

Heat Capacity and Glass Transition of Crystalline Pentachloronitrobenzene[#]

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The heat capacity of crystalline pentachloronitrobenzene was measured by adiabatic calorimetry between 6 and 303 K. A large step in heat capacity was detected around 185 K; this is attributed to a glass transition corresponding to freezing of structural disorder. The observed glass transition temperature was similar to that estimated from the temperature dependence of the dielectric relaxation due to molecular reorientation around the "sixfold axis" of the benzene core.

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 few detected in them. This fact led to the concept of "rigid disorder" suggested by Kitaigorodsky.[1] *p*-Chloronitrobenzene (PCNB) is a compound assumed as an example by him. Recently, the present authors[2] proved that the orientational disorder in crystalline PCNB at room temperature is not "rigid" but dynamical in nature through the new finding of a glass transition arising from freezing of the orientational disorder. Another example, *p*-bromochlorobenzene (PBCB), did not show any anomaly in heat capacity attributable to a glass transition up to the temperature of fusion.[3] 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 the crystalline PBCB may be "rigid". It should be noted that no concrete evidence of molecular reorientation existed before starting calorimetric investigations on them. At this stage, therefore, it seems valuable to study compounds for which reliable results are available concerning molecular reorientation.

The title compound, pentachloronitrobenzene (5CNB), satisfies the requirement. The crystal belongs to a rhombohedral space group R3 with lattice constants $a = 8.751$ Å and $c = 11.111$ Å (hexagonal setting).[4] Molecules lie on threefold axes, which are normal to the benzene plane, namely, the site symmetry is C_3. Owing to the presence of this threefold axis, there is an orientational disorder at least around the axis. The molecule has, however, a seemingly higher symmetry C_{3h}, which was deduced from the distribution of diffraction intensities. This molecular symmetry requires two relative orientations of the nitro group with respect to the benzene ring having effectively the same probability.

Crystalline 5CNB shows a large dielectric relaxation due to molecular reorientation.[5] The temperature dependence of the relaxation frequency f was reported to obey

$$f = 1.58 \cdot 10^{15} \exp\,[-(8100\ \mathrm{K})/T]$$

in the frequency range between 30 Hz to 1 MHz. This dielectric relaxation was attributed to the molecular reorientation around the "sixfold" axis of the benzene core (a crystallographic threefold axis). By identifying the inverse of the relaxation frequency as being the reorientational relaxation time ($\tau = f^{-1}$) and by extrapolating the above temperature dependence to a much lower frequency (longer relaxation time), the glass transition temperature due to the freezing of this motional degree of freedom is predicted. It is generally accepted that a glass transition detected by adiabatic calorimetry corresponds to the relaxation time of $10^3 - 10^4$ s. According to the above formula, the expected temperature is calculated as 200 K for $\tau = 10^3$ s and as 183 K for $\tau = 10^4$ s.

Since there are two types of disorder in crystalline 5CNB, many combinations between ordering leading to phase transition(s) and freezing of disorder resulting in glass transition(s) can be imagined on cooling. In this paper, results of precise calorimetry on crystalline 5CNB are described.

Experimental

Commercially available pentachloronitrobenzene (Tokyo Chemical Industry) was purified by fractional sublimation in a vacuum around 337 K. The elemental analysis on the purified specimen gave C 24.58% (calcd 24.40%), N 4.85 (4.74), and Cl 60.28 (60.02).

The purified sample was loaded into a calorimeter vessel and sealed with a small amount of helium gas (10^5 Pa at room temperature) to promote thermal equilibration within the vessel. The mass of the sample loaded was 4.9391 g after buoyancy correction, which is equivalent to 1.6724×10^{-2} mol based on its molar mass of 295.335 g mol^{-1}. The sealed vessel was set in an adiabatic calorimeter described previously.[6] Heat capacity measurements were

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carried out in a temperature range between 6 and 303 K.

Thermometry was performed using the working thermometers attached to the vessel, which were platinum (Minco, S1055) and germanium (Lake-Shore Cryotronics, GR-200-500B) resistance thermometers. Their temperature scales are based upon the ITS-90.

Results and Discussion

Heat capacity measurements were performed in the range of 6–303 K in three series of runs. Series 1 was carried out up to 303 K after cooling down to 90 K. Since a manifestation of a glass transition had been encountered in series 1, the sample was annealed at 170 K for 13 hours. The calorimeter was then cooled down to 115 K and series 2 was conducted up to 303 K. Series 3 was performed in the range of 6–100 K. The sample contributed 73% at 10 K, 40% at 100 K, and 46% at 300 K to the total heat capacity, including contributions of the calorimeter vessel and helium gas.

