Ab initio structure determination of norbornene from powder diffraction data using molecular packing analysis method

Jinrong Min, Jordi Benet-Buchholz and Roland Boese*

Institut für Anorganische Chemie, Universität-GH Essen, D-45117 Essen, Germany.
E-mail: boese@structchem.uni-essen.de

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The previously unknown crystal structre of the low temperature ordered phase of norbornene was solved from a set of powder diffraction data with severe preferred orientation collected on a laboratory X-ray diffractometer by first predicting the starting model by means of molecular packing analysis method, which was then refined against the experimental data by means of Rietveld method.

Norbornene, bicyclo[2.2.1]-2-heptene, belongs to a family of compounds which have a globular molecular shape, form orientational disordered plastic crystals and undergo phase transitions from high temperature disorderd phases to low temperature ordered phases. During the phase transition, plastic crystals usually shatter and it is very difficult to obtain single crystals from the ordered phases. For norbornane (C_7H_{12}),[1] the crystal structure of the low temperature ordered phase was solved by model building due to the special geometrical arrangement of molecules in the unit cell and refined against high-resolution synchrotron powder diffraction data. For norbornadiene (C_7H_8),[2] the crystal structure of the low temperature ordered phase was solved from single crystal grown by means of the *in situ* technique[3] from solution. This technique, however, failed so far for norbornene.

There is currently a major renaissance in the use of powder diffraction techniques for determining crystal structures at atomic resolution.[4] In this paper, we report the crystal structure of the low temperature ordered phase of norbornene (commercial product) solved from powder diffraction data at 105 K on an ordinary laboratory X-ray diffractometer (Siemens D5000, 7° position-sensitive detector, curved graphite monochromator and Cu-Kα_1 radiation). The structure only exists in an ordered form at low temperatures. The sample was sealed inside a capillary (d = 0.3 mm) and data were collected in steps of 0.0166° from 10.40 to 110.40° in 2θ, counting time 200 s per step. Indexing based on a monoclinic unit cell (TREOR90[5]) and refinement of unit cell dimensions with the whole pattern gave: a = 7.6011(7), b = 8.5985(8), c = 8.7290(8) Å, β = 97.313(3°), V = 565.87(9) Å^3. Systematic absences suggested that the possible space group was $P2_1/c$, although $P2_1$, $P2$, Pc, $P2/c$ could not be excluded for sure in the beginning. $P2/m$, Pm and $P2_1/m$ are excluded from symmetry considerations.

The sample has severe preferred orientation and contains a little impurity of the hexagonal high temperature disordered phase because not all of the sample has transformed into the ordered phase when cooling through the phase transition point at 145.3 K.[6] Preferred orientation, a well known problem that can seriously undermine structure solution attempts, is present in this sample. Therefore, the conventional structure determination method[7] did not succeed in this case, and we turned to molecular packing analysis method.[8] We first predicted structure models by molecular packing analysis method in possible space groups, simulated the diffraction patterns which were then compared to the experimental pattern. Subsequent Rietveld refinement[9] led to a final model.

The only inputs required by molecular packing analysis method are the molecular structure and an intermolecular force field. This method is used to predict the structure of crystals or molecular clusters by energy minimization, based on a variety of published force fields or a user-defined force field. The intermolecular or nonbonded energy of the molecular assembly is represented by a pairwise sum over atoms in different molecules. Crystal lattice sums are accurately evaluated using the accelerated convergence method.[10] The structural variables considered by the program are the rotations and translations of several molecules, and selected internal rotations. Molecules may be related by space group symmetry operations. In our case, we constructed the molecular structure from norbornadiene.[2] The energy minimization was implemented using the fixed unit cell dimensions and on different possible space groups. Rotation and translation parameters of the independent molecule were allowed to vary, while the symmetry-related molecules moved in a dependent way. We just considered the VDW energy term, because Coulomb energy is insignificant for this compound. The final minimized energies are listed in Table 1. From this table, we can see that $P2_1/c$ has the lowest packing energy. These predicted models were used to simulate the powder diffraction patterns, which are shown in Fig. 1. From this figure, we can exclude the space groups $P2$, $P2_1$, and Pc. When we tried to refine the structure in $P2/c$, it did not

Table 1 Molecular packing energies of the low temperature ordered phase of norbornene assuming different space groups at fixed cell dimensions

Space group	$P2_1/c$	$P2/c$	Pc	$P2_1$	$P2$
Packing energy/kJ mol^{-1}	−56.2	−43.9	−32.7	−19.1	22.4

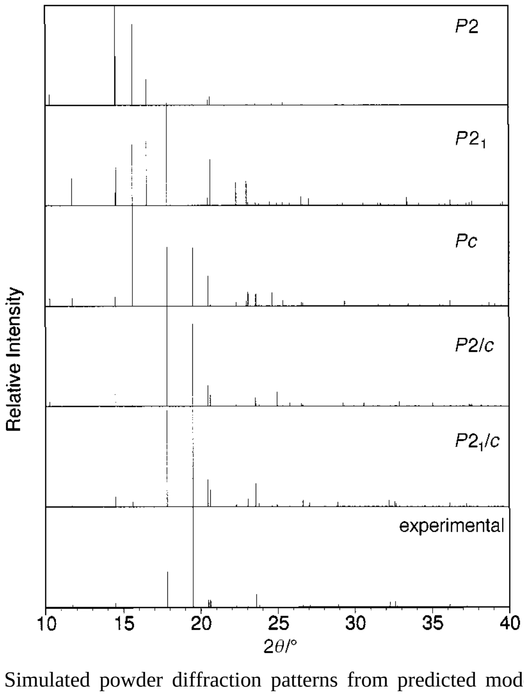

Fig. 1 Simulated powder diffraction patterns from predicted models by molecular packing analysis method on different space groups.

