The Crystal Structure of Norbornane

Andrew N. Fitch*[†][a] and Hervé Jobic[b]

[a] Department of Chemistry, Keele University, Staffordshire, UK ST5 5BG
[b] Institut de Recherches sur la Catalyse, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France

The crystal structure of the low-temperature, ordered phase of norbornane has been solved and refined from high-resolution powder X-ray diffraction data collected using synchrotron radiation.

Norbornane, bicyclo[2.2.1]heptane, is one of the simplest bicyclic aliphatic compounds. The molecule has C_{2v} symmetry, and is slightly strained. The molecular structure has been investigated using electron diffraction, spectroscopy and theoretical approaches,[1,2] but uncertainty remains concerning the relative lengths of the shortest carbon–carbon bonds associated with C(1) on the bridgehead.[2] Like many globular molecules, norbornane is orientationally disordered at ambient temperatures, transforming from cubic to hexagonal at 306 K, and to an ordered phase at 131 K.[3–5] Single crystals of the ordered phase have not been available so the crystal structure has remained undetermined. The thermodynamic, dynamic and spectroscopic properties of norbornane in its solid phases have been of interest.[3–8] A recent vibrational spectroscopic study[8] has addressed the problem of the structure of the ordered phase, and possible orthorhombic and lower-symmetry space groups have been identified. We report here the crystal structure of this phase solved from high-resolution powder X-ray diffraction studies using synchrotron radiation on station 2.3[9,10] at Daresbury Laboratory.[‡]

Because of the parallel-beam optics, the positions of diffraction peaks collected using station 2.3 are insensitive to the effects of specimen transparency and modest sample misalignment. They can therefore be obtained with a high degree of accuracy and are ideal for indexing. In an earlier study[11] the diffraction pattern of ordered norbornane was indexed. However it has become apparent that this phase can suffer from severe preferred orientation which has impeded the solution and refinement of the crystal structure. Several attempts have been necessary to obtain a diffraction pattern in which this effect is reduced to an acceptable level.

The structure is shown in Fig. 1. Although from a crystal structure an accurate molecular structure should also be

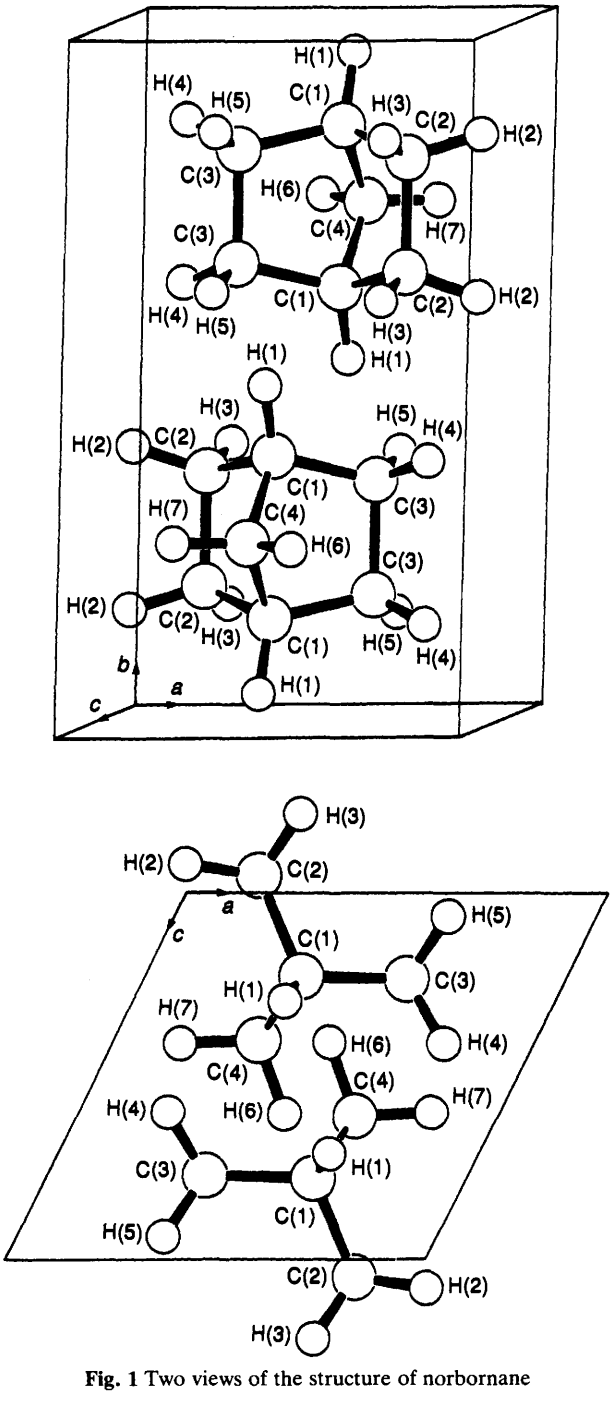

Fig. 1 Two views of the structure of norbornane

[†] *Present address*: ESRF, BP 220, 38043 Grenoble Cedex, France.

