Thermodynamic Consideration on a Series of Compounds $(CH_3)_nCCl_{4-n}$: Correlation between Molecular Sphericity, Configurational Order/Disorder, and Molecular Packing in Plastically Crystalline and Liquid Phases

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Heat capacities of *tert*-butyl chloride and 2,2-dichloropropane were measured with adiabatic calorimeters in the temperature ranges between 13 and 300 K and between 6 and 300 K, respectively, and the standard thermodynamic functions were evaluated. In a series of compounds, $(CH_3)_nCCl_{4-n}$ ($n = 0-4$), the absolute entropy, after subtraction of the contribution due to the exchange between positions of the methyl group and chlorine atom within each molecule, showed its n dependence of a curve with a downward convex in both the plastically crystalline and liquid phases. The volume per molecule, as taken from literature data, showed its n dependence of a curve with a similar downward convex in both phases. These were interpreted to indicate that the positional and/or orientational short-range order of molecules develops with the increasing deviation of the molecular shape from spherical in both phases. Taking also into consideration the fact that the entropy of fusion decreased gradually as the shape of molecule deviated from a spherical one, it is indicated further that the development is more remarkable in the liquid phase without any long-range order than in the plastically crystalline phase with long-range positional order of molecules. It follows, from these considerations for nonspherical molecules, that provided a particular molecule is *fixed* in its orientation, the time-averaged orientational configuration of the surrounding molecules would not fulfill, at the lattice site of the particular molecule, the site symmetry expected from the space group of the plastically crystalline phase.

Introduction

The state of molecular aggregation is characterized by detail of the arrangement of molecules with respect to their positional and orientational degrees of freedom. The molecules in the liquid and complete crystal are recognized to be arranged in the disordered and ordered, respectively, ways concerning the two degrees of freedom. The plastically crystalline state is between the liquid and complete crystal: The molecules are fixed positionally with three-dimensional long-range order and are disordered over several energetically rather equivalent orientations. The plastically crystalline phase is thus generally realized in the systems of molecules having rather spherical shape and possesses one of highly symmetric crystallographic space groups such as a face-centered cubic lattice system. The fusion entropy of plastic crystals is usually considered to be small since the disordering proceeds only with respect to the positional degree of freedom of molecules, and Timmermans really characterized plastic crystals as giving an entropy of fusion smaller than 21 J K^{-1} mol^{-1}.[1,2] The entropy is comparable with the fusion entropy, 14 J K^{-1} mol^{-1}, of rare gas crystals. These considerations are based rather on the assumptions that liquid has completely disordered structure with respect to both the positional and orientational degrees of freedom of molecules and that each molecule in the plastically crystalline phase exhibits, irrespective of the orientations of neighboring molecules, the orientational disorder to fulfill the site symmetry expected from the symmetry of space group. It is not clear at the present time, however, to what extent the order/disorder with respect to the two degrees of freedom of molecules develops in real plastically crystalline and liquid states. It is known only that there exist no orientational *long-range* order in the former and neither orientational nor positional *long-range* order in the latter phase.

The thermodynamic properties have been studied so far for many compounds showing plastically crystalline phase.[3,4] To elucidate the detailed state of aggregation of the molecules, then it is attractive to examine the dependence of some physical quantities on the deviation of molecular shape from the sphere. Nakamura et al.[5] in fact examined the relation between the molecular shape and some thermodynamic quantities and pointed out that nonsphericity of the constituent molecules operates to diminish the value of the fusion entropy and to narrow the temperature range of the plastically crystalline phase. The pointing-out has been found to hold as well for a series of compounds of adamantane, 1-chloroadamantane, and 1-bromoadamantane.[6-9] As the substituent of the 1-position of adamantane becomes large in their van der Waals radii, the temperature range of the stable plastically crystalline phase becomes narrow and the fusion entropy decreases.

The reason this happens is intriguing in considering the configurational order/disorder of molecules in each phase and should be either of following: (a) in the plastically crystalline phase, the orientational short-range order of molecules is reduced and/or the partial positional disordering of molecules proceeds in nonspherical molecules; (b) in the liquid phase, the positional and/or orientational short-range order of molecules rather develops in nonspherical molecules. For example, Nakamura et al. discussed that a less symmetric molecule takes a greater,

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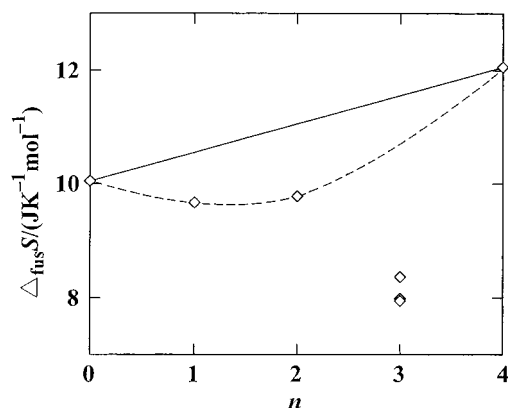
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Figure 1. n dependence of the entropies of fusion for a series of compounds $(CH_3)_nCCl_{4-n}$.

than a symmetric molecule, number of its orientations in order to fulfill the high crystallographic symmetry at the lattice site and possesses partial positional disordering concomitantly with the orientational disordering already in the plastically crystalline phase. This consideration is close to the former of the two reasonings. A series of compounds $(CH_3)_nCCl_{4-n}$ ($n = 0$, CCl_4; $n = 1$, CH_3CCl_3; $n = 2$, $(CH_3)_2CCl_2$; $n = 3$, $(CH_3)_3CCl$; $n = 4$, $(CH_3)_4C$), which all have a face-centered cubic unit cell in the plastically crystalline phase,[10−12] are interesting systems for gaining insight into the real reasoning. The heat capacities[13−20] have been hitherto measured in the temperature range between 3 and 300 K for compounds with $n = 0$, 1, and 4 and between 90 and 280 K for those with $n = 2$ and 3. Figure 1 shows the n dependence of the derived entropies of fusion. It is recognized that the entropies of fusion show dependence of a curve with a downward convex. In view of the fact that carbon tetrachloride and 2,2-dimethylpropane molecules, CCl_4 ($n = 0$) and $(CH_3)_4C$ ($n = 4$), are of rather higher symmetry than the others, this dependence is just the result expected above.

