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Orientational Disorder in Simple Benzene Derivatives: Glass Transition of Crystalline Pentachloronitrobenzene

Many simple derivatives of benzene form orientationally disordered crystals at room temperature. In contrast to expectation based on the third law of thermodynamics, however, ordering phase transitions are scarcely detected in them. This fact probably leaded to the suggestion "rigid disorder" by A. I. Kitaigorodsky. *p*-Chloronitrobenzene (PCNB) is a compound assumed to be an example by him. Recently, we proved that the orientational disorder in crystalline PCNB is not "rigid" but dynamical in nature through detecting a glass transition arising from freezing of the orientational disorder [*J. Chem. Phys.*, **112,** 2355 (2000)]. Another example, *p*-bromochlorobenzene (PBCB), did not show any anomaly in heat capacity attributable to a glass transition [*Bull. Chem. Soc. Jpn.*, **73,** 2279 (2000)]. The residual entropy was compatible with the freezing of the head-to-tail disorder reported in structural studies. The absence of a glass transition implies that the orientational disorder in crystalline PBCB may be "rigid". It is noted that no concrete evidence of molecular reorientation existed before starting calorimetric investigation on them. At this stage, therefore, it seems meaningful to study the compound for which a reliable result is available concerning molecular reorientation.

Pentachloronitrobenzene (5CNB) satisfies the requirement. Crystalline 5CNB shows a large dielectric dispersion due to molecular reorientation. The temperature and frequency to observe this dielectric dispersion are in suitable ranges where no special instruments are necessary. Indeed, this compound is used as a test sample of student experiment (on molecular dynamics in solids) in Tokyo Metropolitan University (Department of Chemistry). The molecular orientation is highly disordered in crystal at room temperature. The site symmetry of the 5CNB molecule is reported to be C_3 with an

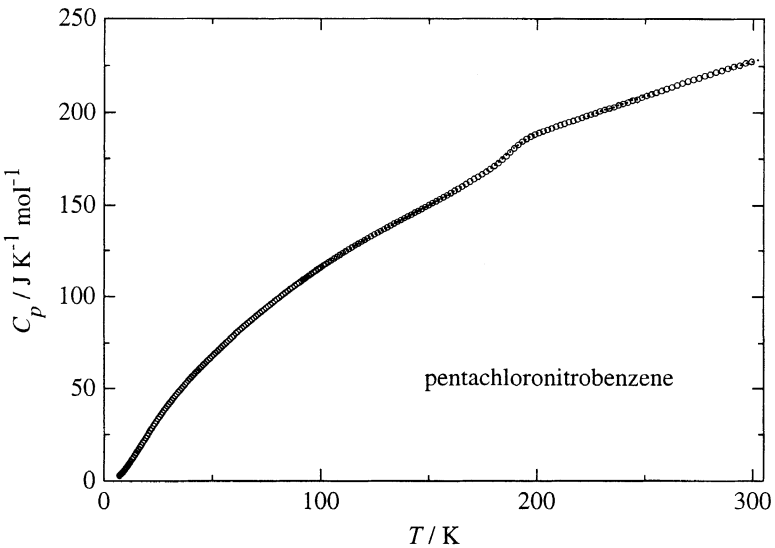

Fig. 1. Measured molar heat capacities of pentachloronitrobenzene.

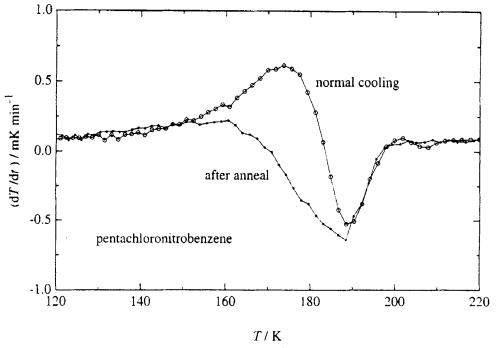

Fig. 2. Drifts in equilibration periods in normal series and that after anealing.

apparent molecular symmetry of C_{3h}, which requires two relative orientation of the nitro group with effectively the same probability. On cooling crystalline 5CNB, thus, many combinations between ordering phase transition(s) and freezing glass transition(s) may be imagined according to the presence of two disordered degrees of freedom.

The measured heat capacities are shown in Fig. 1. There is a large step in the heat capacity around 185 K. Considering the disordered crystal structure, it is natural to attribute this step anomaly to a glass transition arising from the structural freezing. To confirm this assignment, the temperature drifts in a normal measurement and a measurement after annealing at 170 K for 13 h are compared in Fig. 2. The temperature dependence and the effect of the annealing are fully consistent with the assignment of the step to a glass transition. The extrapolation of the temperature dependence of the relaxation time determined in the dielectric measurement [A. Aihara, et al. *Bull. Chem. Soc. Jpn.*, **43,** 3750 (1970)] yields the relaxation time of about 7000 s at the observed glass transition temperature. It is therefore concluded that the observed glass transition arises from the freezing of the reorientation of whole molecule. No anomaly assignable to the ordering and/or freezing of reorientation of nitro group was detected. This is rationalized if we assume one of the followings: Freezing takes place also at 185 K concerning the orientational disorder of the nitro group, or reorientational motion of the nitro groups survives down to low temperatures.

Presentation

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The orientational disorder and reorientational motion at room temperature in crystalline 5CNB results in the presence of the glass transition in contrast to PBCB. Different behaviors presented by PCNB, PBCB and 5CNB imply that the molecular dynamics is govered by the details of molecular and crystal structures and intermolecular interactions. The molecular structures mentioned here are certainly simple in compounds on the earth. The third law of thermodynamics, though it has a clear statistical-physical meaning, may be seemingly violated in most real compounds.

(Z.-C. Tan & K. Saito)