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Pressure-induced Phase Transition and Compressive Behavior of Substituted Adamantanes

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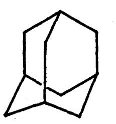
The compressive behavior of adamantane and its secondary monosubstituted derivatives; adamantanone, 2-methyladamantane, and 2-bromoadamantane was measured at various temperatures in a piston-cylinder apparatus. A first-order solid-solid phase transition was found under pressure in each system. The transition pressures, the equilibrium pressures, the volume changes, and the entropy changes for the transition were determined. The compression data for the low pressure phases were fitted to an equation of the form $-\Delta V/V_0 = a_0 + a_1P + a_2P^2$. The effects of substituent groups on the entropy changes of the transitions of these molecular crystals were discussed.

The first-order phase transitions undergone by crystals containing globular (or cage-like) molecules that form plastic crystals have been studied from various viewpoints. Adamantane is one of the few compounds whose phase transition is fully characterized at atmospheric pressure. This compound is known to undergo a phase transition under pressure from a disordered face-centered cubic (fcc) structure to an ordered body centered tetragonal structure,[1)] which is the same as the temperature-induced transition at 208.62 K.[2,3)] The transition pressure was determined as 4.8 kbar at 20 °C by X-ray measurement. The volume change for the transition ΔV is reported to be $-1.8\ \mathrm{cm^3\ mol^{-1}}$ at 4.1 kbar and 20 °C by Pistorius and Resing[4)] and $-\Delta V/V_0$ is 1.4% at 4.1 kbar and 25 °C by Breitling, Jones, and Boyd.[5)] For adamantanone and 2-methyladamantane, as reported in our previous papers,[6–8)] the analogous phase transitions from fcc to tetragonal structure were found at high pressures. For 2-bromoadamantane the high pressure phase was not determined, although the atmospheric phase was fcc.

Such a simple crystal structure in the low pressure phase is not only due to the high symmetrical globular, cage-like molecular structure, but also due to the disordered phase, where the molecules are able to rotate rather freely[9)] or to assume different and hence random orientation on the lattice sites. By the application of pressure the transition from the disordered phase to the ordered phase is expected.

We report here the pressure-induced phase transitions of adamantane, or tricyclo[3.3.1.1^{3,7}]decane (**1**) and its secondary monosubstituted derivatives, *i.e.* adamantanone (**2**), 2-methyladamantane (**3**), and 2-bromoadamantane (**4**).



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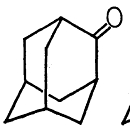

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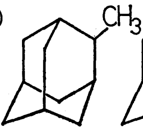

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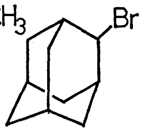

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Precise measurements were made of the pressures of the transitions and the volume changes of the transitions at various temperatures. The entropy changes were calculated. Such thermodynamic data characterize phase transitions and are particularly useful in interpreting solid-solid transformations in which order-disorder effects are predominant.

Experimental

Materials. Guaranteed-grade adamantane (**1**) (Nakarai Chem. Co.) was repeatedly recrystallized from light petroleum and dried *in vacuo*. Adamantanone (**2**) (Aldrich Chem. Co.) and 2-bromoadamantane (**4**) (Aldrich Chem. Co.) were recrystallized from ethanol. 2-Methyladamantane (**3**) was prepared from adamantanone by published procedures[10)] and purified by recrystallization from ethanol. No impurity was detectable in gas-chromatographic analysis of the purified samples.

Measurements. The phase transitions and compression data were obtained in a piston-cylinder device, using a tungsten carbide piston and a 12 mm i.d., 50 mm o.d. cylinder of hardened maraging steel supported by Ni–Cr–Mo steel. The pressure was generated by a 60 t hydraulic press. Extrusion was prevented by the gasket rings which are made from hardened maraging steel. The oil pressure in the press was measured to about 0.1 bar by a 250 bar Heise bourdon gauge. A thin coat of Moly-Kote which was lubricated on the piston and inside of the cylinder as friction reducer has little effect on the transition pressures. The same sample length with a mass of about 1.54 g was used throughout. The transition pressure was affected by the sample length within *ca.* 9% for (**2**).

