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Crystal lattices of the plastic crystals norbornadiene, norbornylene and norbornane.

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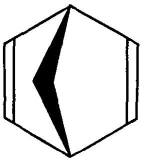
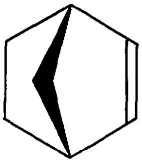
The crystal lattices of the plastic crystals norbornadiene, norbornylene and norbornane have been determined using an X-ray powder technique. Norbornadiene and norbornylene each exhibit only one plastic phase, characterized by a hexagonal close-packed structure. The results obtained show that for norbornadiene $a = 5{\cdot}89$, $c = 9{\cdot}51$ Å and for norbornylene $a = 6{\cdot}08$, $c = 9{\cdot}81$ Å. Norbornane has two distinct plastic phases. The one at lower temperature has a hexagonal close-packed structure, $a = 6{\cdot}17$, $c = 10{\cdot}03$ Å, while above the phase transition at 306 °K an f.c.c. structure, $a = 8{\cdot}73$ Å, is observed.

Crystals composed of globular molecules normally exhibit a high temperature solid phase in which the molecules undergo rapid isotropic reorientation, and the crystals are easily deformed mechanically. This plastic phase is usually bounded at high temperatures by the melting point and at low temperatures by a transition to a structure of lower symmetry with greatly restricted molecular mobility. The crystal structure of the plastic phase of many molecular crystals has been determined and it is usually found that the molecules are located on a lattice characterized as f.c.c. or b.c.c. (*e.g.* Dunning 1961). Only one example so far reported is known to the authors: cyclopentane, which has h.c.p. structure (Post, Schwartz & Fankuchen, 1951).

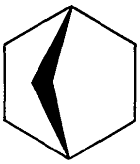
We report the crystal structure determination of three organic molecular crystals, norbornadiene (bicyclo[2,2,1]-heptadiene-2,5), norbornylene (bicyclo[2,2,1]heptene-2) and norbornane (bicyclo[2,2,1]heptane), each measured in the plastic phase. These are all composed of bridged cyclic molecules, differing only by the existence of double bonds as indicated schematically in the diagram. Their thermodynamic properties, however, differ considerably (Westrum, 1969). Norbornane is particularly unusual in that there is a phase transition (involving the very low entropy change of 0·06 cal.mol^{-1}.deg^{-1}) at 306 °K which divides two plastic phases.



Norbornadiene



Norbornylene



Norbornane

Unit cells were determined using a Debye–Scherrer powder camera with a Philips PW1008 X-ray generator using Cu $K\alpha$ radiation. All three compounds were found to produce powder photographs which were indexed as hexagonal, except the upper temperature phase of norbornane, which was found to be f.c.c.

Norbornadiene

The plastic phase exists from 202 to 254 °K. Measurements at 228 ± 8 °K gave nine lines which were fitted by lattice parameters $a = 5{\cdot}89$, $c = 9{\cdot}51$ Å.

Norbornylene

The plastic phase exists from 129 to 320 °K. Measurements at 297 ± 1 °K gave fifteen lines which were fitted by $a = 6{\cdot}08$ and $c = 9{\cdot}81$ Å.

Norbornane

The low temperature plastic phase exists from 131 to 306 °K and at 297 ± 1 °K fourteen lines were obtained and fitted by $a = 6{\cdot}17$ and $c = 10{\cdot}03$ Å.

In all three cases above, $c/a = 1{\cdot}63$ to within the accuracy (1 %) of the measurements. The structures are therefore close packed hexagonal.

In the upper temperature phase of norbornane, existing from 306 to 360 °K we find at 313 ± 5 °K an f.c.c. lattice with $a = 8{\cdot}73$ Å. Ten lines were observed and fitted to this structure. For both plastic phases, the distance between nearest neighbour molecules is 6·17 Å. The small specific heat anomaly and low entropy change associated with the transition (Westrum, 1969) is therefore associated with structural rearrangement from h.c.p. to f.c.c. (not b.c.c to f.c.c. as has been suggested by Guthrie & McCullough, 1961). We note that this structural change has only a small effect on activation energies and absolute magnitudes of translational and reorientational motion of the molecules as determined in the two phases by nuclear magnetic resonance (Folland, Jackson & Strange, 1972).

It is perhaps surprising that so few plastic molecular crystals have h.c.p. structure. The plastic phases of substances with similar molecular structures such as 3-azabicyclo[3,2,2]nonane, 1,4-diazabicyclo[2,2,2]octane, 1-azabicyclo[2,2,2]octane and bicyclo[2,2,2]octane all exhibit an f.c.c. structure. Calculations, using a Lennard-Jones potential for the simplest molecular crystals, the solid rare gases, suggest that the energy difference between h.c.p. and f.c.c. structures is very small, but h.c.p. is favoured (Meyer, 1969). All these solids, except solid helium, crystallize as f.c.c. However, impurities can produce hexagonal close packing, but usually at higher temperatures. We note that in norbornane the low temperature phase is hexagonal and not the high temperature phase.

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