

## Determination of a Molecular Crystal Structure by X-Ray Powder Diffraction on a Conventional Laboratory Instrument

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The crystal structure of formylurea, C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, has been solved and refined from X-ray powder diffraction data collected on a conventional laboratory diffractometer; this is the first previously unknown organic structure containing only light atoms to be solved by this technique, and suggests that powder diffraction has much to offer in the structure determination of organic molecular crystals.

Although a number of inorganic crystal structures have been solved using X-ray powder diffraction data,<sup>1-5</sup> very little has been achieved in the field of organic and organometallic structure determination by the powder method. Indeed, until very recently, the powder technique had only been applied to known molecular structures: Wilson<sup>6</sup> demonstrated the use of a Patterson search method employing poor quality laboratory data in the solution of two simple organic compounds, and Cernik *et al.*<sup>7</sup> solved the structure of the drug cimetidine, C<sub>10</sub>H<sub>16</sub>N<sub>6</sub>S, using very high quality powder diffraction data from a synchrotron source. The latter is probably the most complex structure to have been solved by powder diffraction to date. More recently, Lightfoot *et al.*<sup>8</sup> have demonstrated the use of a modern high-resolution laboratory-based powder diffractometer in the solution and refinement of two previously unknown molecular structures; [(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>3</sub>)]<sup>+</sup>I<sup>-</sup> and *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>. It is clear that the routine determination of simple molecular crystal structures on laboratory-based instruments represents a major challenge in the application of powder diffraction techniques. Success in this aim will open up the field to a much wider community of users, and provide invaluable structural information to chemists when crystals of sufficient size and quality for conventional single crystal X-ray diffraction studies are not available.

The problems encountered in the solution of 'equal-atom' structures (*i.e.* organic compounds, such as formylurea,

containing no elements heavier than oxygen) are particularly severe. In such cases, traditional direct methods of structure determination must be employed and these must operate on more limited data than is the case when single crystal diffraction data are used. In effect the information obtained in a single crystal experiment is condensed into one dimension in a powder pattern and the inevitable overlap of reflections leads to a severe loss of information. Moreover, in the case of 'equal-atom' structures, a more significant fraction (at least 50%) of the structure must be determined directly from the solution stage of the data analysis—*i.e.* prior to Rietveld refinement. In the case of *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>, for example, only three atoms were located *via* direct methods,<sup>8</sup> the remainder of the structure being built up by difference Fourier methods applied to Rietveld analysis of the whole diffraction profile. It is important to explore the limitations of direct methods solutions from powder diffraction data, and with this aim we have begun to study a range of organic compounds of increasing complexity in order to define the current boundaries of this approach. Here, we present the crystal structure of formylurea, the first previously unknown, 'equal-atom' organic structure to be solved from powder diffraction data recorded on a conventional laboratory instrument.

The sample of formylurea (Lancaster) was used directly as received, ground and placed between transparent tape. Data were collected in transmission mode on a Stoe STADI/P high-resolution X-ray powder diffractometer using Ge-