All the data obtained in this study are shown in Fig. 1. The standard thermodynamic quantities are determined by smoothing out the primary data and integrating the resultant heat capacity curve. The contribution below the low temperature limit of the heat capacity data was estimated by smooth extrapolation of the heat capacity curve to satisfy the Debye law in the low temperature limit. The selected values of the standard

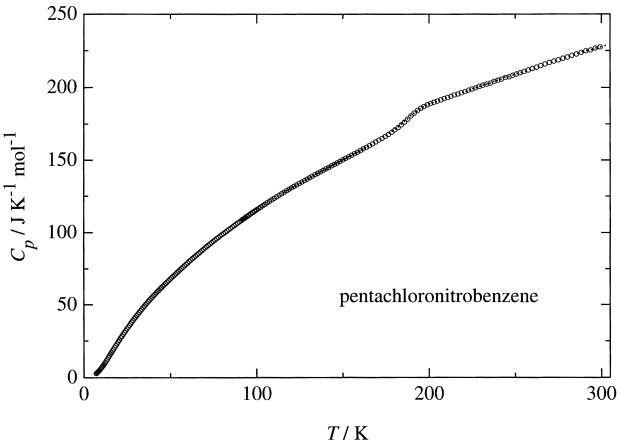

Fig. 1. Measured molar heat capacities of pentachloronitrobenzene.

Table 1. Standard Thermodynamic Quantities of Pentachloronitrobenzene

T	C_p°	$[H^\circ(T) - H^\circ(0)]/T$	$S^\circ(T) - S^\circ(0)$	$-[G^\circ(T) - H^\circ(0)]/T$[a)]
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}
10	6.47	1.94	2.44	0.50
20	24.61	8.62	12.31	3.69
30	41.67	16.88	25.62	8.74
40	55.83	24.90	39.60	14.70
50	67.98	32.33	53.39	21.07
60	79.00	39.20	66.78	27.58
70	89.19	45.62	79.73	34.11
80	98.65	51.67	92.26	40.60
90	107.47	57.38	104.40	47.02
100	115.72	62.81	116.15	53.35
110	123.43	67.97	127.55	59.58
120	130.64	72.90	138.60	65.70
130	137.41	77.60	149.33	71.73
140	143.90	82.11	159.75	77.64
150	150.20	86.44	169.89	83.46
160	156.47	90.62	179.79	89.17
170	163.17	94.68	189.47	94.78
180	170.82	98.70	199.01	100.31
190	181.10	102.76	208.51	105.75
200	188.59	106.88	218.01	111.13
210	192.74	110.88	227.32	116.44
220	196.89	114.69	236.38	121.69
230	201.01	118.35	245.22	126.87
240	204.99	121.88	253.86	131.98
250	208.95	125.29	262.31	137.03
260	212.96	128.58	270.58	142.00
270	216.89	131.78	278.70	146.92
280	220.64	134.89	286.65	151.77
290	224.31	137.91	294.46	156.55
300	227.71	140.85	302.12	161.28
298.15	227.16	140.31	300.72	160.41

a) This entry is $-[G^\circ(T) - H^\circ(0)]/T - S^\circ(0)$ in reality because $S^\circ(0)$ is non-vanishing due to the orientational disorder.

quantities are given in Table 1 at round temperatures.

As seen in Fig. 1, there is a large step in the heat capacity around 185 K. A portion of the step is magnified in Fig. 2. The step extends between 170 and 200 K. The magnitude of the step exceeds 15 J K^{-1} mol^{-1}. There is no appreciable difference between the data obtained in series 1 (open circle) and series 2 (closed circle). Considering the disordered crystal structure, it is natural to attribute this step anomaly to a glass transition arising from the structural freezing.

In order to confirm the anomaly around 185 K as a glass transition, the temperature drifts in a normal measurement and a measurement after annealing at 170 K for 13 h (series 2) are compared in Fig. 3. In a glass transition region, the temperature drift under nominal "adiabatic condition" shows a characteristic feature in adiabatic calorimetry.[7] The drifts shown here were determined by the least-squares fitting of the temperature readings between 7 and 12 min after the vessel heater was turned off. The drift in series 1 (cooling rate is ca. −1.3 K min^{-1} around 185 K) is stationary up to 150 K, shows an exothermic peak around 170 K, turns into decrease, shows an endothermic peak around 190 K, then returns to the stationary level around 200 K. On the other hand, the drift after annealing remains essentially stationary up to 160 K, and turns into a decrease, shows an endothermic peak around 190 K, and recovers the stationary level around 200 K. These trends are fully consistent with the expected behavior for the enthalpy relaxation phenomenon characteristic of a glass transition region.[7] The glass transition temperature T_g is determined as 185 K from the temperature where the drift in normal measurements (series 1 in reality) changes its sign from plus (exothermic) to minus (endothermic).

