Analyzing Carboxylic Acid and Amine-Nitro Hydrogen-Bond Geometry in the Cocrystal of 4-Aminobenzoic Acid and 3,5-Dinitrobenzoic Acid by use of 298 K X-ray and 15 K Neutron Diffraction

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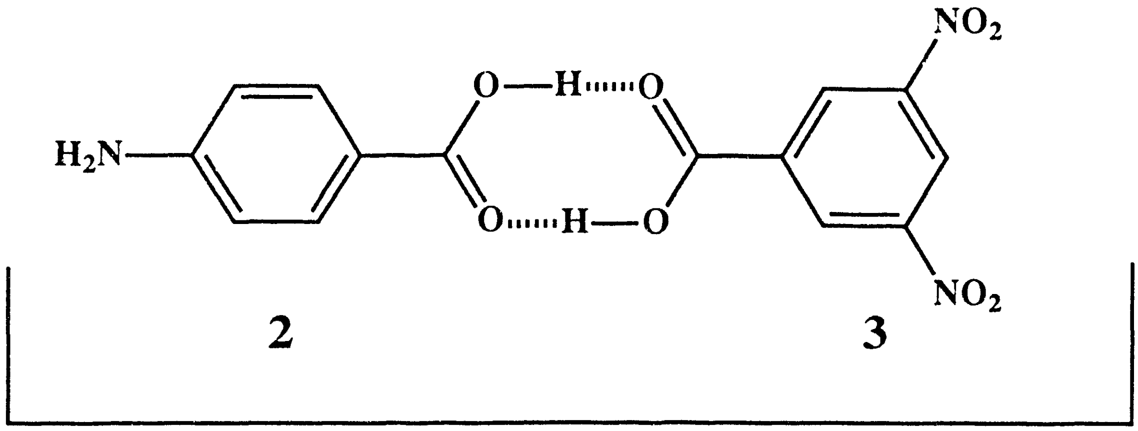
Abstract. The structure of the cocrystal (**1**) of 4-aminobenzoic acid (**2**) and 3,5-dinitrobenzoic acid (**3**), $C_7H_7NO_2 \cdot C_7H_4N_2O_6$, $M_r = 349.26$, has been determined at 298 K by use of X-ray diffraction and at 15 K by use of neutron diffraction techniques. X-ray diffraction structure: Fdd2, $a = 21.49$ (3), $b = 7.041$ (7), $c = 20.65$ (2) Å, V= 3120 (1) Å^3, $Z = 8$, $D_x = 1.48$ Mg•m^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 1.17$ cm^{-1}, F(000) = 1440, $R(F_o) = 0.032$, $R_w(F_o) = 0.029$. Neutron diffraction structure: $a = 21.135$ (3), $b = 6.8567$ (7), $c = 20.602$ (2) Å, V= 2985.6 (6) Å^3, $Z = 8$, $D_x = 1.5541$ Mg•m^{-3}, time of flight neutron diffraction, $\lambda = 0.7$-4.2 Å, $\mu = 0.968$-2.896 cm^{-1}, $R(F_o) = 0.061$, $R_w(F_o^2) = 0.118$. In **1**, hydrogen-bond formation between the acid groups of **2** and **3** results in a cyclic heterodimer. Neutron diffraction data were collected to accurately locate the acid protons and to determine the geometry of the hydrogen bonds. The two acid hydrogen bonds are related by a two-fold crystallographic rotation axis and the protons are disordered over two sites. The heterodimers are organized into two-dimensional polar arrays as a consequence of hydrogen bonding between an amine group and nitro groups on neighboring heterodimers. Determining the structure of **1** at two different temperatures revealed significant changes in the amino-nitro hydrogen-bond geometry, but virtually no change in the acid-acid hydrogen-bond geometry.

Introduction: The X-ray crystal structure of the acid heterodimer (**1**) composed of 4-aminobenzoic acid (**2**) and 3,5-dinitrobenzoic acid (**3**), scheme *i*, was previously solved as part of a study of the relationship between the structure, particularly the hydrogen-bond network, and nonlinear optical properties of **1** (Etter & Frankenbach, 1989). Hydrogen bonds were located between the acid groups of **2** and **3** producing a cyclic heterodimer, scheme *i*. Acid heterodimers have not been studied in detail which prompted our interest in determining the details of the carboxylic acid hydrogen bonds as well as the amino-nitro hydrogen bonds in **1**.



Heterodimer 1

Acid homodimers typically crystallize such that the inversion center of the homodimer and the crystal coincide (Leiserowitz, 1976). Disorder of the acid protons is often accommodated by the coincidence of these inversion centers. Acid heterodimers can not have an inversion center, so proton disorder was not expected to occur in **1**. However, the X-ray structure revealed that the two-fold axis of heterodimer **1** coincides with a crystallographic two-fold axis. The acid protons were assumed to be disordered to accommodate this symmetry operation. Neutron diffraction was used to confirm the location of the protons in **1**.