In the present study, we measure heat capacities of *tert*-butyl chloride $(CH_3)_3CCl$ ($n = 3$) and 2,2-dichloropropane $(CH_3)_2$-CCl_2 ($n = 2$) with adiabatic calorimeters in the temperature ranges between 6 and 300 K and between 13 and 300 K, respectively, and determine precise thermodynamic functions of these compounds. The aim is, based on the n dependence of the absolute entropies in the liquid and plastically crystalline phases, to investigate any essential feature concerning short-range order with respect to molecular positions and orientations as the molecular shape deviates from a sphere in the series of compounds $(CH_3)_nCCl_{4-n}$. The feature of the short-range order is also discussed on the basis of the n dependence of the volumes per molecule in each phase.

Experiment

Special-grade reagent *tert*-butyl chloride (Tokyo Chemical Industry Co., Ltd., Special-grade) was fractionally distilled under low pressure (3 kPa) at 315 K by means of a concentric rectifier having more than 30 theoretical plates. The mole-fraction purity of *tert*-butyl chloride thus refined was determined to be 0.9998 by gas chromatography (gc) and 0.9993 by an equilibrium fractional-melting method described below. 2,2-Dichloropropane (Aldrich Chemical Co., Inc., Special-grade) was subjected to essentially the same purification procedure. The mole-fraction purity was determined to be 0.9999 by gc and 0.9995 by an equilibrium fractional-melting method.

The sample was loaded into a calorimeter cell under an atmosphere of He gas and sealed with indium wire. The inner

volume of the cell was 19.696 cm^3, and the amounts of *tert*-butyl chloride and 2,2-dichloropropane used were 16.382 g ($\cong$0.149 01 mol) and 16.898 g ($\cong$0.161 85 mol), respectively. Heat capacities were measured by an intermittent heating method under adiabatic conditions:[21,22] The initial temperature, T_i, of the cell was determined by following the temperature for 15 min; then a known quantity of electrical energy, ΔE, was supplied into the cell, and the final temperature, T_f, of the cell was determined by following the temperature for another 15 min. The gross heat capacity value, C, was evaluated to be $C = \Delta E/(T_f - T_i)$ at $T_{av} = (T_f + T_i)/2$. The final rating of the temperature served as the initial rating in the next set of heat capacity measurements. Heat capacities of *tert*-butyl chloride were measured in the temperature range between 13 and 300 K with an adiabatic calorimeter.[8] A platinum resistance thermometer was used in this series. Heat capacities of 2,2-dichloropropane were measured in the temperature range between 6 and 300 K with another adiabatic calorimeter.[21] A (rhodium + iron) resistance thermometer (Oxford Instruments Cryogenic Calibration Co.) was used after the temperature scale was transferred from another thermometer calibrated on the ITS-90.[23] The imprecision and the inaccuracy of the results were estimated to be within ±0.04% and ±0.2% for the former[8] and ±0.06% and ±0.3% for the latter calorimeter.[21]

Results

Heat Capacities of *tert*-Butyl Chloride and 2,2-Dichloropropane. The experimental molar heat capacities obtained for *tert*-butyl chloride and 2,2-dichloropropane are tabulated in Tables 1 and 2 and shown in Figure 2. The ordinate for *tert*-butyl chloride is shifted upward by 50 J K^{-1} mol^{-1} for the sake of clarity. The heat capacity curve against temperature for *tert*-butyl chloride showed three anomalies around 183, 219, and 248 K. The anomalies are attributed to crystalline-to-crystalline, crystalline-to-plastically crystalline, and plastically crystalline-to-liquid phase transitions, respectively. For 2,2-dichloropropane, crystalline-to-plastically crystalline and plastically crystalline-to-liquid phase transitions were observed at around 188 and 239 K, respectively, and another heat capacity anomaly was found at 171 K. The crystalline phases of *tert*-butyl chloride and 2,2-dichloropropane were numbered I, II, and III in the order of decreasing temperature, as the phase sequences were described in the following; for *tert*-butyl chloride, phase III (183 K) phase II (219 K) phase I (248 K) L, and for 2,2-dichloropropane, phase III (171 K) phase II (188 K) phase I (239 K) L, where L denotes the liquid phase.

Fusion and Calorimetric Determination of Purity of *tert*-Butyl Chloride and 2,2-Dichloropropane. The fusion temperatures and purities of *tert*-butyl chloride and 2,2-dichloropropane were determined by the fractional melting method. This method is based on the thermodynamics of the crystal + liquid equilibrium. The spontaneous negative drift due to fusion was followed for 2 h after each energy input, and the equilibrium temperature during fusion was easily estimated by exponential extrapolation of the temperature-against-time curve to infinite time because the equilibration time was relatively short. The estimated temperatures for *tert*-butyl chloride and 2,2-dichloropropane were plotted as a function of the reciprocal of the fraction melted, f, in Figure 3a,b, respectively. These points were fitted in terms of a straight line and analyzed by the van't Hoff equation.[24] The fusion temperature and the mole-fraction purity were determined to be 248.6 ± 0.1 K and 0.9993 for *tert*-butyl chloride, and 239.6 ± 0.1 K and 0.9995 for 2,2-dichloropropane, respectively. The enthalpy and entropy of fusion were measured

TABLE 1: Molar Heat Capacities of *tert*-Butyl Chloride; $R = 8.314\,51$ J K^{-1} mol^{-1}

