

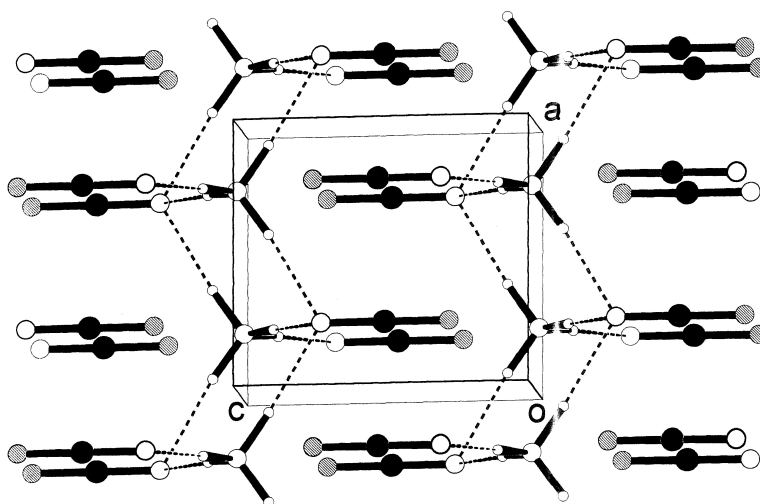
Article

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## Ammonium Cyanate Shows N–H···N Hydrogen Bonding, Not N–H···O

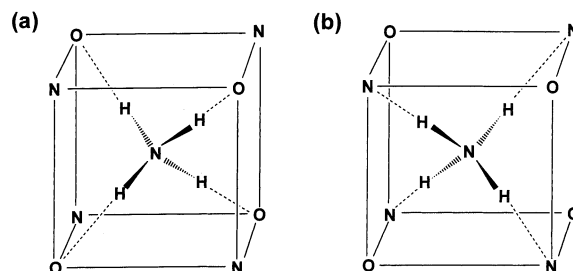
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**Abstract:** The transformation of ammonium cyanate into urea, first studied over 170 years ago by Wöhler and Liebig, has an important place in the history of chemistry. To understand the nature of this solid state reaction, knowledge of the crystal structure of ammonium cyanate is a prerequisite. Employing neutron powder diffraction, we demonstrate conclusively that, in the structure of ammonium cyanate, the  $\text{NH}_4^+$  cation forms N–H···N hydrogen bonds to four cyanate N atoms at alternate corners of a distorted cube, rather than our previously proposed alternative arrangement with N–H···O hydrogen bonds to cyanate O atoms at the other four corners.

Through the work of Wöhler and Liebig in the late 1820s, the transformation of ammonium cyanate into urea occupies an important place in the history of chemistry.<sup>1</sup> Recently, we reported<sup>2</sup> a study of the crystal structure of ammonium cyanate, based on Rietveld refinement of laboratory X-ray powder diffraction data. With two formula units  $\text{NH}_4\text{NCO}$  in the tetragonal unit cell ( $a = b = 5.15 \text{ \AA}$ ,  $c = 5.56 \text{ \AA}$ ) in space group  $P4/nmm$  or  $P4/n$ ,<sup>3</sup> the linear cyanate anions lie along the 4-fold axes, and the N atom of the ammonium cation is located on a site of  $\bar{4}$  symmetry. Within this structure, the  $\text{NH}_4^+$  cation could form four N–H···O hydrogen bonds to four cyanate O atoms at alternate corners of a distorted cube (**A**; Figure 1a), or four N–H···N hydrogen bonds to cyanate N atoms at the other four corners (**B**; Figure 1b), and there could be disorder (dynamic or static) between situations **A** and **B**, which are interconverted by  $90^\circ$  reorientation of the cation about one of its 2-fold axes. Our Rietveld refinement of the laboratory X-ray powder diffraction data<sup>2</sup> led to a description in which the  $\text{NH}_4^+$  cation forms four N–H···O hydrogen bonds (i.e., **A**) rather than four N–H···N hydrogen bonds (i.e., **B**). Apparent support for the N–H···O model was also obtained from the results of energy calculations,<sup>4</sup> which indicated a  $10 \text{ kcal mol}^{-1}$  preference for this structure over the alternative one with inverted orientation of the