Each sample was precompressed to the maximum pressure before each run. The displacement of piston was measured by a dial micrometer accurate to ±0.001 mm. It should

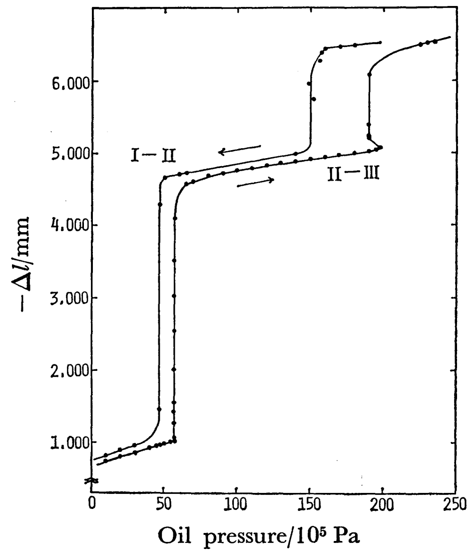

Fig. 1. Piston displacement against pressure for NH_4F used as the fixed points of pressure calibration.

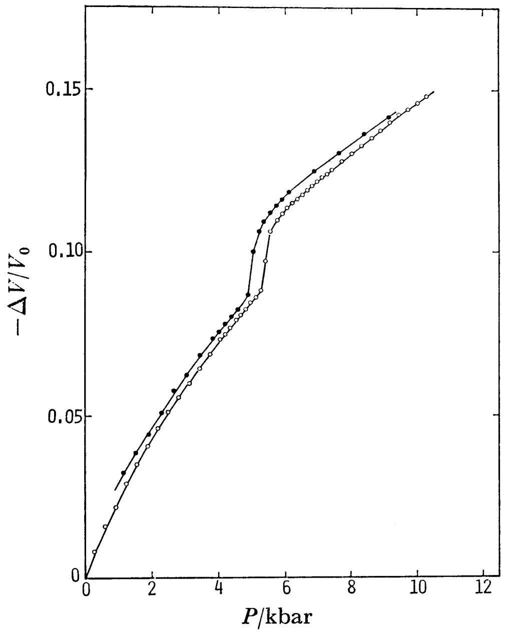

Fig. 2. (a) Compressive behavior of **1** at 22.4 °C. ○: Compression cycle, ●: decompression cycle.

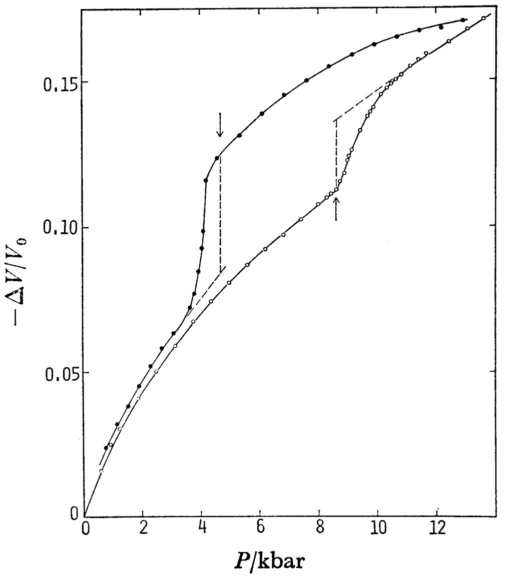

Fig. 2. (b) Compressive behavior of **2** at 21.5 °C. ○: Compression cycle, ●: decompression cycle.

be mentioned that the correction was made for the compression of piston as a function of pressure. The effective area was taken as that of cylinder. The effect of elastic distortion of the cylinder on the volume is less than 0.7% at 10 kbar. The internal pressure was calibrated with I-II and II-III transitions of NH_4F, which is shown in Fig. 1. The transition pressures at 25 °C are 3.605 kbar and 11.531 kbar,† respectively.11) The friction of this apparatus was symmetrical between compression and decompression cycles.