$\langle T \rangle$/K	$C_{s,m}/R$	$\langle T \rangle$/K	$C_{s,m}/R$	$\langle T \rangle$/K	$C_{s,m}/R$	$\langle T \rangle$/K	$C_{s,m}/R$
Crystal							
11.02	0.3990	38.16	4.042	85.34	7.138	138.85	10.61
11.26	0.4321	39.42	4.152	86.79	7.234	140.67	10.73
11.64	0.4766	40.70	4.259	88.24	7.331	142.50	10.86
12.11	0.5404	42.00	4.364	89.69	7.424	144.35	10.99
12.59	0.5994	43.31	4.467	91.13	7.517	146.20	11.11
13.13	0.6768	44.65	4.568	92.58	7.612	148.07	11.24
13.74	0.7577	46.00	4.666	94.05	7.704	149.94	11.37
14.30	0.8382	47.37	4.763	95.54	7.799	151.72	11.49
14.86	0.9156	48.75	4.859	97.04	7.896	153.41	11.62
15.40	0.9892	50.15	4.952	98.55	7.999	155.13	11.75
16.01	1.075	51.56	5.044	100.08	8.094	156.14	11.81
16.78	1.185	52.98	5.135	101.63	8.194	157.81	11.93
17.47	1.302	54.41	5.225	103.18	8.298	158.66	12.01
18.09	1.404	55.85	5.315	104.76	8.399	160.47	12.15
18.98	1.553	57.30	5.405	106.34	8.504	162.30	12.30
20.04	1.731	58.77	5.495	107.94	8.614	164.16	12.46
21.03	1.889	60.24	5.583	109.56	8.712	166.05	12.62
21.98	2.039	61.72	5.673	111.18	8.815	167.96	12.79
22.89	2.182	63.22	5.764	112.82	8.926	169.89	12.98
23.77	2.324	64.72	5.856	114.48	9.037	171.84	13.17
24.63	2.462	66.23	5.949	116.14	9.144	173.82	13.39
25.37	2.581	67.75	6.042	117.82	9.243	175.31	13.55
25.99	2.663	69.28	6.135	119.51	9.356	176.64	13.71
26.87	2.778	70.81	6.228	121.21	9.474	177.82	13.86
28.00	2.920	72.36	6.323	122.92	9.589	178.75	13.98
29.11	3.060	73.91	6.419	124.64	9.698	179.93	14.15
30.19	3.194	75.47	6.515	126.38	9.811	181.23	14.34
31.27	3.326	77.04	6.613	128.12	9.919	181.87	14.45
32.33	3.451	78.62	6.712	129.88	10.03	181.87	14.45
33.40	3.571	79.52	6.765	131.65	10.14	182.52	14.55
34.46	3.684	80.98	6.860	133.44	10.26	182.86	17.51
35.63	3.801	82.43	6.952	135.23	10.38	183.05	26.46
36.90	3.926	83.89	7.041	137.03	10.50		
Phase Transition							
183.88	21.08	192.25	12.86	204.21	13.64	212.16	14.30
184.46	12.77	193.91	12.96	205.98	13.76	213.92	14.49
185.38	12.49	195.59	13.08	206.94	13.84	215.52	14.68
186.37	12.53	197.28	13.18	207.76	13.90	216.94	14.86
187.61	12.60	198.99	13.29	209.56	14.04		
188.99	12.67	200.71	13.40	210.41	14.13		
190.61	12.77	202.45	13.53	211.37	14.21		
Plastic Crystal							
220.44	15.49	226.34	15.65	233.70	15.82	242.15	16.13
221.55	15.52	228.07	15.69	235.71	15.87	244.42	16.41
223.08	15.57	229.88	15.73	237.79	15.93	246.64	19.28
224.67	15.61	231.75	15.78	239.94	16.00		
Liquid							
249.47	18.24	262.13	18.52	273.62	18.78	288.32	19.16
251.69	18.28	263.97	18.55	275.64	18.84	290.62	19.24
253.36	18.32	265.85	18.60	277.69	18.88	292.94	19.30
255.05	18.35	267.75	18.65	279.76	18.94	295.29	19.38
257.25	18.40	269.68	18.69	281.86	19.00	297.66	19.46
259.16	18.44	271.44	18.73	283.80	19.03	300.05	19.55
260.32	18.47	273.62	18.78	286.05	19.10		

TABLE 2: Molar Heat Capacities of 2,2-Dichloropropane; $R = 8.314\,51$ J K^{-1} mol^{-1}

