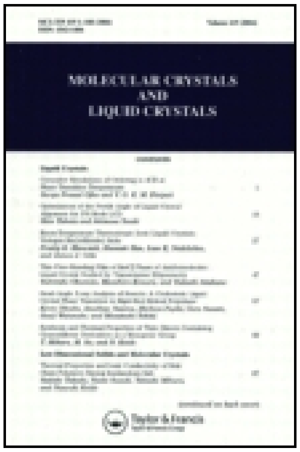

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Heat Capacity Anomaly in Chrysene

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Heat Capacity Anomaly in Chrysene‡

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Single crystals of phenanthrene were found to exhibit a heat capacity anomaly and anomalous electrical effect in the vicinity of 72°C.[1,2] A heat capacity anomaly was also found in this material in powder form. As a result of calculations[3] and other measurements[4] it is quite possible that the source of the anomalous behavior of phenanthrene is the crowded hydrogen atoms at the 4,5 positions of the molecule. A calorimetric survey was made of some other hydrocarbons with crowded hydrogens in the hope of finding materials which exhibit similar behavior.

The materials studied were anthracene, 1:2 benzanthracene, chrysene, pyrene, triphenylene, 5:6 benzoquinoline, fluorene and fluoranthene. The latter two materials, obtained from Eastman Organic Chemicals, were purified by zone refining in an atmosphere of purified nitrogen for forty passes. The remaining chemicals were obtained from the K & K Chemical Company and were purified by chromatography, vacuum sublimation and zone refining. Although these purification processes may not remove all impurities from every material tested, it has been shown that technical grade phenanthrene, as received and with no further

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purification, still exhibited a substantial heat capacity anomaly.[5]

The measurements were performed using a high precision microcalorimeter of the differential type characterized by a linear temperature rise.[6] At heating rates of 1°C/min this calorimeter is capable of detecting energy absorption differences between a sample and dummy of about 0.005 cal. One side of the calorimeter was loaded with 0.3–0.5 gm of the sample in a sealed copper cylinder and the other side contained iron, which is essentially inert at the temperatures of interest. From −60°C to 40°C a mixture of dry ice and methanol was used as the ambient and from room temperature to the melting point of the sample silicone oil was the ambient. A small piece of pure indium was used to calibrate the calorimeter. Possible errors in estimating base lines and measurements of recorder-trace areas account for an error of about 5%.

Of the materials tested, anthracene and pyrene were run as controls and no heat capacity anomaly was found in these from −60°C to their melting points. Furthermore, of all the others, only chrysene was found to exhibit an anomaly. In the vicinity of 230°C an anomalous absorption of energy of 860 ± 40 cal/mole was found. This result is not inconsistent with the premise that the crowded hydrogen atoms are responsible for the anomalous behavior. It is possible that, in the cases where no anomaly was found, either weak intermolecular forces allow the transition to take place at temperatures lower than −60°C or strong intermolecular forces force a transition to take place above the melting point.

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