

result ($\Delta H^* = 41.4 \text{ kJ mol}^{-1}$). At temperatures near the melting point the NMR relaxation measurements, interpreted using a vacancy diffusion model (Roeder and Douglass 1970), give values for the diffusion coefficient which are more than two orders of magnitude lower than radiotracer measurements. Tanner (private communication) has recently measured the self diffusion coefficient in cyclohexane using the pulsed field gradient NMR technique which shows good agreement with values calculated from the NMR relaxation results.

A powerful method with which to investigate the nature of the defect responsible for self diffusion in solids is to study the pressure dependence of a diffusion controlled process. Such measurements can be interpreted in terms of an activation volume, ΔV^* , for the diffusion process. In the case of metals, activation volumes are frequently found to be less than their respective molar volumes, V_m . This is taken to indicate inward relaxation of the surrounding atoms into a vacancy. Only one experimental investigation of the pressure dependence of self diffusion in organic molecular crystals has been reported previously (Anderson and Slichter 1966b). Very small activation volumes were found, with $\Delta V^*/V_m \approx 0.08-0.15$.

We have measured $T_{1\rho}$ for hexamethylethane and norbornylene at 296 K and for cyclohexane at 270 K, for hydrostatic pressures up to 2.8 kbar. Over most of this range $T_{1\rho}$ is entirely determined by modulation of intermolecular dipolar interactions by the relative translational motion of molecules. Impurity levels, estimated by vapour phase chromatography, for cyclohexane and norbornylene were less than 1000 ppm and 500 ppm respectively. The sample of hexamethylethane was that used previously (Chezeau *et al* 1971). Samples were degassed and contained in a glass cylinder sealed with a Kel-F plunger to transmit the pressure. Measurements were made at a Larmor frequency of 14.3 MHz and RF field strengths, H_1 , of 2.0 and 10.0 G. The spin-lattice relaxation times T_1 were also measured. T_1 is controlled by endospherical molecular reorientation over most of the pressure range investigated. Results for cyclohexane are shown in figure 1. The three substances chosen have different crystal structures as shown in table 1.

Table 1. Comparison of activation volumes ΔV^* with molar volumes V_m

	Crystal structure	ΔV^* ml mol ⁻¹	V_m ml mol ⁻¹	$\frac{\Delta V^*}{V_m}$	ΔH^* kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹
Hexamethylethane	BCC ^a $a_0 = 7.69 \text{ \AA}$	164	137	1.20	82.0 ^d	20.0 ^e
Norbornylene	HCP ^b $a = 6.08 \text{ \AA}$ $c = 9.81 \text{ \AA}$	86.4	94.6	0.90	48.9 ^e	10.1 ^h
Cyclohexane	FCC ^c $a_0 = 8.76 \text{ \AA}$	71.1	101	0.70	41.4 ^f	9.2 ⁱ

^a West (1934)

^b Jackson and Strange (1972)

^c Hassel and Sommerfeldt (1938)

^d Chezeau *et al* (1971)

^e Folland *et al* (1972, to be published)

^f Roeder and Douglass (1970)

^g Scott *et al* (1952)

^h Westrum (1969)

ⁱ Staveley (1962)