$\langle T \rangle$/K	$C_{s,m}/R$	$\langle T \rangle$/K	$C_{s,m}/R$	$\langle T \rangle$/K	$C_{s,m}/R$	$\langle T \rangle$/K	$C_{s,m}/R$
Crystal							
5.37	0.0401	43.48	4.537	94.60	7.536	146.77	10.52
6.01	0.0586	44.85	4.633	96.14	7.625	148.53	10.62
6.59	0.0808	46.23	4.727	97.68	7.715	150.30	10.72
7.19	0.1064	47.61	4.817	99.24	7.807	152.08	10.82
7.88	0.1463	49.00	4.906	100.80	7.899	153.86	10.93
8.71	0.2061	50.40	4.993	101.24	7.927	155.66	11.04
9.53	0.2762	51.80	5.079	102.38	7.993	157.26	11.11
10.31	0.3560	53.21	5.163	103.97	8.086	158.34	11.20
11.13	0.4527	54.62	5.247	105.57	8.179	159.42	11.25
11.95	0.5596	56.04	5.329	107.19	8.273	160.26	11.32
12.77	0.6752	57.47	5.411	108.81	8.368	161.03	11.37
13.64	0.8041	58.90	5.491	110.45	8.462	162.09	11.44
14.54	0.9464	60.34	5.572	112.10	8.558	163.15	11.51
15.47	1.100	61.79	5.652	113.76	8.653	164.20	11.58
16.43	1.260	63.24	5.732	115.43	8.748	165.26	11.66
17.44	1.433	64.69	5.813	117.11	8.846	166.30	11.73
18.55	1.622	66.16	5.895	117.17	8.848	167.12	11.79
19.70	1.815	67.63	5.977	118.80	8.937	167.74	11.86
20.81	1.999	69.10	6.061	120.26	9.023	168.38	11.93
21.92	2.177	70.58	6.144	121.82	9.111	168.90	12.00
23.03	2.355	72.07	6.229	123.40	9.199	169.41	12.08
24.16	2.533	73.56	6.315	124.99	9.291	169.92	12.19
25.33	2.712	75.06	6.401	126.59	9.379	170.43	12.35
26.52	2.879	76.57	6.488	128.20	9.472	170.93	12.56
27.74	3.024	78.08	6.576	129.83	9.559	171.43	12.76
28.99	3.170	79.60	6.664	131.47	9.660	171.93	12.28
30.25	3.330	81.12	6.754	133.12	9.748	172.44	12.14
31.53	3.477	82.66	6.842	134.79	9.838	173.96	12.25
32.82	3.620	84.19	6.931	136.46	9.936	176.07	12.41
34.12	3.756	85.30	6.992	137.76	10.01	178.19	12.58
35.43	3.885	86.02	7.035	138.70	10.07	179.37	12.67
36.75	4.007	87.14	7.100	139.85	10.13	180.85	12.80
38.08	4.123	88.61	7.188	139.91	10.13	182.70	12.98
39.42	4.232	90.09	7.274	141.57	10.22	185.15	13.24
40.77	4.337	91.58	7.361	143.29	10.32		
42.12	4.438	93.09	7.449	145.02	10.42		
Plastic Crystal							
190.08	15.26	201.52	15.50	211.31	15.76	222.57	16.14
192.33	15.29	203.17	15.54	212.80	15.80	225.06	16.23
194.19	15.33	204.43	15.57	214.32	15.85	227.56	16.34
195.60	15.36	205.83	15.61	215.89	15.90	230.08	16.46
197.04	15.40	207.06	15.64	217.67	15.96	232.62	16.59
198.51	15.43	208.44	15.68	217.68	15.95	235.18	16.73
200.00	15.47	209.85	15.72	220.11	16.04	236.77	16.85
Liquid							
240.73	17.65	256.96	17.91	271.91	18.12	289.28	18.42
242.54	17.68	258.66	17.94	274.04	18.15	291.65	18.47
244.37	17.71	260.41	17.96	276.21	18.18	294.06	18.51
246.23	17.73	262.19	17.98	278.03	18.22	296.51	18.56
248.11	17.77	264.02	18.00	280.20	18.26	298.99	18.60
250.58	17.80	265.90	18.03	282.41	18.30	301.52	18.65
252.11	17.83	267.77	18.05	284.66	18.34		
254.65	17.87	269.82	18.08	286.95	18.38		

twice to be 1.92 ± 0.03 kJ mol^{-1} and 7.7 ± 0.1 J K^{-1} mol^{-1} for *tert*-butyl chloride and 2.39 ± 0.03 kJ mol^{-1} and 10.0 ± 0.1 J K^{-1} mol^{-1} for 2,2-dichloropropane, respectively. The heat capacity baselines (for crystalline phase I and liquid) used in estimating the enthalpy and entropy of fusion for *tert*-butyl chloride were assumed to be expressed by

$$C_{p,m}(T)/(\text{J K}^{-1}\,\text{mol}^{-1}) = 82.849 + 2.087 \times 10^{-1}(T/\text{K}) \quad (1)$$

and

$$C_{p,m}(T)/(\text{J K}^{-1}\,\text{mol}^{-1}) = 174.855 - 3.453 \times 10^{-1}(T/\text{K}) + 1.012 \times 10^{-3}(T^2/\text{K}^2) \quad (2)$$

respectively, and those for 2,2-dichloropropane by

$$C_{p,m}(T)/(\text{J K}^{-1}\,\text{mol}^{-1}) = 61.702 + 3.257 \times 10^{-1}(T/\text{K}) \quad (3)$$

and

$$C_{p,m}(T)/(\text{J K}^{-1}\,\text{mol}^{-1}) = 142.742 - 7.689 \times 10^{-2}(T/\text{K}) + 3.905 \times 10^{-4}(T^2/\text{K}^2) \quad (4)$$

respectively.

Crystalline III-to-II and II-to-I Phase Transitions. The anomalous heat-capacity contributions due to III-to-II and II-to-I phase transitions for *tert*-butyl chloride and II-to-I phase transition for 2,2-dichloropropane were assessed as usually done
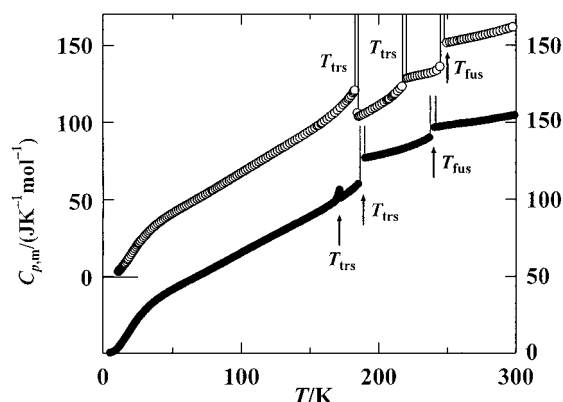
Figure 2. Experimental molar heat capacities, $C_{p,m}$, of *tert*-butyl chloride (upper curve) and 2,2-dichloropropane (lower curve). The ordinate for *tert*-butyl chloride is shifted upward by 50 J K^{-1} mol^{-1} for the sake of clarity.
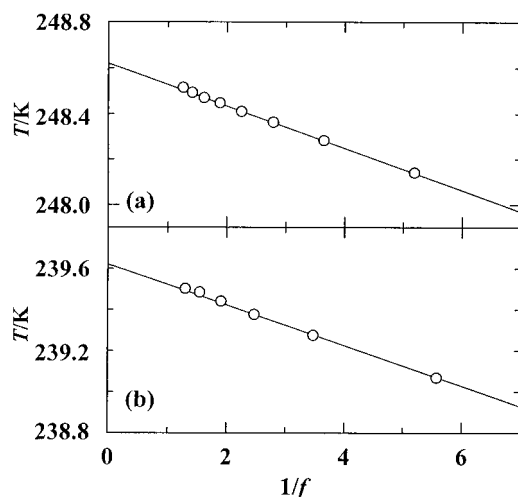

Figure 3. Equilibrium temperature against the reciprocal of the fraction melted, f, in (a) *tert*-butyl chloride and (b) 2,2-dichloropropane.