A comparison with the relaxation time determined in the dielectric measurement[5] gives an insight concerning the frozen-in degree(s) of freedom. The extrapolation of the temperature dependence of the relaxation time determined in the dielectric measurement yields the relaxation time of about 7000 s at the observed glass transition temperature, as shown in Fig. 4. On the other hand, it is generally accepted that the time scale of the adiabatic calorimetry of the present type is some thousands s. From this coincidence between these two quantities, it is very likely that the molecular reorientation as a whole is, at least, involved in the frozen-in degree(s) of freedom. This assignment suggests that for this compound a deviation from the so-called Arrhenius behavior is weak, i.e., the crystal of 5CNB above the glass transition is "strong"[8] if terminology from the scientific field of liquid-quenched glasses is adopted. It seems unnecessary to assume an ideal glass (phase) transition to exist in a strong "liquid", because the elongation of the relaxation

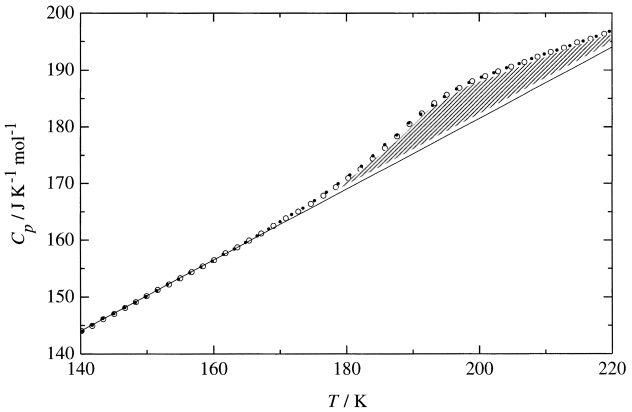

Fig. 2. Measured molar heat capacities of pentachloronitrobenzene in the vicinity of the glass transition. Open circle, data obtained after normal cooling; closed circle, data obtained after annealing at 170 K for 13 h and the successive cooling. A solid curve is an extrapolation of the heat capacity of the glassy state. As for the shaded area, see the text.

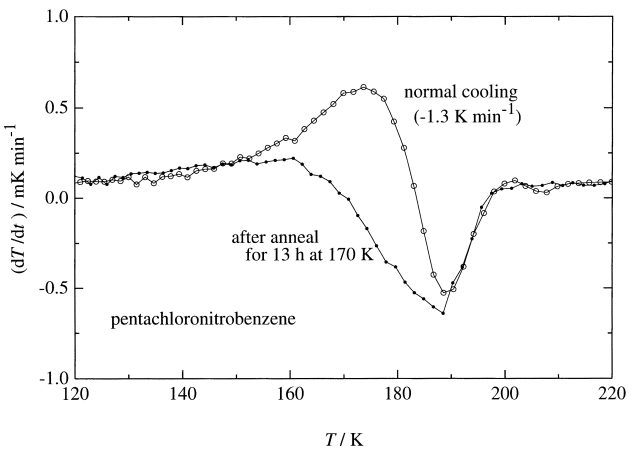

Fig. 3. Temperature drifts in two series of heat capacity measurements of pentachloronitrobezene. Open circle, data obtained after normal cooling; closed circle, data obtained after annealing at 170 K for 13 h and the successive cooling.

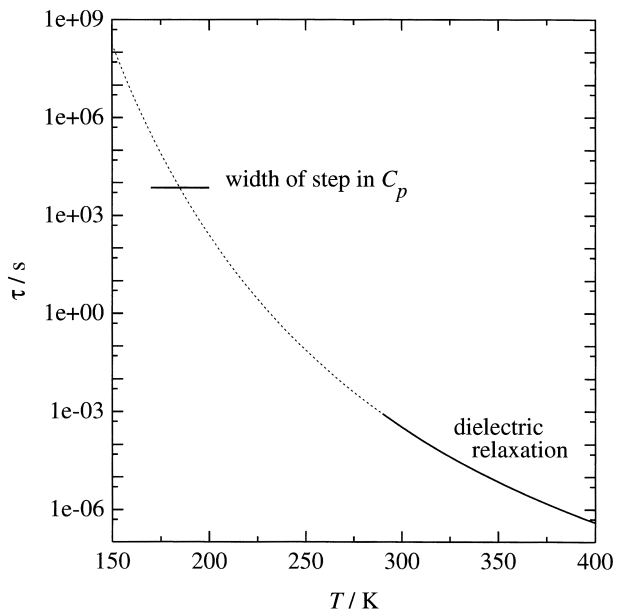

Fig. 4. Reorientational relaxation time of pentachloronitrobenzene. The relaxation time is shown by solid curve for the region covered by the dielectric study.[5] The extrapolation assuming an Arrhenius behavior is drawn by dotted line.

time with decreasing temperature alone can account for properties of its glass transition.

