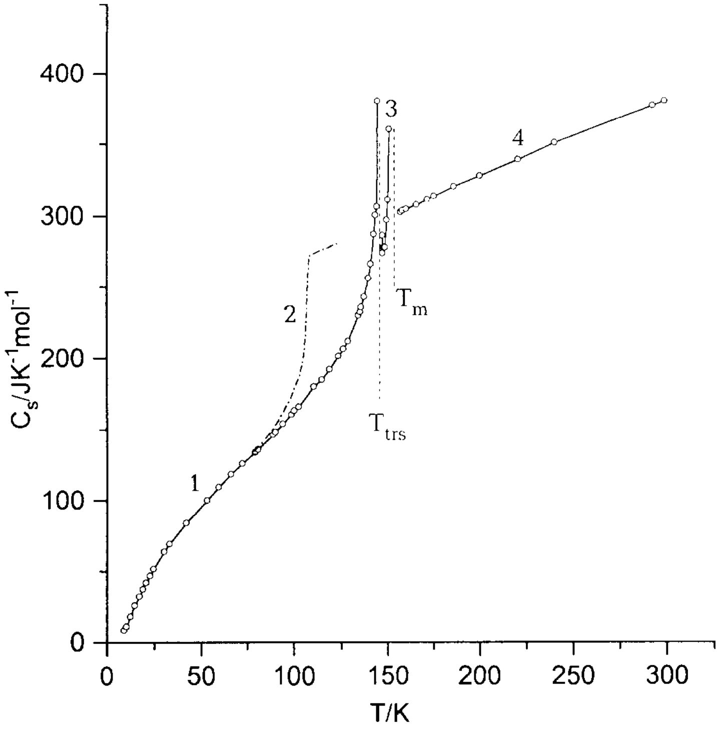

Fig. 1. Heat capacity and phase transitions of $(C_2F_5)_3N$: 1, crystal II; 2, metastable phase (glassy liquid); 3, crystal I; 4, liquid.

For the temperature dependence of the dielectric constant of V, one can see in Fig. 2 that the $C/C_0$ value does not change substantially at $T_{trs}$ and increases sharply only at the melting temperature, when the isotropic rotation begins. Thus, there is no indication of isotropic rotation in the crystal or, in other words, of formation of a plastic crystalline phase at $T_{trs}$. The fusion entropy of perfluorotriethylamine is 35.22 J K$^{-1}$ mol$^{-1}$, significantly greater than $\Delta S^0_{fus}$ of plastic crystals. The relatively small entropy of transition, $10.7 \pm 0.7$ J K$^{-1}$ mol$^{-1}$, is also unusal for plastic crystals. It is worth noting that the ratio $S_{trs}/S_{fus}$ for V is less than 1, which is usual for crystals with axial rotation (see above).

Taking into account all these facts, it can be assumed that at the transition temperature, axial rotation of $(C_2F_5)_3N$ molecules begins about the axis of the pyramid formed by the three C–N bonds. This assumption agrees with the symmetry of the stable conformer of V. It does not contradict the study of dielectric constants, because rotation of polar molecules about a dipole axis should not increase significantly the dielectric constant. Perhaps it is not accidental that the transition entropy, 10.7 J K$^{-1}$ mol$^{-1}$, is approximately equal to $R \ln 3 = 9.13$ J K$^{-1}$ mol$^{-1}$. The absence of phase transitions in crystalline $(C_2F_5)_2NCF_3$ can easily be explained on the basis of this assumption that its molecules hinder axial rotation because of low symmetry.