Neutron diffraction data were collected at a lower temperature than the X-ray diffraction data, providing the opportunity to study changes in the hydrogen-bond network as a function of temperature. The hydrogen-bond network of **1** contains two types of hydrogen bonds; carboxylic acid hydrogen bonds, which are generally short and considered to be strong, and amino-nitro hydrogen bonds, which are generally longer and weaker (some are nearly as long as van der Waals contacts), but still directional (Panunto, Urbañczyk-Lipkowska, Johnson & Etter, 1987). The relative changes as a function of temperature found in these two hydrogen bond types are compared.

Experimental. Equimolar amounts of unpurified **2** (Aldrich) and **3** (Aldrich) were dissolved in methanol. The solution was cooled to 278 K and allowed to sit undisturbed for several weeks. Crystals shaped like trapezoids and rods of **1**, some having faces as large as a few millimeters, grew from this solution. Both types of crystals melt at 477.5-479.0 K. Solid-state UV-vis transmission spectra of **1**, **2**, and **3** were recorded to identify charge-transfer bands. Each compound was ground into a fine powder and mixed with Nujol to form a mull. The mulls were spread between NaCl salt plates and UV-vis spectra were taken using a Hewlett Packard 8452A diode array spectrophotometer.

X-Ray Diffraction. A brilliant, clear, orange trapezoid of dimensions 0.25 x 0.30 x 0.50 mm was used for collecting the X-ray diffraction data at 298 K on an automated Enraf-Nonius CAD-4 diffractometer (graphite monochromator) four-circle diffractometer. Lattice parameters were obtained from least-squares analysis of 25 reflections, 11° < θ < 16°. The space group was obtained from systematic absences. The complete sphere of data, h = -25 to 25, k = -8 to 8, l = -24 to 24, 5205 intensities, was collected. These were averaged assuming space group Fdd2 to give 1309 independent reflections with R_{int} = 0.025. The Friedel pairs were then averaged to give 7[illegible]5 independent reflections with R_{int} = 0.012. As expected with Mo radiation, the Friedel pairs did not differ significantly in measured intensity. No absorption corrections were applied. The change in three standard intensities was less than 1%, over 58.4 hours. The structure was solved by use of direct methods, *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined by full-matrix least-squares procedures. All atoms were refined with anisotropic temperature factors, except for hydrogen atoms which were set at idealized positions with fixed thermal parameters. The acid hydrogen, H(O), was assumed to be disordered and set to 50% occupancy in each position. Corrections for extinction were included in the final least squares refinement. Other experimental details are listed in Table 1.

Neutron Diffraction. Data were obtained at the Argonne Intense Pulsed Neutron Source (INPS) by use of the time of flight single crystal diffractometer (SCD) equipped with a large area (30 x 30 cm^2) position sensitive detector (Schultz, 1987). Three crystals were examined and found to either have a large mosaic spread in their diffraction peaks or had cracks develop upon cooling. One of the crystals, a large trapezoid, was then cut along a crack to obtain a 5.8 mg sample that was glued to an aluminum pin. Although the crystal was cooled slowly on the SCD, by use of a closed cycle helium Displex refrigerator, the crystal cracked slightly again. The peak splitting, however, appeared to be small and a unique octant of data was obtained in a manner described previously (Schultz, Van Derveer, Parker & Baldwin, 1990). Due to the peak splittings the larger-than-usual peak volumes were integrated by use of the ellipsoid contour $\sigma(I)/I$ technique (Wilkinson, Khamis, Stansfield & McIntyre, 1988) rather than a fixed size "shoebox" integration technique. Final unit-cell parameters were obtained from a least-squares refinement of the observed centroid positions of the 1455 strongest reflections from all the data. The initial coordinates for the nonhydrogen atoms were taken from the X-ray structure. All hydrogen atoms were subsequently located in difference Fourier maps. With anisotropic temperature factors and with an isotropic extinction parameter, several atoms refined with nonpositive definite temperature factors. We attribute this to the relatively narrow $(\sin\theta)/\lambda$ range of the data set which was limited by the occurrence of overlapping peaks caused by their splitting and broadening. In the final cycles of least squares refinement, these atoms were refined with isotropic temperature factors. The occupancies of H(1A) and H(1B) were refined with the constraint that their sum equals unity. Other experimental details are listed in Table 1.

Results. Table 1 contains unit cell parameters for the 298 K X-ray and 15 K neutron determined structures. Cooling from 298 K to 15 K produced a 1.7% contraction in the *a* axis, a 2.7% contraction in the *b* axis, but only a 0.2% contraction in the *c* axis.

