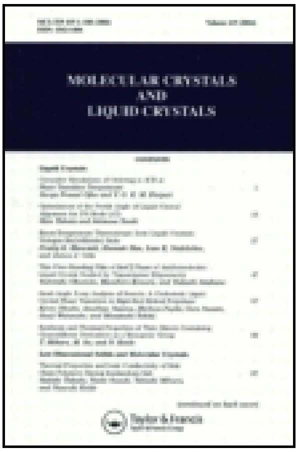

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THE ORDER-DISORDER PHASE TRANSITION IN THE CAGE HYDROCARBON QUADRICYCLANE

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Abstract The phase behavior of quadricyclane has been investigated by differential scanning calorimetry and vibrational spectroscopy. An order-disorder phase transition occurs at 153 K on cooling and at 180 K on heating.

Keywords: order-disorder, phase transition, plastic crystal, quadricyclane

INTRODUCTION

The highly strained cage molecule quadricyclane, tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane, was first reported as the irradiation product of norbornadiene, bicyclo[2.2.1]hepta-2,5-diene.[1,2] This reversible isomerization reaction has been extensively investigated as a potential solar-to-thermal energy conversion system.[3] The seven-membered rigid cage hydrocarbons based on the norbornyl structure are known to have phase transitions to disordered high-temperature crystal structures,[4] but the solid-state properties of quadricyclane are unknown. By analogy with the other members of the series, this compound should also exhibit an order-disorder transition. The results of calorimetric and vibrational spectroscopic studies are reported here.

EXPERIMENTAL

Quadricyclane was purchased from the Aldrich Chemical Company. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 calorimeter, with the temperature and enthalpy scales calibrated against the melting and phase transition of cyclohexane (Aldrich, Gold Label). Infrared spectra were measured on a Nicolet 6000 FT-IR spectrometer with an MCT(B) detector. Raman spectra were recorded on an Instruments S.A. spectrometer with a Jobin-Yvon Ramanor U-1000 double monochromator. The excitation source was the 514.5-nm line of a Spectra Physics model 164, 5-W argon ion laser.

RESULTS AND DISCUSSION

Differential scanning calorimetry revealed the occurrence of a sharp phase transition at 153 K on cooling, 180 K on heating, and the melting transition occurred at 227 K. The entropies of transition and fusion of the bicycloheptyl series of molecules are listed in Table I. The low entropy of fusion of quadricyclane indicates that melting occurs from a disordered phase and that the material can be classified as a plastic crystal.[5]

TABLE I Transition entropies for bicycloheptyl compounds having C_{2v} symmetry.

compound	transition	T_t (K)	ΔS_t ($J\ K^{-1}\ mol^{-1}$)
norbornane	liq. → I	360	12.7*
	I → II	306	0.3*
	II → III	129	31.7
	III → II	130	32.3
norbornadiene	liq. → I	254	5.8
	I → II	175	40.4
	II → I	201	42.8
	I → liq.	254	5.8
quadricyclane	liq. → I	227	4.2
	I → II	153	45.0
	II → I	180	40.0
	I → liq.	228	4.8

*Data from ref. 6.

The entropies of transition in cage hydrocarbons have been interpreted in terms of the number of distinguishable orientations in the two phases plus an excess entropy related to the temperature range of the disordered phase.[7,8] The predicted ratio of distinguishable sites in a face-centered-cubic lattice is 12, which leads to calculated transition entropies of 59.4 and 47.6 J K^{-1} mol^{-1} on cooling and on heating, respectively. Clearly, this approach fails to predict correctly the entropy of transition in the case of quadricyclane. An increased hysteresis in the transition temperature may be responsible for the failure of this and other compounds (including norbornadiene) to follow the predicted behaviour.

The vibrational spectra exhibited few changes on cooling from the liquid state to the disordered phase, but showed abrupt line narrowing and peak splittings at the transition to the ordered phase. Figure 1 shows the low-frequency region of the Raman spectrum. Only the broadened Rayleigh line was observed for phase I, implying isotropic rotation, but at least thirteen lattice peaks occurred for phase II, indicating an ordered, crystalline solid with at least two molecules per unit cell.

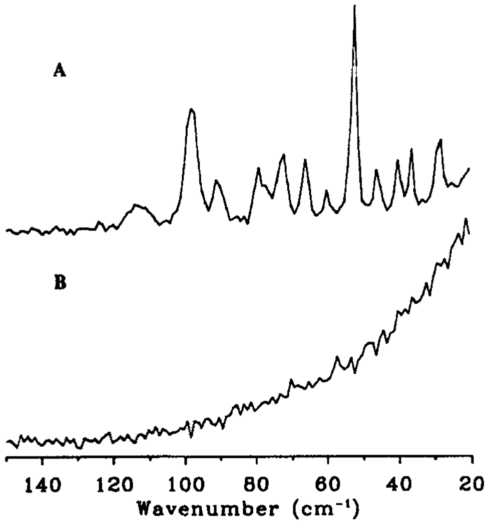

FIGURE 1 Low-frequency Raman spectra of quadricyclane at (A) 43 K (phase II) and (B) 185 K (phase I).

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