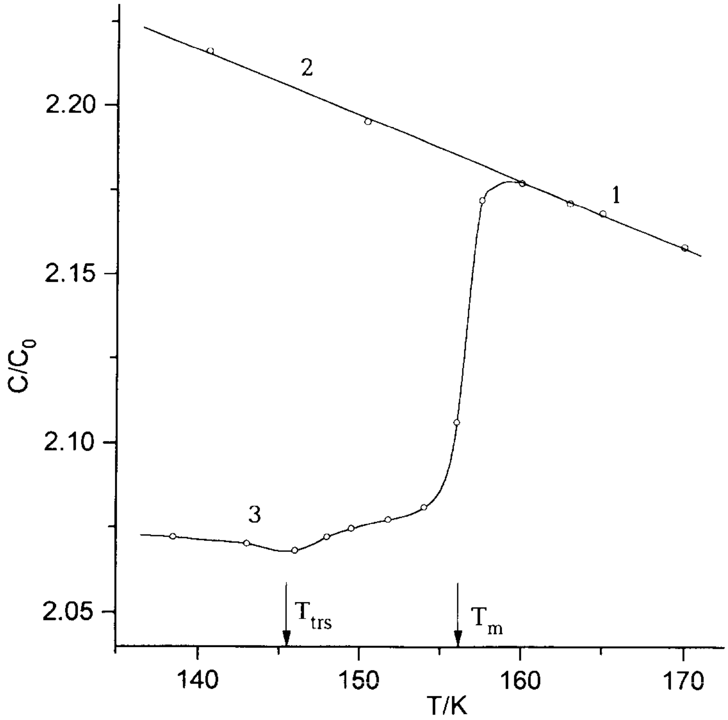

Fig. 2. Temperature dependence of the dielectric constant of $(C_2F_5)_3N$ at a frequency of 1 kHz: 1, liquid; 2, glassy liquid; 3, crystalline phases.

### 2.1.3. *Bicyclic perfluorocarbons*

The heat capacities of perfluorobicyclo[4,4,0]decene-1,6 (**VII**), *cis*-perfluorodecalin (**VIII**) and *trans*-perfluorodecalin (**IX**) have been measured in the range 6–300 K [24, 25]. Solid–solid phase transitions were discovered in **VII** and **VIII**; no thermal anomalies have been found in the $C_S$–$T$ curve of solid **IX**. No glass formation has been detected in the solid phases of these three substances. Unfortunately, no experimental studies of the different crystalline phases of these substances have been accomplished by methods other than calorimetry. Therefore, the interpretation of the phase behaviour of these organic crystals given below is based only on thermodynamic data and is tentative.

Two phase transitions occur in solid perfluorobicyclo[4,4,0]decene-1,6, $C_{10}F_{16}$: crystal **III** → crystal **II** at 200.0 ± 0.2 K, and crystal **II** → crystal **I** at 233.4 ± 0.2 K, with transition entropies of $3.77 \pm 0.15$ and $4.78 \pm 0.11$ J $K^{-1}$ $mol^{-1}$ respectively. The planar molecule $C_{10}F_{16}$ is rather rigid due to the presence of the double bond; therefore there is no reason to connect the transitions with conformational disorder. The isotropic rotation and formation of the plastic crystalline phase is also barely possible, taking into account the rather small sum of the transition entropies, 8.55 J $K^{-1}$ $mol^{-1}$, and the rather large entropy of melting, $39.66 \pm 0.12$ J $K^{-1}$ $mol^{-1}$. It is reasonable to suppose on the grounds of molecular geometry that one of these transitions is associated with the onset of rotation of the $C_{10}F_{16}$ molecule about the axis perpendicular to the plane of the ring. The possibility of this type of disordering of planar molecules in the crystalline phase has been discussed by Wong and Westrum [26]. However, one or two of these transitions can be attributed to a slight change in lattice structure. Such changes are not infrequently accompained by a small transition entropy value. There is no sharp difference between the heat capacity of the low- and high-temperature phases at both transition temperatures [24], which is also usual for slight changes in lattice structure as well as for onset of axial rotation.

The entropy of enantiotropic transition discovered in *cis*-perfluorodecalin at 266.70 ± 0.02 K is equal to 18.24 ± 0.06 J $K^{-1}$ $mol^{-1}$. A rather large transition entropy value indicates a fairly high degree of disorder in crystal **I**. This conclusion has also been confirmed by the considerable jump in heat capacity ($\Delta C_S = 10$ J $K^{-1}$ $mol^{-1}$) at the temperature of transition of crystal **II** to crystal **I**. Therefore, it is difficult to attribute the transition to only the axial rotation of *cis*-$C_{10}F_{18}$ molecules. However, the large melting entropy, 38.63 ± 0.04 J $K^{-1}$ $mol^{-1}$, excludes isotropic rotation and formation of a plastic crystalline phase. Transformation of the isomers or ring conversion are also not possible in solid *cis*-perfluorodecalin because of the high potential barriers of these processes. Thus the origin of this transition remains unexplained. Perhaps it can be attributed to molecular motion which is intermediate between axial and isotropic rotation. A lack of phase transitions in solid *trans*-perfluorodecalin is an example of how sensitive the molecular behaviour in organic crystals is to the shape of the molecules.