The sample temperature could be maintained to within better than ±0.1 °C by circulating the water of constant temperature into the outer jacket of the cylinder. The temperature was measured with a calibrated chromel-alumel thermocouple inserted in the cylinder.

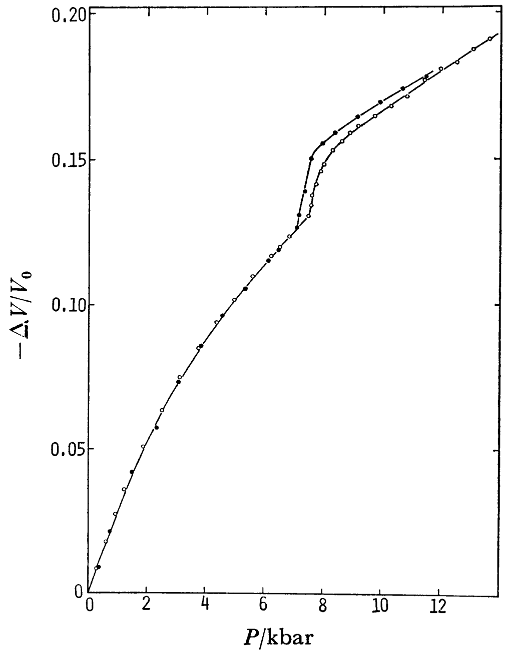

Fig. 2. (c) Compressive behavior of **3** at 20.5 °C. ○: Compression cycle, ●: decompression cycle.

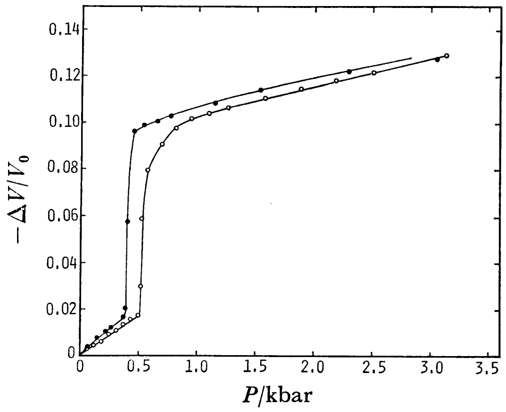

Fig. 2 (d). Compressive behavior of **4** at 20.0 °C. ○: Compression cycle, ●: decompression cycle.

Results

Every compound exhibits a discontinuous volume change at high pressure below 20 kbar, which indicates a first-order phase transition. The relative volume change $-\Delta V/V_0$ against pressure are shown in Fig. 2 (a), (b), (c), and (d) for (**1**), (**2**), (**3**), and (**4**), respectively. They are the results after correcting the friction of apparatus. The curves represent the best fit passing through the experimental points. The inflection point was used to characterize the transition pressure P_t, and the equilibrium pressure P for transition was taken as the average between the transition pressures for the compression and decompression cycles. The volume change at the transition ΔV_t was obtained by extrapolating the compression curve to the inflection pressure and measuring the difference of displacement. The volume change for the transition ΔV was determined as the average

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† 1 bar$=10^5$ Pa.

Table 1. Transition parameters for pressure-induced transitions of substituted adamantanes