in the estimation of the thermodynamic quantities of transitions. The temperature drift after each energy input was followed for 2 h in the temperature range between 170 and 220 K for *tert*-butyl chloride and between 180 and 190 K for 2,2-dichloropropane, respectively. The equilibrium temperature was estimated by extrapolating the drift curve to infinite time in terms of an exponential function. The temperatures of III-to-II and
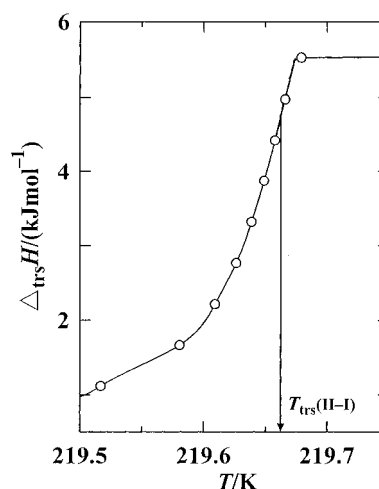

Figure 4. Temperature dependence of the enthalpy of the II-to-I phase transition in *tert*-butyl chloride. The transition temperature was taken to be a point of inflection of the curve.

II-to-I phase transitions for *tert*-butyl chloride and II-to-I phase transition for 2,2-dichloropropane were determined as an inflection point of the anomalous enthalpy-against-temperature curve, i.e., temperature of the maximum of anomalous heat capacities, to be 183.26 ± 0.05, 219.67 ± 0.03, and 188.17 ± 0.03 K, respectively. Figure 4 shows, as an example, the curve for the II-to-I phase transition of *tert*-butyl chloride. The enthalpies of the phase transitions were evaluated to be 1.84 ± 0.01, 5.61 ± 0.02, and 6.08 ± 0.02 kJ mol^{-1}, respectively, and the entropies to be 10.1 ± 0.1, 25.5 ± 0.1, and 32.3 ± 0.1 J K^{-1} mol^{-1}, respectively. The thermodynamic quantities of phase transitions for the series of compounds $(CH_3)_nCCl_{4-n}$ are tabulated in Table 3 together with structural data.

Crystalline III-to-II Phase Transition at Low Temperature in 2,2-Dichloropropane. As described above, a new III-to-II phase transition was observed for 2,2-dichloropropane at a low temperature. It exhibited a relatively sharp peak in the heat capacities and the first-order character. The drift was followed for 1 h after each energy input in the temperature range between 166 and 173 K. Figure 5b shows the drift rates taken at 15 min after the energy input. Heat capacities were evaluated by using the equilibrium temperatures estimated by extrapolation of the drift curve to infinite time in terms of an exponential function. Although the derived heat-capacity curve in Figure 5a indicates that the transition might be of the second order, the phase

TABLE 3: Structural Data and Thermodynamic Quantities of Phase Transitions for a Series of Compounds $(CH_3)_nCCl_{4-n}$; $R = 8.314\ 51$ J K^{-1} mol^{-1}

n	$V_m/\text{Å}^3$	$V_z(I)/\text{Å}^3$	$V_z(L)/\text{Å}^3$	$V_z(L)^\dagger/\text{Å}^3$	T_{trs}/K	$\Delta_{trs}S_m^0/R$	T_{fus}/K	$\Delta_{fus}S_m^0/R$
0	87.98	145.02[b]	159.62[d]	157.91[e]	225.45[h]	2.47[h]	245.6[h]	1.23[h]
1	90.46	147.65[b]	165.55[d]	155.83[f]	224.80[i]	4.01[i]	243.1[i]	1.16[i]
2	92.93	150.84[b]	173.38[d]		188.17[o]	3.89[o]	239.6[o]	1.20[o]
					188[j]	3.83[j]	239.3[j]	1.18[j]
3	95.41	161.80[c]	180.60[d]		183.26[o]	1.21[o]	248.6[o]	0.93[o]
					219.67[o]	3.07[o]		
					182.91[l]	1.23[l]	247.5[l]	1.01[l]
					219.25[l]	3.23[l]		
					183.1[m]	1.22[m]	248.4[m]	0.96[m]
					219.4[m]	3.11[m]		
					183.1[k]	1.13[k]	248.1[k]	0.97[k]
					219.6[k]	3.19[k]		
4	97.88	171.53[b]	198.66[d]	195.31[g]	140.50[n]	2.25[n]	256.75[n]	1.45[n]

[a] V_m, molecular volume evaluated on the basis of the data of interatomic bond lengths and van der Waals radii of atoms and methyl group. $V_z(I)$, volume per molecule calculated from density data in the plastically crystalline phase. $V_z(L)$, volume per molecule calculated from density data in the liquid phase at room temperature. $V_z(L)^\dagger$, volume per molecule evaluated on the assumption that the molecules are arranged in the body-centered cubic system. [b] From ref 11. [c] From ref 10. [d] From Beilstein. [e] From ref 36. [f] From ref 38. [g] From ref 37. [h] From ref 13. [i] From ref 15. [j] From ref 16 [k] From ref 17 [l] From ref 18. [m] From refs 12 and 19. [n] From ref 20. [o] Present results.
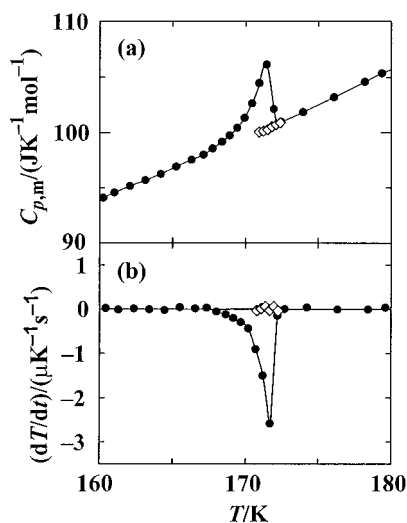
Figure 5. Heat capacities (a) and temperature drift rates (b) in the temperature region of III-to-II phase transition in 2,2-dichloropropane: (●) sample precooled to 80 K; (◇) sample precooled to 170 K.

transition is demonstrated to be of the first order by the effect of supercooling, as is shown in Figure 5a,b. Closed circles in the upper portion (a) represent heat capacities of the sample precooled to 80 K, and those in the lower portion (b) represent the corresponding temperature drift rates observed during the series of heat capacity measurements by the intermittent heating method. The negative (endothermic) effect in the transition temperature region definitely indicates the existence of the jump in the state of molecular aggregation. Diamonds represent heat capacities of the sample precooled to 170 K, and there appears no sign indicating progress of the phase transition as a rise in the heat capacity. The corresponding temperature-drift rates, as plotted with diamonds in the lower portion, exhibit quite the normal behavior as well. The transition temperature was determined as a point of the heat capacity peak to be 171.6 ± 0.1 K. The entropy of the III-to-II phase transition was estimated from the anomalous heat capacities to be 0.06 ± 0.01 J K^{-1} mol^{-1}. The small entropy indicates that the transition is rather associated with slight shifts in the positions or orientations of molecules.