Potential barriers to molecular reorientation in the crystalline phase depend not only on the geometry of the molecules, but also, to a high degree, on molecular interactions. McCullough et al. [27] found a phase transition in solid *cis*-decalin at 216 K with an entropy value of $\Delta S^0_{trs} = 9.22$ J $K^{-1}$ $mol^{-1}$, which is half that of $\Delta S^0_{trs}$ in *cis*-perfluorodecalin. The phase transition in *cis*-$C_{10}H_{18}$ can presumably be interpreted as being associated with the onset of axial rotation of the *cis*-$C_{10}H_{18}$ molecules. The greater entropy of transition of *cis*-$C_{10}F_{18}$ confirms the greater disorder of its crystal **I** compared with crystal **I** of *cis*-$C_{10}H_{18}$ and, consequently, the greater mobility of its molecules. The range of existence of crystal **I** in *cis*-$C_{10}F_{18}$, 34 K, is much greater than that of crystal **I** in *cis*-$C_{10}F_{18}$, 14 K. The fusion entropy of *cis*-$C_{10}F_{18}$, 38.63 J $K^{-1}$ $mol^{-1}$, however, is slightly smaller than that of *cis*-$C_{10}H_{18}$, 42.21 J $K^{-1}$ $mol^{-1}$. These facts also testify to a greater disorder of crystal **I** of the perfluorocompound, as compared with its hydrogen analogue (see also a comparison of the phase transitions in halogen-ethanes with those in their H-analogues, below).

### 2.2. *Halogen derivatives of ethane*

Molecular crystals of ethane-halogen derivatives were expected to have order–disorder transitions involving orientational and conformational disorder. Orientational disorder was possible for most of these compounds in view of their molecular geometry. Conformational disorder attributed to trans–gauche transformations is quite usual for compounds of general formula $CX_2Y$–$CX_2Y$ or related compounds.

Therefore, both types of disordering should be taken into account in the interpretation of phase transitions occurring in halogenated ethanes. Five halogen derivatives of ethane have been studied by low-temperature calorimetry: 1,2-difluoro-1,1,2,2-tetrachloroethane (**X**), 1,1,2,2-tetrafluoro-1,2-dichloroethane (**XI**), 1,1,2-trifluoro-1,2,2-trichloroethane (**XII**), 1,1,2,2-tetrafluoro-1,2-dibromoethane (**XIII**), and 1,1,2,2-tetrachloroethane (**XIV**) [28–31].

A glass-like transition was found in **X** at about 90 K, with a sharp jump in heat capacity $\Delta C_S = 54.4$ J $K^{-1}$ $mol^{-1}$ (Fig. 3). The small entropy of fusion, $\Delta S^0_{fus} = 12.34 \pm 0.04$ J $K^{-1}$ $mol^{-1}$, and the small difference between the heat capacities of the solid and liquid phases at the temperature of fusion indicate a high degree of disorder in the solid, which is characteristic of plastic crystals. The X-ray diffractogram obtained at 10°C by Fogel [28] showed that this phase had a lattice of cubic symmetry. A study of X-ray diffraction patterns carried out later by Kishimoto et al. indicated a body-centred cubic unit cell for this crystal [32]. In addition to a low entropy of fusion and a high symmetry of its crystal lattice, 1,1 difluoro-1,1,2,2-tetrachloroethane also has some other characteristics of plastic crystals: high viscosity, transparency and high vapour pressure. All these features indicate that below its melting point of 299.70 ± 0.03 K, $CFCl_2CFCl_2$ forms a typical plastic crystal. Thus, the glass transition discovered