[‡] *Crystal data* for norbornane (bicyclo[2.2.1]heptane), at 50 K: C_7H_{12}, $M = 96.17$, monoclinic, space group $P2_1/m$, $a = 5.9365(3)$, $b = 9.6818(1)$, $c = 5.7116(3)$ Å, $\beta = 116.356(5)°$, $V = 294.16(2)$ Å^3, $Z = 2$, $D_c = 1.086$ g cm^{-3}. Norbornane (Aldrich, 98%) was ground under liquid nitrogen and loaded onto a flat-plate, copper sample holder and covered with a Kapton foil. The sample was cooled to 50 K and rotated in a liquid-helium-cooled cryostat on the diffractometer 2.3[9,10] at Daresbury laboratory. A powder X-ray diffraction pattern was measured in θ–2θ geometry counting for 2 s per 0.01° step, with a wavelength of 1.39839(4) Å. In an earlier study under similar conditions[11] the unit cell was obtained from the positions of twenty low-angle peaks using the autoindexing program FZON.[12] From the systematic absences $0k0 : k = 2n + 1$ absent, the space groups $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2) appear likely. With the latter, one of the two orthogonal mirror planes of the molecule must be coincident with a mirror plane in the unit cell, at $y = \frac{1}{4}, \frac{3}{4}$. Using the program CERIUS,[13] which allows facile building and display of crystal structures, different arrangements were investigated, and the solution found. The structure was refined with an overall isotropic thermal parameter by the Rietveld[14] method using the program MPROF[15] to restrain the geometry[1,2] to symmetry C_{2v}, with C–C bond distances of 1.536, 1.546 and 1.573 Å, C–H distances of 1.09 Å (restraints weighted ±0.001 Å), and H–C–H angles of 109° ± 0.5°, as the latter tended to become too small. Even with the restraints, the final distances and angles differ slightly from these values. Preferred orientation along [010] and narrower $0k0$ reflections are difficult to eradicate, even with determined grinding and care in mounting the sample. The preferred orientation was modelled using the March–Dollase model.[16] Parts of the diffraction pattern affected by peaks arising from penetration of the X-rays through to the sample holder were excluded. Final R factors, $R_{wp} = 13.8\%$, $R_{exp} = 5.4\%$, $R_1 = 9.1\%$. The observed and calculated profiles are shown in Fig. 2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Cystallographic Data Centre. See Notice to Authors. Issue No. 1.

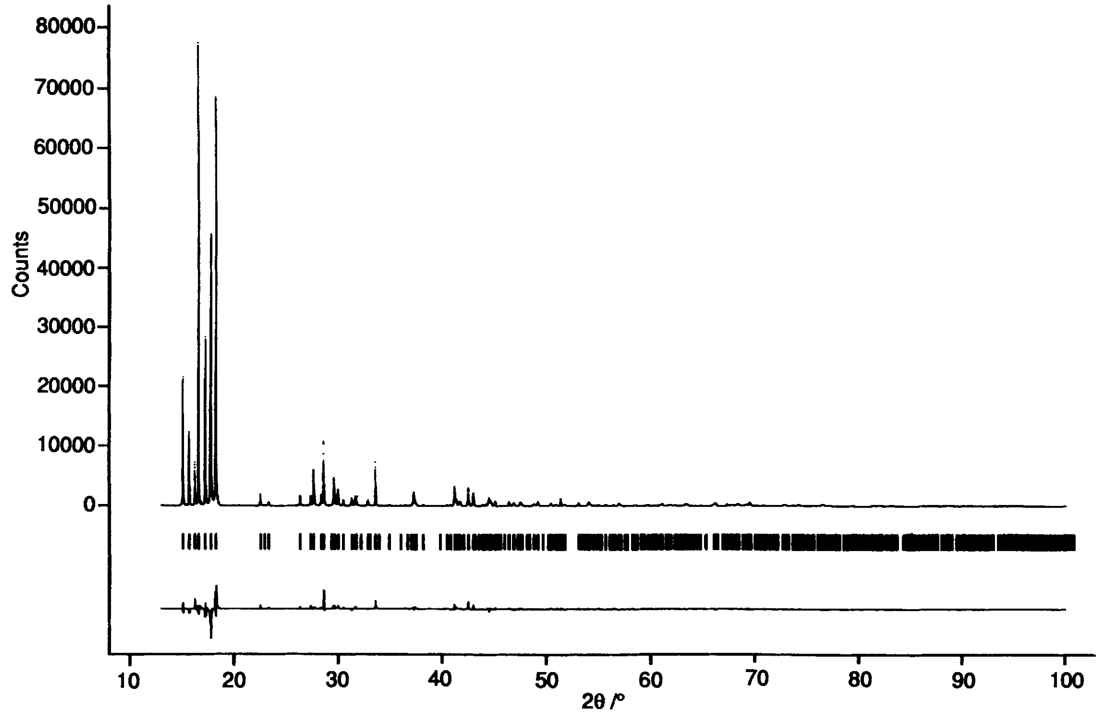

Fig. 2 Observed (points), calculated (full curve) and difference profiles for the ordered phase of norbornane at 50 K. The positions of the peaks contributing to the profile are indicated.

available, the persistence of preferred orientation means that it has been necessary to constrain the molecule to the best geometry available.[1,2] It is expected that future studies employing spinning capillary samples will overcome this problem. The chosen space group for norbornane, $P2_1/m$ (C_{2h}^2), is not one proposed by Kawai *et al.*[8] However the noncentrosymmetric subgroup $P2_1$ (C_2^2) is compatible with the spectroscopic measurements. The latter space group implies the loss of the crystallographic mirror planes at y = ¼, ¾, due to a rotation of the molecule so that the mirror plane of the molecule is no longer parallel with the *ac* plane of the unit cell. If such a rotation is present then it is small, since no evidence for it could be found within the limitations of this study.

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