Compound	T °C	P_t kbar	P kbar	ΔP kbar	$-\Delta V$ cm^3 mol^{-1}	$-\Delta V/V_0$ %	$-\Delta S$ J K^{-1} mol^{-1}	$-\Delta H$ kJ mol^{-1}
1	0.0	4.00	3.80	0.2	2.2_9	1.78	14.2	3.9
	22.4	5.35	5.28		2.2_7	1.73	14.1	4.2
	32.2	5.85	5.75		2.1_9	1.70	13.6	4.2
	41.5	6.45	6.30		2.1_9	1.70	13.6	4.3
	54.5	7.30	7.23		2.1_2	1.65	13.1	4.3
2	0.0	6.80	4.93	4.0	4.6_4	3.5	33.7	9.2
	21.5	8.65	6.68		4.3_7	3.3	31.7	9.4
	32.5	9.30	7.30		3.9_7	3.0	28.8	9.1
	44.5	10.30	8.18		3.9_7	3.0	28.8	9.5
	55.5	11.10	9.00		—	—	—	—
3	0.0	6.00	6.00	≈ 0	2.9_0	2.00	19.4	5.3
	20.5	7.45	7.45		2.8_0	1.93	18.7	5.5
	32.5	8.30	8.30		2.4_4	1.68	16.3	5.0
	42.3	8.80	8.80		2.3_2	1.60	15.5	4.9
	51.5	9.40	9.40		2.1_5	1.48	14.4	4.7
4	14.0		(1 bar)[a]	0.10—0.13				
	20.0	0.55	0.49		11.7_6	7.82	51.3	15.0
	40.0	1.35	1.29		10.6_0	7.05	46.2	14.5
	59.0	2.14	2.10		9.9_0	6.58	43.2	14.3
	78.8	3.05	3.00		9.5_5	6.35	41.6	14.6

a) DSC data at atmospheric pressure.

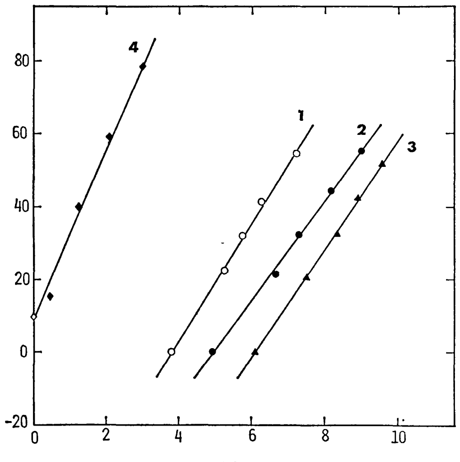

Fig. 3. Phase diagrams of **1**, **2**, **3**, and **4**.

between the volume changes at the transition pressure in compression cycle P_t and that in decompression cycle P_t', *i.e.* $1/2(\Delta V_t+\Delta V_t')$, which is shown in Fig. 2 (b). The volume changes of the transition were determined to an accuracy of 0.2 cm^3 mol^{-1}. The transition pressures, the equilibrium pressures, and the volume changes for the transitions at various temperatures are summarized in Table 1. The transition pressure for (**1**), which has been determined previously from X-ray measurements as 4.8 kbar at 20 °C,[1] is in reasonable agreement with the present equilibrium pressure of 5.1 kbar at 20 °C. But the values of the transition pressure and the volume change reported by Pistorius *et al.*[4] and by Breitling *et al.*[5] are a little lower than those of the present work. Hysteresis, the reproducible difference in the transition pressure between compression and decompression cycles, ΔP is quite large for (**2**), as compared with other compounds. Its temperature dependence was not beyond the experimental errors.

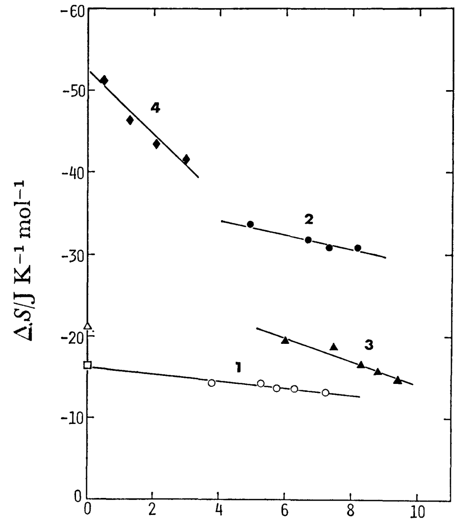

Fig. 4. Entropies of transitions against pressure.

The obtained phase diagrams are shown in Fig. 3. The slopes ($\mathrm{d}P/\mathrm{d}T$) of the equilibrium lines were obtained by means of least square fit. They were used in conjunction with ΔV to determine the entropies and enthalpies of transitions by the Clausius-Clapeyron equation.