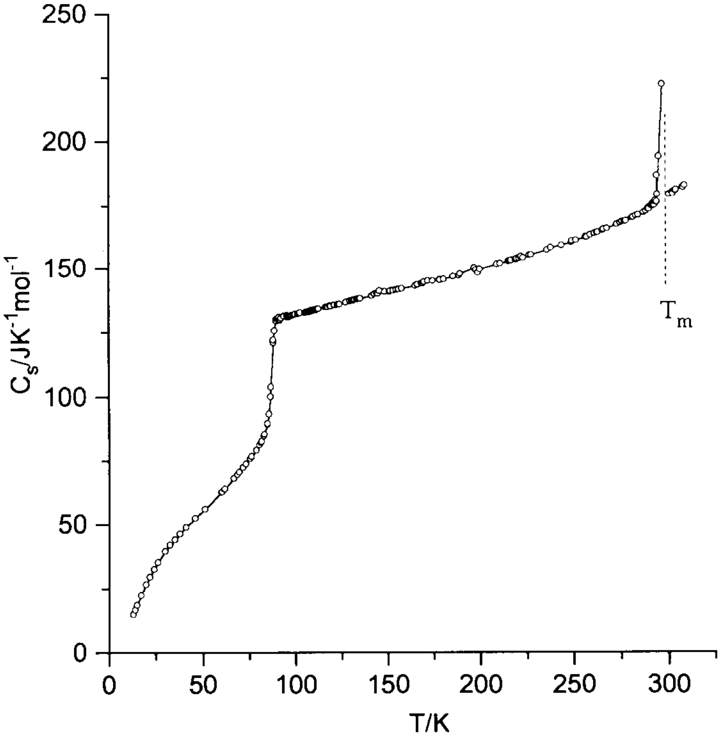

Fig. 3. Heat capacity and glass transition of $CFCl_2CFCl_2$.

near 90 K is obviously associated with the freezing of orientational degrees of freedom of the plastic crystalline phase and below the glass transition point, $CFCl_2CFCl_2$ becomes a glassy crystal.

Usually, plastic crystals undergo one or more solid-state transitions to a more ordered phase with rather high changes in enthalpy and entropy. But no such transitions in solid $CFCl_2CFCl_2$ were found [28], although some attempt were made to obtain a more ordered and more stable crystalline phase, (a) by variation of the cooling rate, and (b) by exposing the crystal near the melting point. After prolonged exposition of the sample just below $T_m$ and slow cooling (the procedure was carried out repeatedly), the heat capacity of $CFCl_2CFCl_2$ in the range from 108 to 187 K was 0.7–2.5% lower than the average $C_S$–$T$ curve. A small quantity of stable phase was probably obtained during this procedure. Another anomaly found in the course of the heat capacity measurement was a slow thermal equilibrium and abnormal discrepancy of results (up to 0.37%) in the range 90–230 K. Above 230 K, no relaxation effects were found and the reproducibility of the results was normal for a solid phase with no transitions. Therefore, it was concluded [28] that, above 230 K, the plastic crystalline phase of $CFCl_2CFCl_2$ is definitely stable. In a region somewhere below 230 K, very slow ordering processes begin, and the range of existence of the undercooled plastic crystal lies below this region up to the glass transition point.

The temperature of the ordering transition in $CFCl_2CFCl_2$ was later defined more precisely by Kishimoto et al. They investigated the unusual behaviour of this substance in the solid state and carried out a thorough calorimetric study of its transition phenomena [32]. The essential features of their results were in agreement with those obtained before [28]: they confirmed the existence of a plastic crystalline phase below $T_m$ and its transition into a glassy crystalline state at around 90 K. The Japanese authors also made thorough attempts to obtain a stable phase with ordered molecular orientations. They cooled the sample to 13 K and then annealed it in the range 77–160 K for 50 days. The heat capacity of the annealed sample revealed a sharp peak at 170 K which was obviously the temperature of transition of the plastic crystalline phase into the ordered phase. The percentage of plastic crystalline phase transformed into ordered phase by this procedure was estimated to be about 2–3%; thus only traces of low-temperature phase were formed, even following a very long annealing. Obviously, an extremely long equilibrium time is required for the phase transformation [32].

It was shown in studies of the IR, Raman and NMR spectra of crystalline $CFCl_2CFCl_2$ that in the temperature range 77–85 K, its molecules exist in two forms: gauche and trans [33–35]. The transformation of plastic crystal into an ordered phase should be attributed to rearrangement of the molecules to the most stable conformer (more likely the trans-conformer). Kishimoto et al. [32] believed that the reason for the extremely slow phase transition into an ordered phase was the slow rate of the trans–gauche conversion resulting from steric hindrance of the bulky halogen atoms in this highly halogenated ethane.