Standard Thermodynamic Functions of *tert*-Butyl Chloride and 2,2-Dichloropropane. Standard thermodynamic functions of *tert*-butyl chloride and 2,2-dichloropropane were evaluated from experimental heat capacities and are summarized in Tables 4 and 5, respectively. Heat capacities below 15 K were then derived by fitting an expression: $C_{p,\mathrm{m}}(T)/(\mathrm{J\ K}^{-1}$ mol$^{-1}) = a(T/\mathrm{K})^3 + b(T/\mathrm{K})$,[5] to the experimental results in the temperature range between 6 and 20 K for *tert*-butyl chloride and between 13 and 20 K for 2,2-dichloropropane, respectively. The constants a and b were determined to be 2.941×10^{-3} and -2.914×10^{-6}, respectively, for *tert*-butyl chloride and 3.169×10^{-3} and -3.057×10^{-6}, respectively, for 2,2-dichloropropane.

Discussion

Correlation between Molecular Sphericity and Configurational Order/Disorder in Plastically Crystalline and Liquid Phases. The n dependence of the entropies of fusion in a series of plastically crystalline compounds $(CH_3)_nCCl_{4-n}$ indicated that, as shown in Figure 1, the entropies decrease as the deviation of molecular shape from a sphere increases. However, the dependence does not explain directlywhy it happens. Information on the configurational degree of freedom of molecules can be

TABLE 4: Standard Molar Thermodynamic Functions of *tert*-Butyl Chloride; $R = 8.314\ 51$ J K^{-1} mol^{-1}

| T/K	$C_{s,\mathrm{m}}^0/R$	$\Delta_0^T H_\mathrm{m}^0/R\cdot$K	$\Delta_0^T S_\mathrm{m}^0/R$	Φ_m^{0a}/R
		Crystal		
0	0	0	0	0
10	0.333	0.878	0.118	0.030
20	1.717	10.48	0.728	0.204
30	3.175	35.37	1.717	0.538
40	4.203	72.58	2.781	0.966
50	4.943	118.4	3.801	1.432
60	5.569	171.0	4.758	1.907
70	6.178	229.8	5.662	2.380
80	6.798	294.6	6.527	2.845
90	7.441	365.8	7.365	3.300
100	8.091	443.5	8.183	3.748
110	8.742	527.7	8.985	4.188
120	9.393	618.3	9.774	4.621
130	10.04	715.5	10.55	5.048
140	10.69	819.1	11.32	5.468
150	11.37	929.4	12.08	5.883
160	12.11	1047	12.84	6.294
170	13.01	1172	13.60	6.700
180	14.09	1308	14.37	7.105
183.26	14.44	1355	14.63	7.236
		Phase Transition		
183.26	14.47	1577	15.84	7.236
190	12.74	1662	16.32	7.571
200	13.34	1792	16.99	8.025
210	14.10	1929	17.66	8.468
219.67	14.89	2071	18.31	8.887
		Plastic Crystal		
219.67	15.48	2745	21.38	8.887
220	15.49	2750	21.40	8.906
230	15.74	2906	22.10	9.464
240	15.99	3064	22.77	10.01
248.61	16.21	3203	23.34	10.46
		Liquid		
248.61	18.23	3434	24.27	10.46
250	18.26	3459	24.46	10.62
260	18.46	3643	25.18	11.17
270	18.69	3829	25.88	11.70
280	18.95	4017	26.56	12.22
290	19.22	4208	27.23	12.72
298.15	19.47	4365	27.77	13.13
300	19.53	4401	27.89	13.22

^{a} $\Phi_\mathrm{m}^0/R = (\Delta_0^T S_\mathrm{m}^0 - \Delta_0^T H_\mathrm{m}^0/T)/R$.

examined from the consideration on the absolute entropies in the plastically crystalline and liquid phases.

Figure 6 shows the standard entropy data derived for the series of compounds $(CH_3)_nCCl_{4-n}$. The data were plotted with downward shifts by 50 J K^{-1} mol^{-1} in the order of increasing n for the sake of clarity. Here, we supposed the third law of thermodynamics to hold; namely, the molecular orientation is perfectly ordered at $T = 0$ K for each compound. The standard entropies of carbon tetrachloride ($n = 0$) were evaluated from experimental heat capacities reported by Hicks et al.[13] between 17 and 300 K and by Atake et al.[14] between 3 and 50 K. Heat capacities at $T < 3$ K were then derived by fitting an expression, $C_{p,\mathrm{m}}(T)/(\mathrm{J\ K}^{-1}$ mol$^{-1}) = a(T/\mathrm{K})^3 + b(T/\mathrm{K})$,[5] to the experimental results[14] in the temperature range between 3 and 17 K. The constants a and b were determined to be 5.711×10^{-3} and -7.082×10^{-6}, respectively. The standard entropies of 2,2-dimethylpropane ($n = 4$) were evaluated from experimental heat capacities reported between 13 K and the boiling point ($T_b = 282.61$ K) by Aston et al.,[25] and between 4 and 20 K and between 60 and 260 K by Enokido et al.,[20] respectively. Heat capacities at $T < 4$ K were derived by the same method as carbon tetrachloride using the experimental results[20] in the