The transition temperature of 14.0 °C for (**4**) at atmospheric pressure was determined by the differential scanning calorimetry (dsc).

The entropy changes ΔS and enthalpy changes ΔH of the transitions are listed in Table 1. The values of ΔS are plotted against the pressure in Fig. 4. The value of ΔS for (**1**) obtained from the dsc at atmospheric pressure by Chang *et al.* (16.2 J K^{-1} mol^{-1})[12] is just on the extrapolated line of the present data. As for (**3**) the value from the dsc by Clark *et al.*[13] is smaller than the extrapolated value.

Discussion

It is interesting to note that by the application of pressure all of the secondary monosubstituted adamantanes examined here, which have disordered fcc structure at atmospheric pressure, undergo the phase transitions to ordered body centered tetragonal structure. The structural results were reported previously.[7,8] We found that (**4**) underwent the corresponding phase transition at atmospheric pressure and that the phase diagram could be determined to atmospheric pressure. Presumably, for both (**2**) and (**3**) the temperature-induced transition with the same structural change will appear at low temperature on the extrapolated line of the phase diagram just in the similar way as (**4**).

Figure 4 indicates that ΔS increases with pressure, *i.e.*

$$\frac{\partial \Delta S}{\partial P}=\frac{\partial S(\mathrm{h})}{\partial P}-\frac{\partial S(\mathrm{l})}{\partial P}>0,$$

where S(h) and S(l) refer to the entropy of high pressure phase and that of low pressure phase, respectively. This means a normal phenomenon that the pressure dependence of entropy is higher in the low pressure phase than in the high pressure phase, since $(\partial S/\partial P)<0$ for the most substances. On the other hand, we can see in Table 1 that the temperature dependence of ΔH, which indicates ΔC_p, is too small to find a comprehensive trend.

Compressibility and Crystal Density of Low Pressure Phase. The compression data of the low pressure phases at around 20 °C shown in Fig. 2 were fitted to the following equation by using the method of least squares.

$$\mathbf{1}:\quad -\frac{\Delta V}{V_0}=1.94\times10^{-3}+2.26\times10^{-5}P-1.22\times10^{-9}P^2,$$

$$\mathbf{2}:\quad -\frac{\Delta V}{V_0}=5.80\times10^{-3}+1.93\times10^{-5}P-0.83\times10^{-9}P^2,$$

$$\mathbf{3}:\quad -\frac{\Delta V}{V_0}=1.85\times10^{-3}+2.80\times10^{-5}P-1.51\times10^{-9}P^2,$$

where V_0 is the volume of the crystal under atmospheric pressure and the unit of P is bar. For (**4**) the transition pressure was too low to get the reliable compression data of low pressure phase. The initial compressibility β_0, which is given by

$$\beta_0=-\frac{1}{V_0}\left(\frac{\mathrm{d}V}{\mathrm{d}P}\right)_{P=0},$$

and the crystal density that was obtained from the measurement of the sample size are listed in Table 2. The size of the unit cell and the crystal desity calculated from X-ray data are also included in Table 2. The agreement between both data of the crystal density is satisfactory. We can find a correlation that the higher compressibility corresponds to the structure with the larger unit cell parameter, or the loose structure. This correlation may confirm an evidence that in molecular crystals hydrostatic compression causes the contraction of intermolecular free volume in the crystal especially in an early stage of compression and that the contraction of molecules themselves (or electron clouds) is negligible in the first approximation.

TABLE 2. INITIAL COMPRESSIBILITY AND CRYSTAL DENSITY

Compound	Initial compressibility β_0 / 10^{-6} bar^{-1}	Crystal density ρ / g cm^{-3} A[a)]	B[b)]
1	22.7	1.06	1.08
2	19.3	1.13	1.14
3	28.0	1.03	0.99
4	—	1.43	1.40

a) Determined in the present work. b) Calculated from the X-ray data.