Two solid–solid enantiotropic phase transitions were found in $CF_2ClCF_2Cl$ (**XI**) at temperatures of $109.3 \pm 0.2$ K and $134.6 \pm 0.1$ K, with entropies of transition of $11.1 \pm 0.1$ and $19.52 \pm 0.04$ J $K^{-1}$ $mol^{-1}$, respectively (Fig. 4) [29]. Study of the IR absorption spectra of the three crystalline phases of **XI** revealed that crystals **I** and **II**

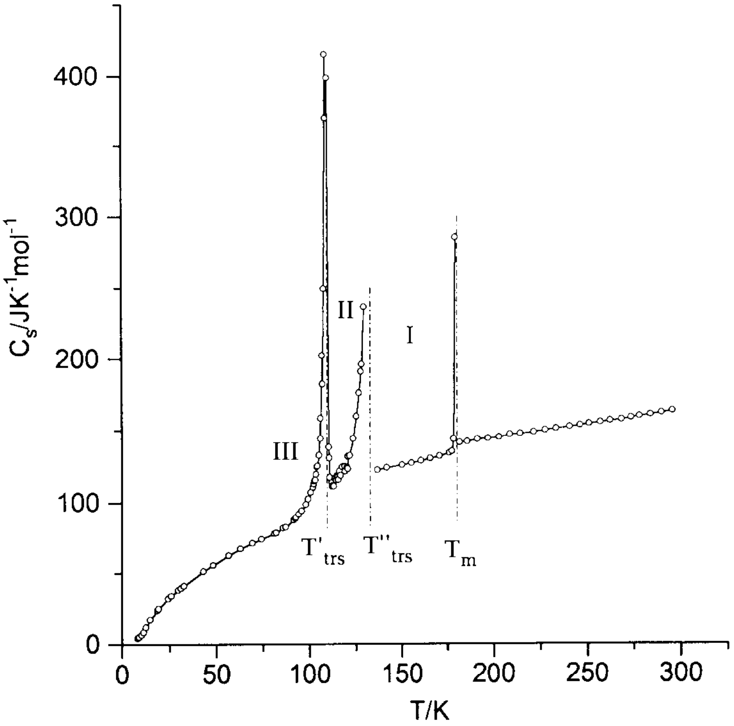

Fig. 4. Heat capacity and phase transitions of $CF_2ClCF_2Cl$.

exist as mixtures of trans- and gauche-conformers. Taking into account the small entropy of fusion, 8.37 ± 0.04 J K$^{-1}$ mol$^{-1}$, and the small difference in $C_S$ values of liquid and crystalline $CF_2ClCF_2Cl$ at $T_m$, it is reasonable to assume that crystal **I** is highly disordered. Probably, molecular rotation in the lattice sites was started and the plastic crystalline phase was formed at the crystal II-to-crystal I transition temperature.

The IR spectrum of crystal **III** was significantly different from the spectrum of crystal **II** and it was evident that only one trans-conformer remains in crystal **III**. This conclusion was in agreement with data of Kagarise [36] who studied IR absorption spectra of $CF_2ClCF_2Cl$ and discovered only the trans-conformer in the solid state at 103 K, i.e. in the existence range of crystal **III**. Thus, the crystal III-to-crystal II transition at 109.3 K is obviously associated with the onset of internal rotation in $CF_2ClCF_2Cl$ molecules and with the appearance of the gauche-conformer. Perhaps, this conformational disorder alone created the necessary preconditions for the onset of orientational disordering at 134.6 K.

Only one enantiotropic phase transition was discovered at 82.5 ± 0.5 K in the measurement of the heat capacity of $CF_2ClCFCl_2$ (**XII**) in the range from 6 to 300 K (Fig. 5), the entropy of transition being 10.1 ± 0.2 J K$^{-1}$ mol$^{-1}$ [29].