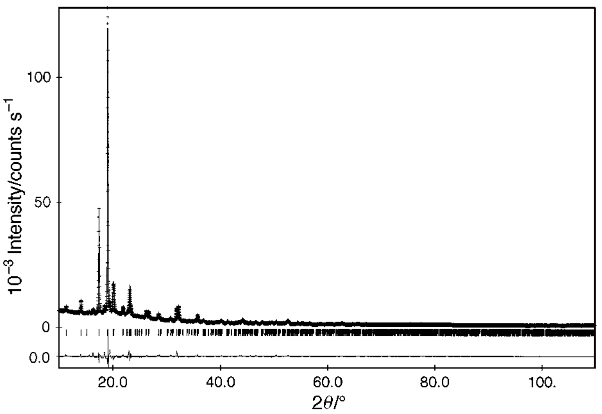

Fig. 2 Observed (plus marked line), calculated (solid line) and difference patterns (at the bottom) for the low temperature ordered phase of norbornene at 105 K. The short vertical lines mark the positions of possible Brag reflections.

converge. Therefore, we can conclude that the correct space group of the low temperature phase of norbornene is $P2_1/c$.

The atomic coordinates of the model predicted by molecular packing analysis method were input into the Rietveld refinement program FULLPROF.[11] A pseudo-Voigt profile function was selected to describe the diffraction peak profiles. After some cycles of refinement, the difference pattern between the observed and calculated patterns shows obvious preferred orientation along [111], which was modelled using Marsh–Dollase function.[12] At the beginning of refinement, only the positions of the carbon atoms were refined with an overall isotropic thermal parameter and without any constraints on the bond distances. After some cycles, one C–C bond became remarkably shorter than the other C–C bonds, indicating its double bond characteristic. The positions of the hydrogen atoms were generated using the SHELXTL utilities XP[13] on the ideal positions after each cycle of refinement of carbon atoms. Fig. 2 shows the Rietveld refinement pattern. The remarkably good fit between the observed and calculated patterns supports the structure model.[14] Fig. 3 shows the molecular structure of the low temperature ordered phase of norbornene.

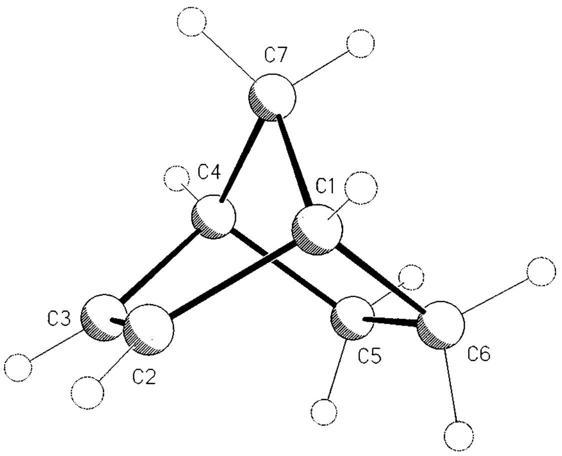

Fig. 3 Molcular structure of low temperature ordered phase of norbornene.

In summary, from the successful structure determination of norbornene, we wish to encourage the scientific community to exploit the structural information which can be readily obtained from powder diffraction data with inhouse techniques.

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Notes and references

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14 *Crystal data* for norbornene at 105 K: C_7H_{10}, M = 94.16, monoclinic, space group $P2_1/c$, a = 7.6011(7), b = 8.5985(8), c = 8.7290(8) Å, β = 97.313(3)°, V = 565.87(9) Å^3, Z = 4, D_c = 1.105 g cm^{-3}. Overall isotropic thermal parameter B = 3.2(1) Å^2. Final Rietveld refinement converted to R_p = 4.66%, R_{wp} = 6.48%, R_b = 10.0%, R_{exp} = 2.00%, χ^2 = 10.5 for 35 variables and 715 reflections distributed over 6025 profile points. Bond lengths (Å): C(1)–C(2) 1.524(1), C(3)–C(4) 1.522(1), C(2)–C(3) 1.334(1), C(4)–C(5) 1.563(1), C(1)–C(6) 1.562(1), C(5)–C(6) 1.557(1), C(1)–C(7) 1.547(1), C(4)–C(7) 1.545(1). See http://www.rsc.org/suppdata/cc/1999/2751/ for listing of bond lengths and angles and atomic coordinates.

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