TABLE 5: Standard Molar Thermodynamic Functions of 2,2-Dichloropropane; $R = 8.314\ 51$ **J K**$^{-1}$ **mol**$^{-1}$

T/K	$C^0_{s,m}/R$	$\Delta_0^T H^0_m/R\cdot K$	$\Delta_0^T S^0_m/R$	Φ^{0a}_m/R
		Crystal		
0	0	0	0	0
10	0.330	0.842	0.112	0.028
20	1.868	11.25	0.771	0.208
30	3.306	37.55	1.817	0.566
40	4.279	75.78	2.911	1.016
50	4.967	122.2	3.943	1.499
60	5.550	174.8	4.901	1.987
70	6.112	233.1	5.799	2.469
80	6.685	297.1	6.652	2.939
90	7.271	366.9	7.474	3.397
100	7.848	442.5	8.270	3.845
110	8.440	523.9	9.046	4.283
120	9.008	611.2	9.805	4.712
130	9.566	704.0	10.55	5.132
140	10.14	802.6	11.28	5.545
150	10.71	906.8	12.00	5.951
160	11.33	1017	12.71	6.352
170	11.99	1133	13.41	6.747
180	12.70	1257	14.12	7.136
188.17	13.28	1362	14.69	7.452
		Plastic Crystal		
188.17	13.31	2094	18.58	7.452
190	15.26	2122	18.69	7.523
200	15.46	2276	19.48	8.101
210	15.72	2432	20.24	8.662
220	16.05	2590	20.98	9.205
230	16.44	2753	21.70	9.732
239.6	16.81	2913	22.38	10.23
		Liquid		
239.6	16.88	3201	23.58	10.23
240	17.65	3208	23.61	10.25
250	17.79	3385	24.34	10.80
260	17.94	3563	25.04	11.33
270	18.10	3744	25.72	11.85
280	18.26	3925	26.38	12.36
290	18.44	4109	27.02	12.85
298.15	18.59	4260	27.54	13.25
300	18.62	4294	27.65	13.34
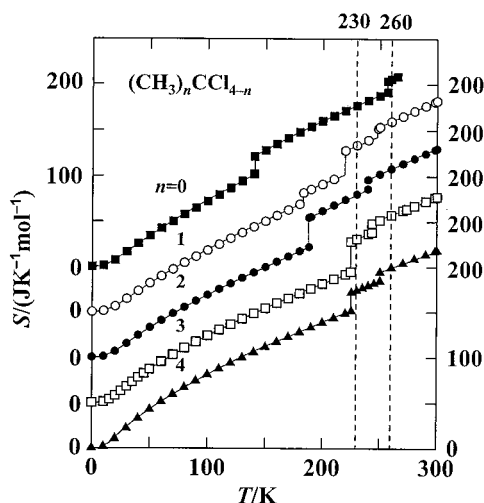
Figure 6. Molar entropies of the series of compounds $(CH_3)_nCCl_{4-n}$. The ordinate is shifted upward by 50 J K^{-1} mol^{-1} in the order of decreasing n for the sake of clarity: (■) $n = 0$; (○) $n = 1$; (●) $n = 2$; (□) $n = 3$; (▲) $n = 4$.

temperature range between 5 and 19 K. The constants a and b were determined to be 3.662×10^{-3} and -4.015×10^{-6}, respectively. For 1,1,1-trichloroethane ($n = 1$), the data by Andon et al.[15] were used. The constants a and b were 3.791×10^{-3} and -3.499×10^{-6}, respectively.
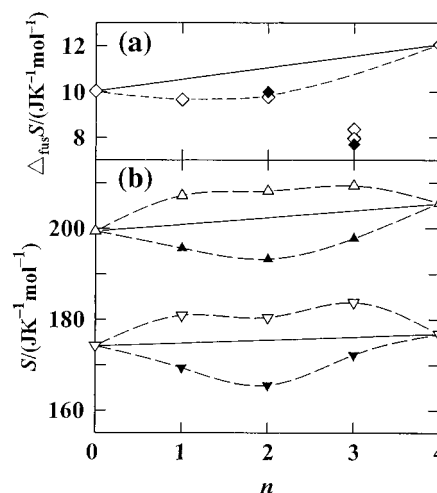
Figure 7. n dependence of (a) entropies of fusion and (b) standard entropies at 230 K in the plastically crystalline phase and at 260 K in the liquid phase of compounds $(CH_3)_nCCl_{4-n}$: (◆) entropies of fusion obtained in the present work; (◇) literature data;[13-15,20,25] (▽) standard entropies at 230 K; (▼) entropies (at 230 K) after subtraction, from the standard entropies, of the contributions due to the exchange between positions of methyl group and chlorine atom within each molecule; (△) standard entropies at 260 K; (▲) entropies (at 260 K) after subtraction, from the standard entropies, of the contributions due to the exchange between positions of methyl group and chlorine atom within each molecule.

Figure 7a shows the n dependence of the entropies of fusion for the series of compounds $(CH_3)_nCCl_{4-n}$ together with the literature data: solid diamonds represent our results, while open diamonds represent the literature data.[12,13-20] The dependence exhibits a curve with a downward convex, as described above. The lower portion of Figure 7b shows the n dependence of the absolute, standard entropies at 230 K in the plastically crystalline phase with inverted open triangles, and the upper portion shows the n dependence at 260 K in the liquid phase with open triangles, respectively. The entropies, however, involve the contributions due to the exchange between positions of methyl group and chlorine atom within each molecule. The contributions are evaluated by a following method: On introducing the distinction between the methyl group and chlorine atom, the number of different molecular orientations is estimated to be $_4C_1 = 4$ for 1,1,1-trichloroethane and *tert*-butyl chloride, and to be $_4C_2 = 6$ for 2,2-dichloropropane, respectively. This orientational disorder of molecules gives rise to an excess entropy of $R \ln 4 = 11.5$ J K^{-1} mol^{-1} for the former group of compounds and $R \ln 6 = 14.9$ J K^{-1} mol^{-1} for the latter. Solid triangles and inverted solid triangles in Figure 7b represent the entropies derived by subtracting the contributions from the experimental values indicated by the open triangles and inverted open triangles, respectively.