The entropy of fusion was 10.42 ± 0.04 J K$^{-1}$ mol$^{-1}$, and the difference between the $C_S$ values of liquid $CF_2ClCFCl_2$ and crystal **I** at $T_m$ was also rather small (Fig. 5). It

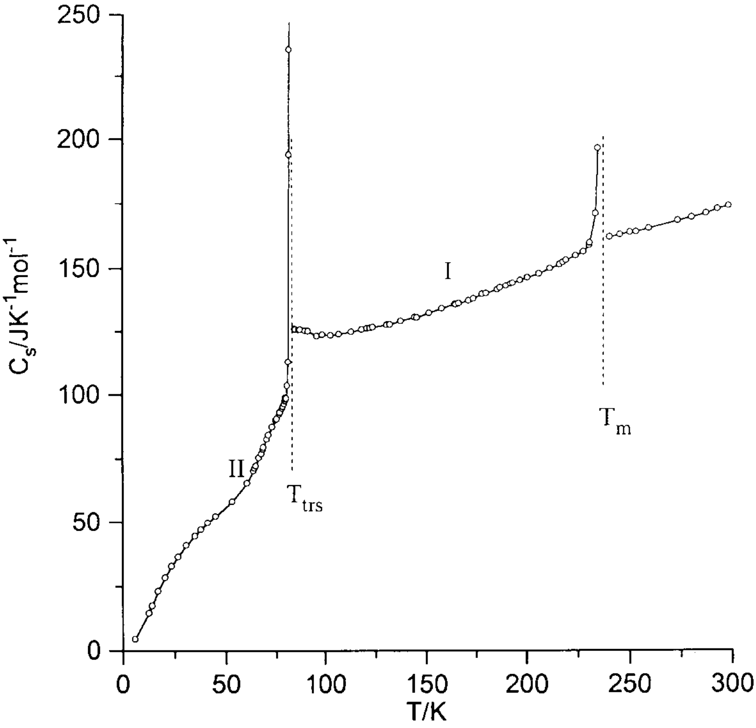

Fig. 5. Heat capacity and phase transitions of $CF_2ClCFCl_2$.

seems obvious that below the temperature of melting, $CF_2ClCFCl_2$ forms a plastic crystalline phase. The high viscosity and high vapour pressure of this substance are also characteristics of plastic crystals.

The high-temperature modification of **XII** (crystal **I**) was easily undercooled on rapid cooling through the transition region. A glass-like transition (not shown in Fig. 5) was found on the $C_S$–$T$ curve of this metastable phase. Obviously, at $T_g$ the undercooled plastic crystal undergoes transition to glassy crystalline phase with frozen-in molecular orientations. The temperature of this transition (about 70 K) and the heat capacity of the metastable phase depended on the cooling rate of crystal **I**, or in other words, on the content of residual non-transformed crystal **I**. Spontaneous transformation of metastable phase into crystal **II** occurred with significant heat evolution at a temperature which varied from 74 to 78 K and also which depended on the previous thermal treatment. To obtain stable crystal **II** without any residue of crystal **I**, it was necessary to cool the sample gradually to the liquid nitrogen temperature and then to expose it in the pre-transition region, at 3–4 K below $T_{trs}$, for 10–14 h.

Hallam and Ray [37], by studying the IR spectra of $CF_2ClCFCl_2$ in the temperature interval from 173 to 353 K, found that in the solid and liquid states this substance comprises a mixture of trans- and gauche-conformers. Unfortunately the IR spectrum of crystal **II** was not studied. Thus the nature of the crystal II-to-crystal I transition remains unexplained. Perhaps it is due to crystal lattice rebuilding.

For $CF_2ClCFCl_2$, $\Delta S_{trs} + \Delta S_{fus} = 20.5$ J $K^{-1}$ $mol^{-1}$, whereas the sum of the transition and fusion entropies is usually about 42–50 J $K^{-1}$ $mol^{-1}$ for organic crystals. It is reasonable to assume that crystal **II** has a significant residual entropy. Indeed, the difference between the calorimetric entropy, calculated for the gaseous state at 198.15 K and 101.325 kPa, and the spectroscopic entropy, obtained by Higgins and Lielmers [38], equals 10.1 J $K^{-1}$ $mol^{-1}$ and represents the residual entropy of crystal **II** [29]. The mixture of trans- and gauche-conformers existing in crystal **I** was probably frozen at low temperature. The maximum entropy change caused by disorder of this type, $R \ln 3 = 9.1$ J $K^{-1}$ $mol^{-1}$, is rather close to the obtained value of $S_0$.

In contrast to the three fluorochloroethanes described in this section, no peaks corresponding to solid–solid phase transitions have been found on the $C_S$–$T$ curve of 1,1,2,2-tetrafluorodibromoethane up to the melting point, 162.83 ± 0.02 K. An abnormal growth of heat capacity, which began at rather low temperatures and could not be explained only by the presence of impurities, was the only peculiarity on the $C_S$–$T$ curve. The $T_i$–$1/F_i$ dependence studied in the course of fractional melting was also represented by a very unusual curve [30]. These facts could be explained if, for example, some endothermic processes occurred in the solid substance far below the melting point.