**Figure 1.** Schematic illustration of the distorted cube in the crystal structure of ammonium cyanate, with O and N atoms of cyanate anions at alternate corners. Two different orientations of the ammonium cations are shown, corresponding to: (a) the formation of N–H···O hydrogen bonds (situation **A**), and (b) the formation of N–H···N hydrogen bonds (situation **B**).

tetrahedral cation. However, in sobering contrast, our subsequent Rietveld analysis of improved X-ray powder diffraction data from a synchrotron source,<sup>5</sup> discussed below, has led to virtually indistinguishable quality of fit for the two possible orientations of the  $\text{NH}_4^+$  tetrahedron,<sup>6</sup> and further energy calculations with several computational schemes have shown that the relative energies of

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(1) Wöhler, F. *Pogg. Ann.* **1828**, *12*, 253.

(2) Dunitz, J. D.; Harris, K. D. M.; Johnston, R. L.; Kariuki, B. M.; MacLean, E. J.; Psallidas, K.; Schweizer, W. B.; Tykwinski, R. R. *J. Am. Chem. Soc.*, **1998**, *120*, 13 274.

(3) The initial X-ray analysis was based on the assumption of the lower symmetry space group  $P4/n$  but the deviation of the derived structure from  $P4/nmm$  was insignificant.

(4) Periodic Hartree–Fock calculations with 6-31G\*\* basis set, using the CRYSTAL95 program.

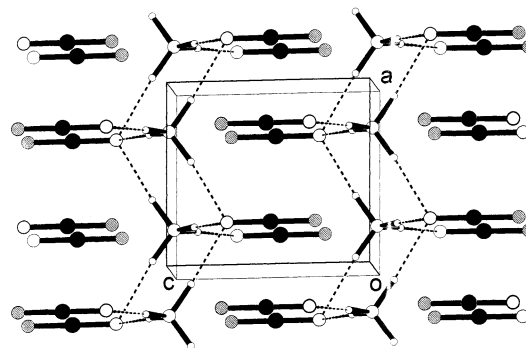
(5) Synchrotron X-ray powder diffraction data were recorded (for both  $\text{NH}_4\text{NCO}$  and  $\text{ND}_4\text{NCO}$  samples) on Station 2.3 at the Synchrotron Radiation Source, Daresbury Laboratory [ $\lambda = 1.400 \text{ \AA}$ ; capillary (1 mm diameter) sample holder; beam size  $1 \times 10 \text{ mm}^2$ ]. The total  $2\theta$  range was  $10^\circ$  to  $80^\circ$  measured in  $0.01^\circ$  steps, and collected over 1 h. The data were normalized for beam decay. There were no distinguishable differences between the data recorded for  $\text{NH}_4\text{NCO}$  and  $\text{ND}_4\text{NCO}$ : the results reported refer to analysis of the data for the deuterated material. Rietveld refinement of the synchrotron X-ray powder diffraction data was carried out using the program MPROF (A. D. Murray, A. N. Fitch, University College London, 1989).