It is noted that the n dependences of the corrected, absolute entropies for the series of compounds $(CH_3)_nCCl_{4-n}$ at 230 K in the plastically crystalline phase and at 260 K in the liquid phase definitely exhibit curves with downward convex. The dependences indicate that the orientational disorder due to the exchange between the methyl group and chlorine atom has not fully evolved in both phases and that some short-range order with respect to the positional and/or orientational degrees of freedom of molecules develops, on the basis of intermolecular interaction, as the nonsphericity of the molecular shape increases.

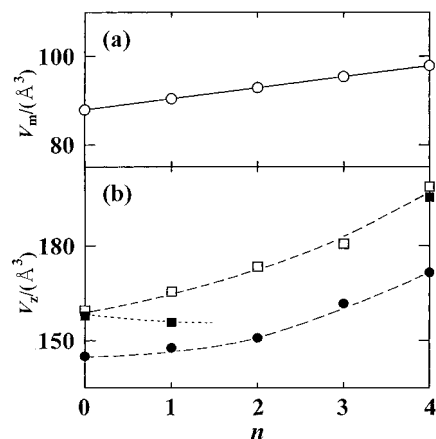**Correlation between Molecular Sphericity and Dense Packing in Plastically Crystalline and Liquid Phases.** To

Figure 8. (a) Molecular volume, V_m, and (b) volume, V_z, per molecule calculated from density: (●) plastically crystalline phase; (□) liquid phase at room temperature; (■) volume per molecule calculated from structural literature data[27−29] in the liquid phase at room temperature.

examine whether some short-range order with respect to the molecular positions and/or orientations really develops in the plastically crystalline and liquid phases, volume data of the series of compounds $(CH_3)_nCCl_{4-n}$ are considered in this section. Many structural investigations[10−12,26−38] have been so far reported for the series of compounds: All the compounds have a face-centered cubic unit cell in the plastically crystalline phase. The volume data are tabulated in Table 3 together with the entropy data mentioned above. Figure 8a shows the n dependence of the molecular volume: The molecular volumes, V_m, were calculated by using known interatomic bond lengths in the molecules and the van der Waals radii of chlorine atom and methyl group,[12,39−41] which may be treated, to a good approximation, as the "methyl atom".[41] The n dependence of the volume is then expressed by

$$V_m/\text{Å}^3 = 2.275n + 87.98 \qquad (5)$$

Figure 8b shows volumes, V_z, per molecule in the plastically crystalline and liquid phases. The volumes per molecule in the plastically crystalline phase were calculated from the density data and are represented by solid circles. The n dependence shows a curve of a downward convex; namely, the values at $n = 1, 2$, and 3 are rather smaller than expected from a linear relation between the values at $n = 0$ and 4. The volumes per molecule in the liquid phase, derived in the same way and represented by open squares, show an n dependence similar to that in the plastically crystalline phase. These results are quite consistent with the indication derived from the consideration on the absolute entropy; that is, there exists some short-range order with respect to the molecular positions and/or orientations on the basis of intermolecular interaction including the non-sphericity of molecular shape.

Here, Nishikawa et al.[35−38] interestingly point out that the scattering intensities of tetrahedral-molecular liquids such as carbon tetrachloride, 1,1,1-trichloroethane, and 2,2-dimethyl-propane were reproduced rather well by the body-centered cubic local lattice structure model. By assuming that the molecules form the model structure and that the distance between neighboring molecules is given by the data of Nishikawa et al., the volumes per molecule in the liquid phase of the above three compounds $n = 0, 1$, and 4 are evaluated as represented by solid squares in Figure 8b. The dotted line is drawn as a guide for the eyes. The feature of the n dependence is the same as derived above from the density data, while the extent of the

downward convex is rather remarkable as compared with that derived from the density. Thus it is concluded that the "nonspherical" molecules with $n = 1, 2$, and 3 are rather more densely packed than expected from the properties of rather "spherical" molecules with $n = 0$ and 4. This indicates that the short-range order with respect to the positions and/or orientations of molecules develops as the shape of molecule deviates from the spherical one, and the development of the short-range order could be responsible for the fact that the entropy of fusion decreases with the increasing nonsphericity of molecular shape.

Conclusion

The reason the entropies of fusion of plastic crystals decrease with the increasing deviation of molecular shape from sphere should be either one of two: (a) in the plastically crystalline phase, the orientational short-range order of molecules is reduced and/or the partial positional disorder of molecules rather proceeds in nonspherical molecules; (b) in the liquid phase, the positional and/or orientational short-range order of molecules rather develops in nonspherical molecules. A series of compounds $(CH_3)_nCCl_{4-n}$ ($n = 0$, CCl_4; $n = 1$, CH_3CCl_3; $n = 2$, $(CH_3)_2CCl_2$; $n = 3$, $(CH_3)_3CCl$; $n = 4$, $(CH_3)_4C$), which all have a face-centered cubic unit cell in the plastically crystalline phase,[10−12] were examined for making insight into the real reasoning. From n dependences of the absolute entropy and the volume per molecule, it was concluded that the short-range order with respect to the positions and/or orientations of molecules develops as the shape of molecule deviates from the spherical one, and this situation could be responsible for the fact that the entropy of fusion decreases with the increasing nonsphericity of molecular shape. This also means for nonspherical molecules that, provided that the orientation of a particular molecule is *fixed*, the site symmetry expected from the space group of a plastically crystalline phase would not be fulfilled at the lattice site of the particular molecule with respect to the time-averaged orientations of the surrounding molecules.

In molecular compounds, the liquid state is characterized by the disordered arrangements in both the orientations and positions of molecules. So far, it has been discussed that some short-range and often medium-range order among the molecules is present and plays an important role in the determination of structural relaxation properties at low temperatures of the supercooled plastically crystalline phase and the supercooled liquid phase. The detail of how the short-range ordering, above indicated to exist even in the stable plastically crystalline and liquid phases, is connected with or distinguished from the low-temperature ordering is attractive and should be investigated in the future. That would certainly help understanding the complicated relaxation properties in such disordered molecular-arrangement systems.[42,43]

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