Usually, order–disorder processes take place in a narrow temperature interval and can be discovered through the presence of sharp anomalies, e.g. peaks on the $C_S$–$T$ curve. However, gradually developing processes of disordering not accompanied by sharp heat capacity anomalies are also possible [4]. To explain the unusual phenomena discovered during heat capacity measurement, the IR spectra of solid $CF_2BrCF_2Br$ were obtained in the temperature range from 90 K to $T_m$ [30]. Only bands of the trans-conformer were discovered in the range 90–133 K, in agreement with the data in Refs. [33, 39]. At temperatures higher than 133 K, bands of the gauche-conformer appeared in the IR spectrum. This phase, comprising a mixture of trans- and gauche-conformers, existed up to the melting temperature. Bands of gauche-conformer have also been revealed in the Raman spectrum in the range from 148 K to $T_m$, parallel with the trans-conformer bands. The bands of the gauche-conformer disappeared on cooling in both the IR and Raman spectra, indicating an equilibrium of the process. Thus the unusual heat capacity growth and unusual appearance of the $T_i$ versus $1/F_i$ graph can obviously be attributed to the gradual transformation of trans-conformer into gauche-conformer. This compound represents one of very few examples of gradual disordering not accompained by sharp heat capacity anomalies.

Unlike other halogen-ethanes described above, 1,1,2,2-tetrachloroethane forms two crystalline modifications, **1** and **2**, which undergo $\lambda$-type transitions with $C_S$ maxima at 207.3 and 204.8 K (Fig. 6) and with entropies of transition of 2.62 ± 0.36 and 1.74 ± 0.29 J $K^{-1}$ $mol^{-1}$ respectively [31]. The existence of two polymorphic modifications of $CHCl_2CHCl_2$ was also stated before by Brasch [40]. Modification **1** was reported in Ref. [31] as being obtained by prolonged annealing of the sample in the pre-melting region. The temperatures and entropies of melting also differed noticeably for these modifications: 230.5 ± 0.1 K and 39.79 ± 0.12 J $K^{-1}$ $mol^{-1}$ for **1** and 229.2 ± 0.3 K and 41.54 ± 0.38 J $K^{-1}$ $mol^{-1}$ for **2**. The rather small entropies of transition, large entropies

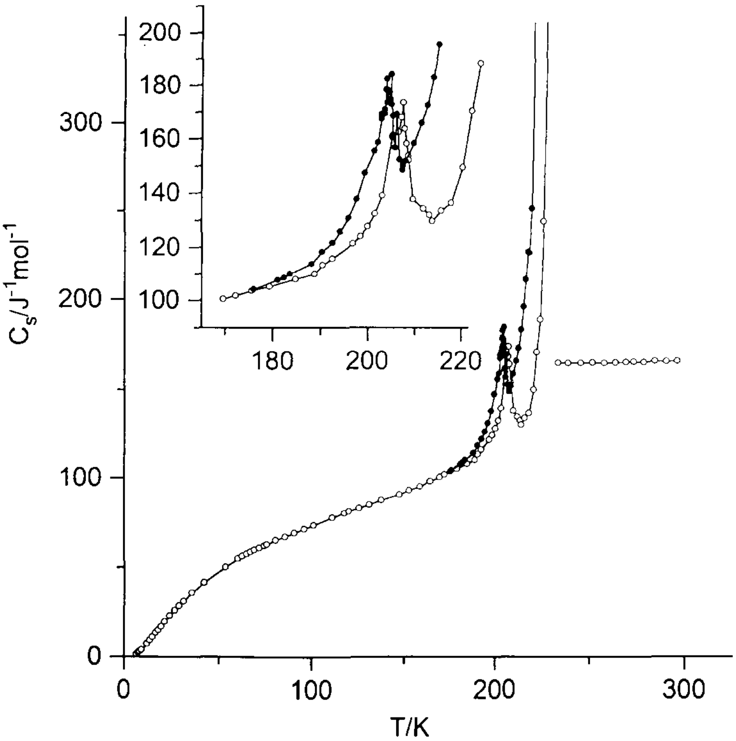

Fig. 6. Heat capacity and phase transitions of $CHCl_2CHCl_2$: ○, modification 1 and liquid; ●, modification 2.