(6) Although there is usually no difficulty about localizing H atoms in X-ray analysis based on single-crystal diffraction data (apart from the characteristic systematic contraction of apparent X–H bond distances), the reduction of information inherent in powder diffraction patterns can make H atom localization from analysis of X-ray powder diffraction data much more problematic.

the two possible structures are highly sensitive to details of the calculation and are hence unreliable.<sup>7</sup>

We first consider the Rietveld refinement calculations on the synchrotron X-ray powder diffraction data. Given the need, in general, to impose restraints on molecular geometry during Rietveld refinement of X-ray powder diffraction data, it is important to give consideration to the manner in which the geometry of the cyanate anion is restrained, as this could in principle have a bearing on other aspects of the refinement, such as the location of the H atoms of the  $\text{NH}_4^+$  cation. Thus, two different restrained geometries of the cyanate anion were considered,<sup>8</sup> corresponding to the extremes  $\text{O}=\text{C}=\text{N}^-$  (denoted **1**) and  $^-\text{O}-\text{C}\equiv\text{N}$  (denoted **2**). In each case, Rietveld refinement was carried out for the two different hydrogen bonding arrangements **A** and **B** discussed above. All four refinements give very good fit to the synchrotron X-ray powder diffraction data, with essentially flat difference plots between the experimental and calculated powder diffraction patterns in each case; thus, there are no significant differences in the visual quality of fit obtained in the four refinements, and only small differences in the values of the R-factors.<sup>9</sup> It is clear that because of the low X-ray scattering power of H atoms and the similar scattering powers of O and N atoms, X-ray powder diffraction does not provide a reliable basis for establishing the full details of the crystal structure of ammonium cyanate, particularly with regard to the details of the hydrogen bonding arrangement. This conclusion, together with the further uncertainties arising from our subsequent computational studies,<sup>7</sup> has led us to reinvestigate the details of the hydrogen bonding in ammonium cyanate.

Chastened by our experiences with the use of X-ray powder diffraction to tackle this problem, we turned to neutron powder diffraction of a deuterated sample  $\text{ND}_4\text{NCO}$ .<sup>10–12</sup> Rietveld refinements of the neutron powder diffraction data for  $\text{ND}_4\text{NCO}$  collected



**Figure 2.** Crystal structure of  $\text{ND}_4\text{NCO}$ , refined from neutron powder diffraction data recorded at 14 K, viewed along the  $b$ -axis. The dashed lines represent  $\text{N}-\text{D}\cdots\text{N}$  hydrogen bonds.

**Table 1.** Fractional Coordinates for the Crystal Structure of  $\text{ND}_4\text{NCO}$ , Determined at 14 K from Neutron Powder Diffraction Data [ $P4/nmm$ ;  $a = b = 5.0822(1)$  Å,  $c = 5.5513(1)$  Å; origin at  $\bar{1}$ ]

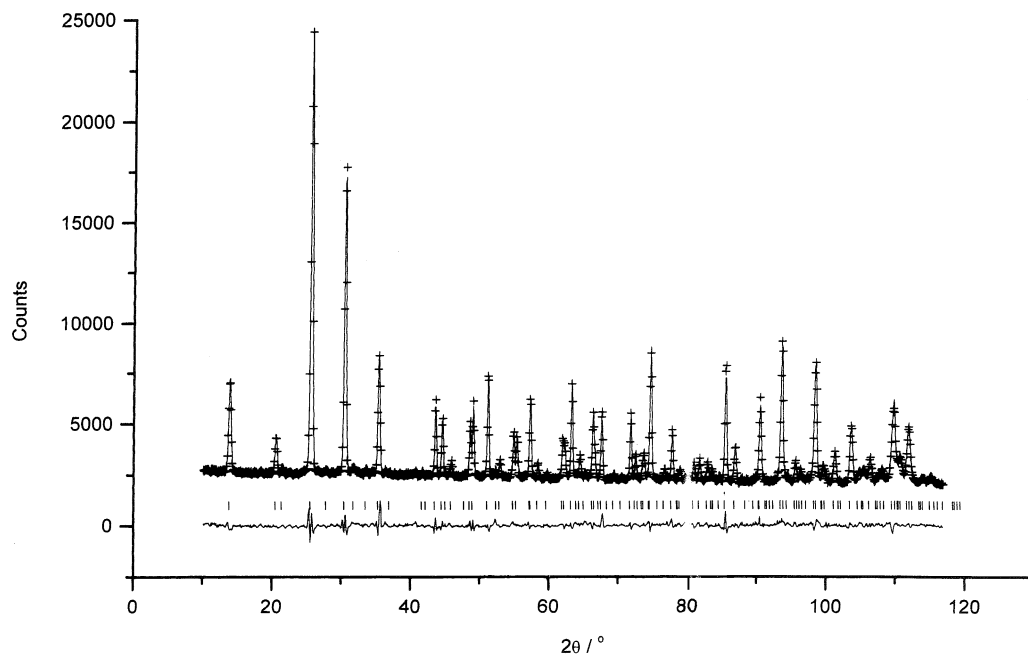
atom	$x$	$y$	$z$	$U_{\text{iso}}/\text{Å}^2$	occupancy
N	1/4	3/4	0	0.0036(5)	1
D	1/4	0.9163(5)	-0.1069(6)	0.0106(8)	0.809(5)
H	1/4	0.9163(5)	-0.1069(6)	0.0106(8)	0.191(5)
O	1/4	1/4	0.2818(9)	0.0040(9)	1
C	1/4	1/4	0.5007(10)	0.0024(6)	1
N	1/4	1/4	0.7153(5)	0.0024(6)	1