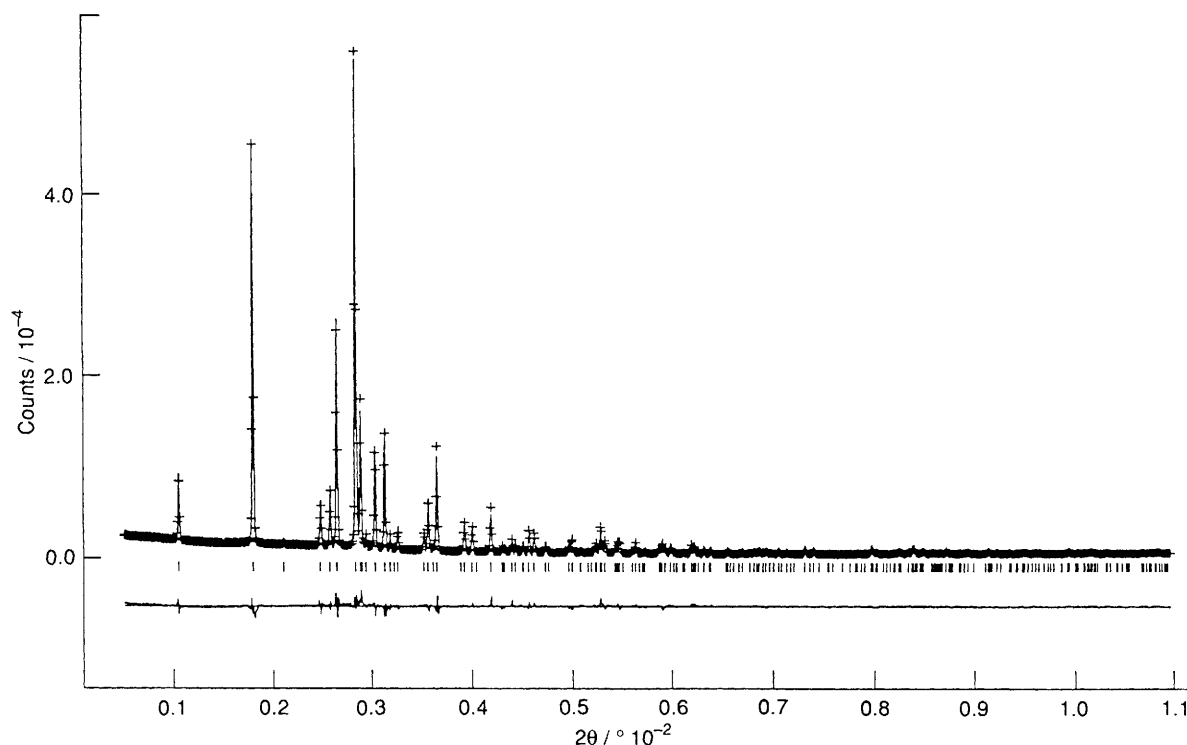


Fig. 1 Final observed (+ marks), calculated (solid line) and difference (below) profiles for the Rietveld refinement of formylurea. Reflection positions are marked.

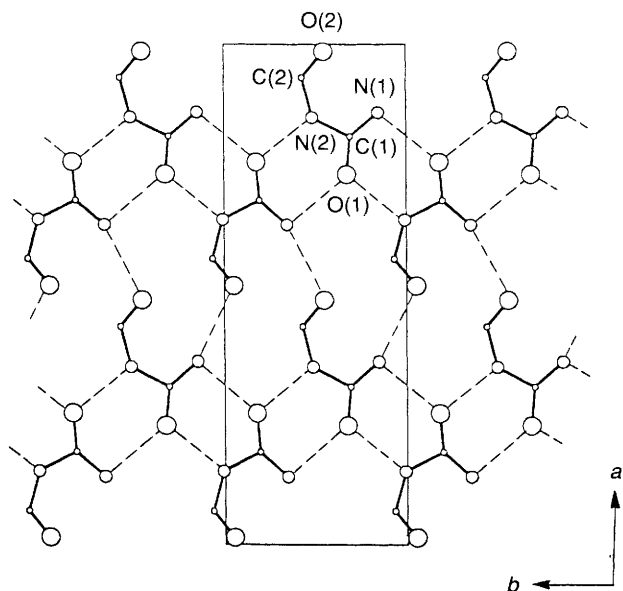


Fig. 2 Crystal structure of formylurea viewed along the *c* axis. The dashed lines represent a probable hydrogen-bonding scheme.

Table 1 Final refined atomic parameters for formylurea, space group  $Pn2_1a$ ,  $a = 16.8156(5)$ ,  $b = 6.0608(1)$ ,  $c = 3.6696(1)$  Å

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (iso)/Å <sup>2</sup>
C(1)	0.314(3)	0.305	0.329(5)	0.025(2)
C(2)	0.433(2)	0.558(5)	0.209(2)	0.032(2)
N(1)	0.361(9)	0.146(4)	0.459(5)	0.034(2)
N(2)	0.352(5)	0.503(7)	0.174(4)	0.031(2)
O(1)	0.238(7)	0.313(7)	0.301(6)	0.046(2)
O(2)	0.486(6)	0.440(3)	0.339(2)	0.056(2)

monochromatised Cu-K $\alpha$ 1 radiation. The total data range was 5–110° in  $2\theta$ , measured in 0.02° steps, and the total data collection time was about 15 h. A position-sensitive detector covering about 6° in  $2\theta$  was employed.

