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PRESSURE-INDUCED PHASE TRANSITION IN 2-METHYLADAMANTANE AND 2-BROMOADAMANTANE

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Pressure-induced phase transitions were found in 2-methyladamantane and 2-bromoadamantane by X-ray studies at high pressures. Their transition pressures were 9 kbar and 0.5 kbar, respectively. The crystal structures of the low-pressure phases for both compounds and the high pressure phase of 2-methyladamantane were determined.

Some molecular crystals composed of globular or cage-like molecules have been known to undergo phase transitions at low temperatures as well as at high pressures. For adamantane, it has been established that the high pressure transition is of the same type as the low temperature disorder-order transition at atmospheric pressure.1)-3) A quite similar phase transition that is from face-centered cubic to tetragonal structure has been reported for adamantanone at high pressure.4)-6)

Here we report the results of X-ray studies at high pressures on 2-methyladamantane and 2-bromoadamantane, in which substituents are at the same position of adamantane. It was found that in both compounds phase transitions take place at high pressures. The structures of the atmospheric phases as well as the high pressure phases were explored. The structural information is especially important for understanding the entropy of transition in the order-disorder transition of such molecular crystals.

2-Methyladamantane was prepared from adamantanone by published procedures7) and purified by recrystallization from ethanol. 2-Bromoadamantane (Aldrich Chem. Co.) was recrystallized from ethanol twice. The X-ray measurements at high pressures were carried out with a gasketed diamond anvil cell for 2-methyladamantane and with a cramp-type X-ray cell for 2-bromoadamantane. Zirconium-filtered MoKα radiation was used. The detailed techniques and procedures of measurements at high pressures will be described elsewhere. The pressure was determined by the 200 line of NaCl that was mixed with each sample as internal standard. The X-ray diffraction pattern at 1 atm was recorded on a rotary target X-ray diffractometer with CuKα radiation.