at 14 K were made for situations **A** and **B** respectively, with fractional occupancy by D and H (i.e.,  $\text{H}_{1-x}\text{D}_x$ ). The refinement for situation **B** led to physically sensible values of the isotropic displacement parameters  $U_{\text{iso}}$  for all atoms and occupancy variable  $x \approx 0.81$  (in close agreement with the level of deuteration deduced by experimental analysis<sup>10</sup>). Similarly, good quality fits to the data at other temperatures were obtained for situation **B**. In contrast, Rietveld refinements for situation **A** led at all temperatures to significantly inferior fits, as well as physically unreasonable values of  $U_{\text{iso}}$  for the cyanate N and O atoms (extremely low for O and high for N<sup>13</sup>) such as to simulate interchange of these atoms. Thus, it appears that the **A** refinement attempts to convert situation **A** into one that mimics situation **B**. Difference Fourier maps based on the parameters from the final Rietveld refinements for situation **B** show no significant features corresponding to H/D atoms in the alternative  $\text{N}-\text{H}\cdots\text{O}$  structure, and thus indicate that there is no appreciable disorder between hydrogen bonding situations **A** and **B**.<sup>14</sup>

The crystal structure (corresponding to situation **B**<sup>15</sup>) at 14 K is shown in Figure 2 (see also Table 1), and the fit to the experimental neutron powder diffraction data is shown in Figure 3. Rietveld refinements of the data collected at higher temperatures lead to essentially the same structure, apart from the expected lattice expansion<sup>16</sup> and minor changes in the interatomic distances. On warming from 14 to 288 K, the  $\text{N}\cdots\text{H/D}$  hydrogen bond distance shows a steady increase from 1.962(1) Å to 2.000(1) Å,<sup>17</sup> the C–N distance stays nearly constant close to 1.19 Å and the C–O distance shows a small but steady decrease from 1.215(5) Å to 1.174(8) Å.