Entropy of Transition. Much information has been obtained about the disordered phases of molecular crystals from the entropies of transition.[14)] There has been an attempt to interpret the entropy of transition of caged hydrocarbon crystals in terms of the Guthrie-McCullough method[15)] which is treated for simple tetrahedral molecules and is based on sets of equivalent, distinguishable molecular orientations obtained by combining the symmetry elements of the crystal lattice with the symmetry elements of the molecule. In this method the orientational disorder is assumed to account for the entropy of transition entirely, all other effect being negligible. This treatment, however, includes some oversimplifications and is invariance with various experimental results except for some typical examples. Clark *et al.*,[13,16)] on the other hand, proposed that the lattice slackening and other effects contribute a significant proportion of the entropy of transition and separated this contribution as excess entropy $\Delta S_{\mathrm{excess}}$ from the orientational entropy.

$$\Delta S=R\ln(N_{\mathrm{I}}/N_{\mathrm{II}})+\Delta S_{\mathrm{excess}},$$

where N_{I} is the number of molecular orientational states statistically occupied in the low pressure disordered phase, N_{II} is the corresponding number in the high pressure ordered phase which is usually unity, and R is the gas constant.

Adamantane is a simple polycyclic saturated hydrocarbon with carbon atoms arranged in a cage-like skelton and has tetrahedral symmetry. Its orientational entropy change based on the Guthrie-McCullough method is $R\ln 2=5.8$ J K^{-1} mol^{-1}, since two distinguishable orientations are allowed in the disordered phase. By comparing with the observed entropy of transition (14.1 J K^{-1} mol^{-1} at 22.4 °C), 8.3 J K^{-1} mol^{-1} is the excess entropy of transition.

By the analogous application of this method, the orientational entropy change of adamantanone should be $R\ln 12=20.7$ J K^{-1} mol^{-1}, since there are six orientations in each one of adamantane. Thus, the excess entropy of 11 J K^{-1} mol^{-1} is obtained by comparing with the observed entropy of transition (31.7 J K^{-1} mol^{-1} at 21.5 °C). This is in accord with the result of Clark *et al.*[16)] that the excess entropy is 10—

15 J K^{-1} mol^{-1}. Namely, the most part of the difference between the transition entropies of adamantane and adamantanone is originated from the difference in the orientational entropy change.

In the case of (**3**) and (**4**), on the other hand, there are two further distinguishable orientations in each one of (**2**), so that the orientational entropy change should be R ln 24=26.4 J K^{-1} mol^{-1}. If we compare the orientational entropy of (**4**) with the observed entropy of transition (51.3 J K^{-1} mol^{-1} at 20.0 °C), the excess entropy becomes 25 J K^{-1} mol^{-1}. This value is beyond the range proposed by Clark *et al.*, although the larger value is expected for the compounds having the larger substituents. By the application of the semiempirical equation of Clark *et al.*, since the temperature range for the orientational disordered phase, $T_m-T=129$ °C is obtained at atmospheric pressure, we get a little lower excess entropy of 16.6 J K^{-1} mol^{-1}. As for (**3**), the value of the observed entropy is much lower than that would be expected. This abnormality may come from the fact that has been pointed out by Clark et al. Thus, the obtained order of $\Delta S_{\mathrm{excess}}$ is (**4**)<(**1**)<(**2**)<(**3**).

The values of $\Delta S_{\mathrm{excess}}$ can be explained if we take the effects of intermolecular ordering and intermolecular forces into account. The value of $\Delta S_{\mathrm{excess}}$ of (**2**) is greater than that of (**1**), although they have almost the same molecular size, and hence must have similar intermolecular ordering. The same is the case for the larger value in (**4**), as compared with (**3**). Thus, we can propose that the dipolar interactions in the ordered crystal are considerably more favorable than those in the disordered phase, increasing $\Delta S_{\mathrm{excess}}$. The intermolecular ordering effect is another striking effect that must be considered. Large substituent groups loosen the ordered crystal lattice. This would be the reason why the values of $\Delta S_{\mathrm{excess}}$ of (**1**) and (**3**) are smaller than (**2**) and (**4**), respectively. We can say conclusively that the molecules with the more sphericity and the higher dipole moment can give more stable ordered crystal.

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