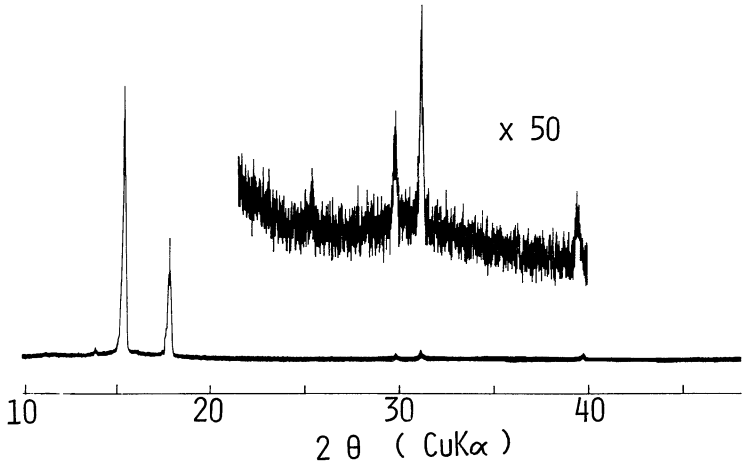

Fig. 1 X-ray diffraction pattern of 2-methyladamantane at 1 atm

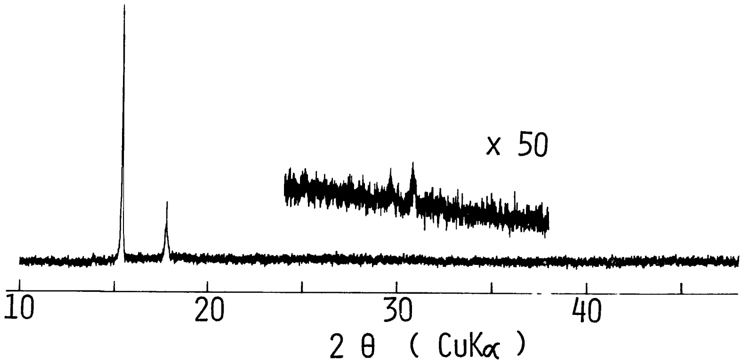

Fig. 2 X-ray diffraction pattern of 2-bromoadamantane at 1 atm

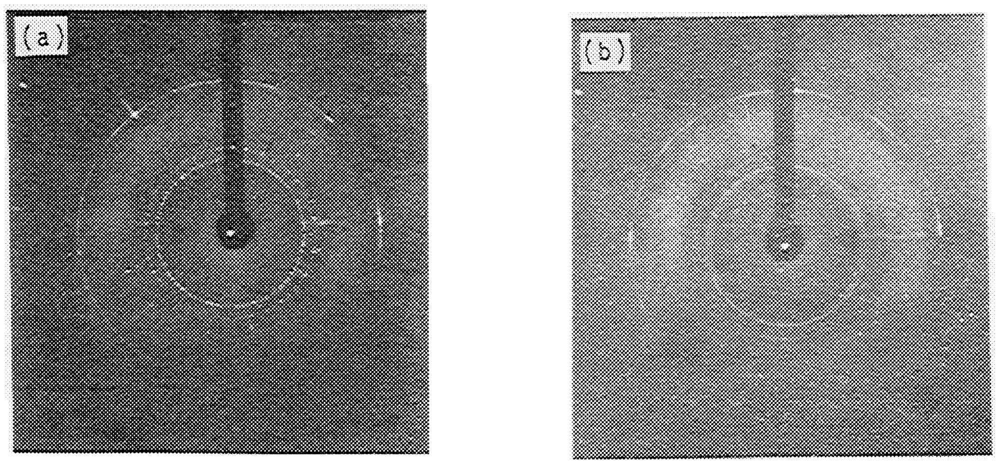

Fig. 3 X-ray exposure of 2-methyladamantane in high pressure cell
(a) 1 atm, (b) 15 kbar

Table 1 X-ray diffraction patterns

Substance	Intensity	hkl	d / Å observed	d / Å calculated
2-Methyladamantane				
Low-pressure phase at 1 atm				
	vs	111	5.767	5.762
	s	200	4.992	4.990
	vw	220	3.517	3.528
	w	113	3.002	3.008
	w	222	2.873	2.880
	vw	331	2.296	2.290
High pressure phase at 15 kbar				
	s	011	5.55	5.59
	vs	110	5.22	5.15
	w	012	4.48	4.49
2-Bromoadamantane				
Low-pressure phase at 1 atm				
	vs	111	5.824	5.814
	s	200	5.063	5.035
	w	113	3.025	3.036
	w	222	2.901	2.907

Table 2 Crystal properties of substituted adamantanes

Substance	Phase	Crystal system	Cell parameters/ Å	Density/gcm^{-3}
2-Methyladamantane	I	cubic	a=9.98	1.00
	II	tetragonal	a=7.3, c=8.8	1.06
2-Bromoadamantane	I	cubic	a=10.07	1.40
	II	——	——	——
Adamantanone6)	I	cubic	a=9.56	1.14
	II	tetragonal	a=7.2, c=7.8	1.25
Adamantane3)	I	cubic	a=9.42	1.08
	II	tetragonal	a=6.54, c=8.82	1.20

I: Low-pressure phase, II: High-pressure phase

The X-ray powder diffraction patterns of 2-methyladamantane and 2-bromoadamantane at atmospheric pressure, which are shown in Figs. 1 and 2, are explained with face-centered cubic cells having dimensions a=9.98Å and a=10.07Å, respectively. The X-ray data are listed in Table 1. Figures 3 (a) and (b) show the X-ray diagrams of 2-methyladamantane at 1 atm in the high pressure cell and at 15 kbar, respectively. Each photograph was exposed for 50h at 20°C. In 2-methyladamantane, the diffraction lines of the high pressure phase could be indexed with a tetragonal cell, as given in Table 1. The obtained cell dimension is not so accurate as that of the atmospheric phase, because of the lower S/N ratio in the high pressure cell. The transition is quite analogous to those of adamantanone and unsubstituted adamantane, though the bulky substituent group is introduced. The transition pressure was determined to be 9 kbar by several exposures around the transition pressure. As for 2-bromoadamantane, the structure of high pressure phase was difficult to be determined. The transition pressure was 0.5 kbar at 20°C. We found also by differential scanning calorimetry that the transition occurred at 14.0°C at 1 atm.

The crystal properties of substituted adamantanes are summarized in Table 2 for comparison. It is natural that the larger unit cell corresponds to the larger substituent for both low-pressure and high-pressure phases. It is noteworthy that 2-bromoadamantane has a quite low transition pressure as compared with other substituted adamantanes. All the compounds concerned have a close packed lattice in the low pressure phases, though the molecular structures are modified by the bulky substituents. These pressure-induced transitions are regarded as the rotational type. In the low pressure phase molecules are able to rotate or to assume different orientations on the lattice points. Consequently, for the molecules with approximately spherical shapes, a close-packed structure results. At high pressures the rotation will be sufficiently restricted to allow the molecules to form a more compact structure permitted by the actual molecular shape.

The increase of pressure has the same effect as the decrease of temperature. Thus, we can predict that 2-methyladamantane will also show the same phase transition at low temperature at 1 atm.

We are still continuing our investigation on the pressure-induced phase transitions of substituted adamantanes.

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