- (7) Periodic Hartree–Fock calculations were carried out using the CRYSTAL95 and CRYSTAL98 packages for a range of different basis sets and a range of values of other parameters controlling the calculation (Posada, A.; Johnston, R. L.; Harris, K. D. M., unpublished results). In some cases, a lower energy was obtained for  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding, in others for  $\text{N}-\text{H}\cdots\text{N}$ . No geometry optimization was carried out, and the positions of all non-hydrogen atoms were fixed at those in the crystal structure. For some calculation conditions, the energetic ordering of the  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{N}$  structures was different depending on whether the coordinates of the non-hydrogen atoms were those determined at 14 K (from the neutron powder diffraction data presented here) or at ambient temperature (reported previously [2] from X-ray powder diffraction data). A more detailed appraisal of computational approaches for investigating this issue is required.
- (8) The restrained values were as follows; Situation **1**: O–C, 1.174 Å, C–N 1.192 Å; Situation **2**: O–C, 1.256 Å, C–N, 1.181 Å. The actual bond lengths obtained in the refinements remained close to these restrained values.
- (9) It is noteworthy that the lowest  $R_{\text{wp}}$  is obtained for situation **B-1** and the next lowest is for situation **A-1**, suggesting, not surprisingly, that the refinement calculations are more sensitive to the geometry of the cyanate anion than to the hydrogen bonding arrangement. The R-factors are: **A-1**,  $R_{\text{wp}} = 13.66\%$ ; **B-1**,  $R_{\text{wp}} = 13.35\%$ ; **A-2**,  $R_{\text{wp}} = 14.02\%$ ; **B-2**,  $R_{\text{wp}} = 13.71\%$ . The Rietveld difference plots for these refinement calculations are included in the Supporting Information.
- (10) Obtained by ion exchange between tetraethylammonium cyanate and ammonium thiocyanate- $d_4$  (Aldrich) in a nitrogen atmosphere. The deuteration level of the product, estimated by electron impact ionization mass spectrometry of samples converted to urea- $d_4$ , was about 77%.
- (11) The advantage of deuterated samples in neutron diffraction comes from the relatively large neutron scattering power of  $^2\text{H}$  compared with  $^1\text{H}$  and the strong incoherent neutron scattering of the latter.
- (12) Neutron powder diffraction data were collected on the C2 powder diffractometer at the NRU reactor (Chalk River, Ontario), with the sample packed inside a thin walled cylindrical vanadium tube of 5 mm diameter. The wavelength was 1.3286 Å, generated from the (531) reflection of a silicon monochromator with a takeoff angle of  $2\theta_m = 92.7^\circ$ . Temperature was varied using a closed-cycle refrigerator, measured using Si-diodes and controlled by a home-written temperature-control system. The horizontal incident collimation was  $0.4^\circ$ . Data for both  $\text{NH}_4\text{NCO}$  and  $\text{ND}_4\text{NCO}$  samples were collected at several temperatures (14, 77, 135, 210, 245, 288 K) over the  $2\theta$  range  $5^\circ$  to  $117^\circ$ , with a step size of  $0.1^\circ$  and a total data collection time of about 4 h at each temperature. Rietveld refinement of the neutron powder diffraction data was carried out using the program GSAS (Larson, A. C., Von Dreele, R. B., Los Alamos Laboratory Report No. LA-UR-86-748, 1987).

- (13) The neutron scattering length for N ( $9.36 \times 10^{-15}$  m) is appreciably larger than for O ( $5.805 \times 10^{-15}$  m).
- (14) This conclusion was confirmed by Rietveld refinement calculations for a disorder model comprising  $x$  % of situation **A** and  $(100-x)$  % of situation **B**. In such calculations,  $x$  refines, within experimental errors, to a value of zero.
- (15) Rietveld refinement for situation **B** was also carried out for the lower space group  $P4/n$  but the resulting deviation of the H/D atoms from the mirror planes was insignificant. The description in space group  $P4/nmm$  is therefore preferred.
- (16) Crystal data at higher temperatures (77–288 K) are given in Supporting Tables 2–6.



**Figure 3.** Rietveld refinement ( $R_{wp} = 3.60\%$ ;  $R_p = 2.58\%$ ) of  $\text{ND}_4\text{NCO}$  from the neutron powder diffraction data recorded at 14 K (experimental pattern, + marks; calculated pattern, solid line; difference profile, lower line; tick marks indicate reflection positions).