of melting, and the significant difference in the $C_S$ of liquid and crystalline $CHCl_2CHCl_2$ at $T_m$ indicate that the high-temperature phases of both modifications are rather ordered and definitely not plastic crystals. A study of IR spectra in the range from 90 K to $T_m$ revealed only the gauche-conformer throughout this interval in both modifications. So, the nature of the $\lambda$-transition in $CHCl_2CHCl_2$ remains unexplained. It is obvious, however, that this transition is not attributable to either orientational or conformational disordering.

A comparison of the properties of molecular crystals formed by the fluoroderivatives of ethane and their parent hydrogen-containing compounds made it possible to observe the influence of H- to F-substitution on the molecular mobility. It was shown above that $(CF_2Cl)_2$, $(CFCl_2)_2$ and $CF_2ClCFCl_2$ formed plastic crystalline phases composed of equilibrium mixtures of trans- and gauche-conformers. A conformational mobility was also discovered in crystalline $(CF_2Br)_2$. Meanwhile, only gauche-conformer was detected in solid $(CHCl_2)_2$, and also only one conformer (trans or gauche) was revealed in solids $(CH_2Cl)_2$, $(CH_2Br)_2$ and $CH_2ClCHCl_2$ [40, 41]. No isotropic rotation of molecules or plastic crystals were discovered in these four H-analogues of fluoroderivatives. Only in crystalline $(CH_2Cl)_2$ and $(CH_2Br)_2$ was an axial rotation about the Cl... Cl and Br... Br axes observed [42, 43].

Table 2
Boiling points, enthalpies of vaporization at 298.15 K, and surface tension of some halogenated ethanes

| Compound | $T_b$/K | $\Delta H^0_{vap}$/kJ mol$^{-1}$ | $\sigma$(at 30°C)/N m$^{-1}$ |
|---|---|---|---|
| $(CHCl_2)_2$ | 420.15 [44] | 38.49 ± 0.29 [44] | 34.4 [45] |
| $(CFCl_2)_2$ | 360.02 [46] | 30.8 ± 0.4 [46] | 23 [47] |
| $CHCl_2CH_2Cl$ | 362.82 [44] | 33.0 ± 0.4 [44] | 32.24 [45] |
| $CFCl_2CF_2Cl$ | 320.77 [46] | 26.8 ± 0.4 [46] | 18.1 [47] |
| $(CH_2Cl)_2$ | 356.53 [44] | 32.2 ± 0.2 [44] | 30.8 [45] |
| $(CF_2Cl)_2$ | 277.15 [44] | 23.4 [44] | 12–13 [47] |
| $(CH_2Br)_2$ | 404.85 [44] | 41.8 ± 0.4 [44] | – |
| $(CF_2Br)_2$ | 319.65 [44] | 28.4 ± 0.8 [44] | – |

Thus, it is obvious that substitution of hydrogen atoms by fluorine in this series of halogen derivatives of ethane increases the possibility of intramolecular and intermolecular motion. The increasing molecular mobility in fluoroderivatives can probably be attributed to a weakening of molecular attraction due to the absence of hydrogen bonds in completely halogenated ethanes and to the intense decrease in dipole–dipole and quadripole–quadripole interactions. Substitution of H atoms by F atoms in this series of compounds also causes a change in some physicochemical properties of the liquids which correlates with the change in molecular mobility in the solids. For example, normal boiling temperatures, enthalpies of vaporization and surface tension of the compounds under consideration are listed in Table 2. One can see from this table that in all cases the $T_b$, $\Delta H^0_{vap}$ and $\sigma$ values of fluoroderivatives are significantly lower than these values for their parent H compounds. The analogous increase in molecular mobility in crystalline *cis*-perfluorodecalin as compared with *cis*-decalin was mentioned above.

## 3. Conclusions

The study of the phase transitions occurring in some compounds with cage structures and in some halogenated ethanes has emphasized the importance of thermodynamic data based on calorimetric measurements in the interpretation of the phase behaviour of these solid substances. Attempts at this interpretation also demonstrated that, in most cases, using other physicochemical methods in addition to calorimetry can supply the necessary data for a complete understanding of the processes occurring during phase transformations.

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