Now we try to analyze the magnitude of the jump in heat capacity at the glass transition. It is noted that the site symmetry (C_3) is compatible with any apparent molecular symmetries higher than it, e.g., C_{3v}, C_{3h}, C_6, D_6, and so on, which result in the numbers of equivalent orientations (around the "sixfold" axis of the benzene core) being 3, 3, 6, 6, etc. Here, however, we assume C_{3h} as a possible "molecular" symmetry considering the result of crystallographic study.[4] The heat capacity contributions of most intramolecular vibrations change only slightly upon molecular reorientation, because the intramolecular interaction is much stronger than intermolecular interaction. The consideration of energy states corresponding to molecular orientations is thus sufficient in the following.

There is a subtle point in analysis of the magnitude of the step in heat capacity for the present case. What state is correct or wrong is clear for the disorder in ordered phases, but it is unclear for cases of the disorder in disordered phases such as the present case. A simple scheme for the disorder in ordered phase is temporarily assumed here. According to the third-law of thermodynamics, the orientation of 5CNB molecules should be ordered in a crystal at absolute zero when the system is in thermodynamic equilibrium. This ordered state is assumed as a reference. In fact, this ordered state cannot be realized due to the freezing of the molecular reorientation at the glass transition. The molecules, however, feel their local environment, which is formed as a result of relative orientations of neighboring molecules. Then, one out of the three orientations equivalent at room temperature is selected as the lowest-energy orientation. The remaining two orientations are assumed to have equal higher energies. The crystal of 5CNB is approximated by the ensemble of two-level systems with the degeneracy ratio 1:2. The maximum heat capacity of this system is about 6.3 J K^{-1} mol^{-1}. This simple model, therefore, cannot account for a step in heat capacity as large as 15 J K^{-1} mol^{-1}. It is noted that even if a higher symmetry that allows 6 orientations is assumed the maximum heat capacity (12 J K^{-1} mol^{-1}) is still smaller than the observed.

In crystalline 5CNB there is another structural disorder, i.e., the orientation of the nitro group with respect to the benzene ring. The apparent molecular symmetry C_{3h} deduced in the crystallographic study[4] implies that two orientations of the nitro group have effectively equal probabilities at room temperature. Since this disorder does not contribute to the establishment of the space group symmetry, the disorder is classified as "the disorder in ordered phases" in the sense described above. The crystal is then approximated by an ensemble of simple two-level systems as far as only this degree of freedom is concerned. The maximum heat capacity of this system is about 3.6 J K^{-1} mol^{-1}.

If the two types of disorder accidentally afford the maximum heat capacities at the same temperature and if the glass transition temperature for both degrees of freedom is common, the magnitude of the step in heat capacity will amount to about 10 J K^{-1} mol^{-1}. This is still smaller than the observed step. Besides, the equal probability of two orientations of the nitro group at room temperature implies that the energy difference between the two is smaller than thermal energy at room temperature. Since the maximum heat capacity of this model appears around 0.4 times of the energy difference, the above possibility is ruled out. These difficulties seem to be easily removed by assuming the presence of an (unobservable) phase transition. If the intermolecular interaction tending to order the orientation exists, an ordering transition is expected to occur at some (low) temperature. In this case, the large step of heat capacity may be regarded as being a high-temperature tail of the thermal anomaly due to this virtual ordering transition. The expected entropy of transition is the sum of those for the orientational disorder of a molecule as a whole ($R\ln 3 \approx 9.1$ J K^{-1} mol^{-1}) and of the nitro group ($R\ln 2 \approx 5.8$ J K^{-1} mol^{-1}). Considering the entropy gain corresponding to the frozen-in degrees of freedom (ca. 4 J K^{-1} mol^{-1}), which is estimated by integration of the shadowed portion in Fig. 2 up to room temperature with respect to $\ln T$, the assumption of this unobservable phase transition is acceptable.

It is unnecessary to consider an accidental coincidence between the glass transition and the temperature of the maximum heat capacity in order to explain the magnitude of the step anomaly. No anomaly plausibly assigned to the ordering and/or freezing of reorientation of nitro group was detected in this study. There are two possibilities: One is the accidental coincidence of two glass transitions. The environment of the nitro groups governing the potential energy certainly depends on their orientation and orientational dynamics of neighboring molecules. The freezing of the molecular reorientational motion may bring some effects on orientational dynamics of the nitro groups. The other possibility is that the reorientational motion survives down to low temperatures because of its smallness. In this case, calorimetry at lower temperatures may detect tunneling effects.

Conclusion

Heat capacities of the disordered phase of the crystalline pentachloronitrobezene were precisely measured by adiabatic calorimetry between 6 and 303 K. The standard thermodynamic functions of the compound were established below 300 K. A glass transition around 185 K was clearly detected in the solid state of the compound. The location of the glass transition was compatible with the temperature dependence of the reorientational relaxation time deduced by dielectric study.

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