It is well-known that molecular dimensions obtained by diffraction analysis may appear too short because of the effect of molecular libration,<sup>18</sup> which increases with temperature. Since in this study only isotropic displacement parameters  $U_{iso}$  are available from the Rietveld refinements, it is not possible to correct the bond distances for this effect but the 10-fold increase of  $U_{iso}$  for the O atom from  $0.0040 \text{ \AA}^2$  to  $0.0408 \text{ \AA}^2$  (Tables 1–6<sup>16</sup>) is more pronounced than that of the other atoms, and rough order-of-magnitude calculations encourage us to believe that the apparent shortening of the C–O bond with temperature is mainly, or possibly entirely, due to the effect of thermal motion. At 14 K, the bond distances are as follows: C–N,  $1.191(5) \text{ \AA}$ , C–O,  $1.215(5) \text{ \AA}$ ; at 288 K they are as follows: C–N,  $1.192(7) \text{ \AA}$ , C–O,  $1.174(8) \text{ \AA}$ . We note that the latter are within experimental error the same as in silver cyanate,  $\text{AgNCO}$ , the only other simple cyanate salt for which crystal structure data are available.<sup>19</sup> The bond distances reported here clearly represent a significant revision of those in our initial X-ray study,<sup>2</sup> providing a further salient reminder of the advantages of using neutron diffraction in the present case.

Because of the possibility of isotopic polymorphism, we also analyzed the neutron powder diffraction pattern from the natural isotopic abundance material  $\text{NH}_4\text{NCO}$ . Although the strong incoherent scattering of  $^1\text{H}$  drastically lowers the quality of the data,

Rietveld refinement gives a clear preference for situation **B** (i.e.,  $\text{N-H}\cdots\text{N}$  hydrogen bonding), as in the deuterated compound.

Analysis of neutron powder diffraction data thus leads us to revise our earlier description of the hydrogen bonding. The correct hydrogen bonding pattern is  $\text{N-H}\cdots\text{N}$  not  $\text{N-H}\cdots\text{O}$ . The solid state transformation to urea is presumably triggered by transfer of  $\text{H}^+$  from  $\text{NH}_4^+$  to  $\text{NCO}^-$  via a proton jump along one of the  $\text{N-H}\cdots\text{N}$  hydrogen bonds to form  $\text{H-NCO}$  and  $\text{NH}_3$  in close vicinity to one another in the crystal, followed by nucleophilic attack of  $\text{NH}_3$  on the carbon atom. We are currently applying a range of techniques to explore this issue, together with studies of the dynamic properties of the ammonium cation in the crystalline material.

**Acknowledgment.** We are grateful to CCLRC (U.K.) for the award of beamtime for synchrotron X-ray powder diffraction experiments at Daresbury Laboratory, and to NRC (Canada) for the award of beamtime for neutron powder diffraction experiments at Chalk River.

**Supporting Information Available:** (1) Tables giving crystallographic data (including atomic coordinates) for  $\text{ND}_4\text{NCO}$ , determined from neutron powder diffraction data at the following temperatures: 77, 135, 210, 245, and 288 K; and (2) results from Rietveld refinement of the synchrotron X-ray powder diffraction data recorded at ambient temperature for  $\text{ND}_4\text{NCO}$ , comprising the results for refinements **A-1**, **B-1**, **A-2**, and **B-2** discussed in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(17) This change is accompanied in the high-resolution solid state  $^{15}\text{N}$  NMR spectrum by a systematic increase in the isotropic  $^{15}\text{N}$  NMR chemical shift for the cyanate N without significant change in the isotropic chemical shift for the ammonium N. This may be explained by the fact that hydrogen bonding has a decreased inductive effect on the acceptor N atom of the cyanate anion as the crystal expands. As a consequence, this atom becomes systematically more deshielded as the hydrogen bond distance increases.

(18) For a recent example see Dunitz, J. D. *Chem. Commun.* **1999**, 2547.

(19) Britton, D.; Dunitz, J. D. *Acta Crystallogr.* **1965**, *18*, 424.

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