Diamantane Derivatives, a New Series of Plastically Crystalline Compounds. The Strain Energy of Diamantane

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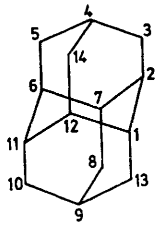
Summary Differential scanning calorimetry reveals that diamantane and several of its derivatives exist in the plastically crystalline phase over wide temperature ranges and that the strain energy of diamantane is larger than that of adamantane, in agreement with earlier theoretical predictions.

Two independent sets of molecular mechanics calculations based on different types of non-bonded potential functions have led to the prediction that diamantane (1) should have a larger strain energy than adamantane.[1,2] However, recently determined heats of formation[3,4] indicate that these two diamondoid systems are in fact about equally strained to the extent of 37·7 kJ mol^{-1}. The experimental heat of formation of diamantane, 165·5 kJ mol^{-1} exothermic,[4] is based on a heat of fusion (at 25°) of 30·1 kJ mol^{-1}, but we now describe an aspect of diamantane chemistry, undiscovered when these data were obtained, which requires that this heat of fusion be increased, making the heat of formation less exothermic.

At −65° adamantane exhibits a solid–solid transition to the plastically crystalline state;[5] the molecules undergo an abrupt change of freedom involving rotational–reorientational types of motion. This behaviour renders adamantane soft and "damp" in appearance at room temperature. In contrast, crystals of diamantane, zone-refined to 99·99% purity, appear sharp-edged and brittle. Between room temperature and 100° diamantane exhibits little physical change; but above 100° the crystal edges begin to round off



(I)

At about 150° an abrupt change occurs, the crystal faces lose their planarity and acquire the matt appearance of adamantane. At 175° there is a second sudden change, although the crystal boundaries are still retained. This state persists until fusion occurs at 251°.

Transitions observed above 25°

	T_1	T_2	Fusion
Diamantane	142	174	251
Diamantan-1-ol	122	135	300
Diamantan-3-ol	152	181	251
Diamantan-4-ol	—	175	211
3-Methyldiamantane . .	—	56	114
1-Bromodiamantane . .	—	67	206
1,4-Dichlorodiamantane . .	—	63	111

The data were obtained with a Du Pont thermal analyser fitted with a d.s.c. cell; the rate of heating in sealed pans was 10°/min.

A differential scanning calorimetry (d.s.c.) curve for diamantane reveals these solid–solid transitions as endotherms of sharpness comparable with that of the final transition to the liquid at temperatures which correspond closely with those observed optically. The thermochemical data, measured from the d.s.c. curve, show that transitions T_1 and T_2 are endothermic by $4{\cdot}48 \pm 0{\cdot}21$ and $7{\cdot}66 \pm 0{\cdot}34$ kJ mol^{-1}, respectively. Consequently, the value of 30·1 kJ mol^{-1} for the heat of fusion of diamantane must now be increased to about 42·3 kJ mol^{-1} to allow for these transitions (this value may require slight alteration when accurate experimental molar heat capacities for diamantane become available). The strain energy of diamantane thus becomes about 49·8 kJ mol^{-1}, making the molecule more strained than adamantane in accord with the molecular mechanics result.

The low entropy of the final transition to the liquid of 17·2 J K^{-1} mol^{-1} establishes that diamantane has indeed a plastically crystalline phase, according to the definition of Timmermans.[6] We have found that this type of behaviour is a quite general phenomenon with a wide range of substituted diamantanes;[7] the transition temperatures of several are given in the Table. Others appear to be already plastically crystalline at room temperature. Although the diamantane crystal structure[8] is known at room temperature, further studies are needed, especially of the crystal structures of the plastically crystalline phases, in order to elucidate these solid–solid transitions in which order-disorder effects are believed to predominate.[9]

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