The powder pattern was indexed on the basis of the first 29 observable peaks using the program TREOR.<sup>9</sup> This produced an orthorhombic unit cell with dimensions  $a = 16.822$  Å,  $b = 6.062$  Å,  $c = 3.670$  Å. Systematic absences were compatible with space groups  $Pnma$  (centrosymmetric) and  $Pn2_1a$  (non-centrosymmetric). Density considerations suggested the presence of four molecules per unit cell, hence requiring all atoms to occupy the special positions ( $x$ ,  $1/4$ ,  $z$ ) if the space group was  $Pnma$ . Such a structure would produce a dominant intensity in the (020) reflection, which was not observed. Hence, the space group could be unambiguously assigned as  $Pn2_1a$ . This assignment was later supported by the standard statistical  $N(Z)$  and  $E$  distribution tests after data reduction; although the results from applying such tests to powder diffraction data should clearly be interpreted with caution, our experience to date suggests that they are in general reliable. A total of 112 integrated intensities were then extracted from the powder pattern over the range  $5^\circ < 2\theta < 75^\circ$  by a modified Rietveld<sup>10</sup> profile-fitting procedure,<sup>11</sup> incorporated into the GSAS<sup>12</sup> program package. This procedure decomposes the overlapping regions of the pattern to give unique integrated intensities for all reflections. In the present case there were 75 non-overlapping or partially overlapping reflections and 37 heavily overlapping reflections. These were used as input to the direct methods program SIR.<sup>13</sup> The best solution produced an E-map in which the five highest peaks gave a recognisable molecular fragment. These were input as equal atoms into a Rietveld refinement of the whole diffraction profile. This model was a sufficiently good starting point to complete the structure solution, despite the fact that the

position of one of the input atoms later proved to be incorrect. The remaining two non-H atoms were found by difference Fourier methods. Final atomic assignments were based on the results of the refined model, using considerations of both intramolecular geometry and intermolecular geometry (*i.e.* the hydrogen-bond arrangement) to distinguish O(1) and N(1). The final Rietveld refinement converged to  $R_{wp} = 7.55\%$ ,  $\chi^2 = 7.8$ , for 41 variables and 345 reflections distributed over 5238 profile points (Fig. 1). The crystal structure is shown in Fig. 2, with a probable hydrogen-bonding scheme indicated. All bond lengths and angles† are within acceptable limits consistent with the precision of the data.

This structure determination demonstrates the feasibility of obtaining reliable and useful structural information on simple organic molecular crystals *ab initio* from powder diffraction data. When single crystals are readily available, and in particular when the most accurate bond lengths and angles are required, then single crystal diffraction methods are clearly preferred. However, for many purposes a knowledge of the molecular geometry and packing arrangement are sufficient, and in these cases powder diffraction data are equally appropriate. Clearly the method applied here has the potential to become more widely and routinely used, although it has yet to be tested on more complex systems, of up to say 25 or 30 atoms in the asymmetric unit.

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† Final refined parameters:  $C_2H_4N_2O_2$ ,  $M_r = 88.07$ , orthorhombic,  $Pn2_1a$ ,  $a = 16.8156(5)$ ,  $b = 6.0608(1)$ ,  $c = 3.6696(1)$  Å,  $V = 374.00$  Å<sup>3</sup>. Individual isotropic thermal parameters. Bond lengths (Å): C(1)–N(1) = 1.34(1), C(1)–N(2) = 1.49(1), C(1)–O(1) = 1.29(1), C(2)–O(2) = 1.23(1), C(2)–N(2) = 1.39. Bond angles (deg): N(1)–C(1)–N(2) = 116(1), N(1)–C(1)–O(1) = 132(1), N(2)–C(1)–O(1) = 112(1), C(1)–N(2)–C(2) = 126(1), O(2)–C(2)–N(2) = 127(1). Intermolecular distances (Å): N(1)–O(1) = 2.91(1), N(1)–O(2) = 2.94(1), N(2)–O(1) = 2.79(1), see also Table 1.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.