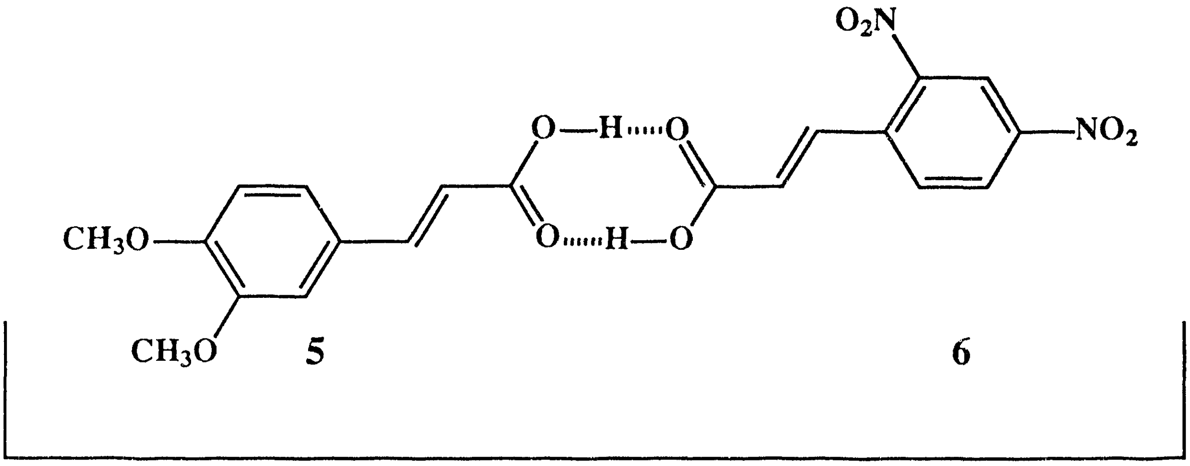
Positional parameters from neutron diffraction data are given in Table 2. Bond distances and angles for both structures are compiled in Table 3. Positional parameters from X-ray diffraction data, anisotropic thermal parameters, and structure factors from the X-ray and neutron diffraction data are deposited as supplementary material.

Hydrogen-bond distances and angles for both structures are given in Table 4. A cyclic heterodimer formed due to hydrogen bonding between the carboxylic acid groups of **2** and **3**, Fig. 1. The heterodimer and crystallographic two-fold axes coincide. In the X-ray structure, the acid protons were not located, but were assumed to be disordered. They were placed in calculated positions and set to 50% occupancy in each position. In the neutron diffraction structure, all hydrogen atoms were located and refinement of the acid proton multipliers gave an occupancy factor of 0.44 (2) for H(1A).

The amine hydrogen atoms form bifurcated hydrogen bonds to nitro oxygen atoms on glide-related heterodimers ($x + 1/4, \bar{y} + 1/4, z + 1/4$). The amino-nitro hydrogen bonds organize the heterodimers into a polar, buckled, two-dimensional array, Fig. 2, in which the amino-nitro hydrogen bond pairs are displaced by ±1/4 in y. The polar arrays pack with the nitro groups oriented in the same direction resulting in a polar and therefore, acentric crystal. The amino-nitro hydrogen bonds shortened upon cooling: at 298 K, N(1A)···O(2B) = 3.227 (3), and N(1A)···O(3B) = 3.330 (3) Å, and at 15 K, N(1A)···O(2B) = 3.156 (5), and N(1A)···O(3B) = 3.198 (4) Å.

The planar heterodimers are stacked perpendicular to the *b* axis. The close overlap between the aromatic rings of **2** and **3** on neighboring heterodimers, *b*/2 = 3.250 Å at 15 K, suggests a charge-transfer interaction. The bright orange color of **1** indicates a transition in the visible spectrum. There are absorptions at λ_{max} = 314 and 222 nm in the solid-state UV-vis transmission spectrum of **1**. Absorptions were found at λ_{max} = 310 and 246 nm in the solid-state spectra of **2** and **3**, respectively. No new absorption which could be attributed to charge transfer was clearly apparent in the spectrum of **1**. However, the peak at 314 nm has a broad shoulder extending to approximately 560 nm which may be a visible charge transfer absorption, or may mask one.

Discussion. The protons of **1** were located by use of the neutron diffraction technique and found to be disordered. Leiserowitz has shown that proton disorder is absent in crystals of homodimers which pack in asymmetric environments (Leiserowitz, 1976). Absence of proton disorder might also be expected in asymmetric heterodimers. For example, in **4**, composed of 3,4-dimethoxycinnamic acid (**5**) and 2,4-dinitrocinnamic acid (**6**) (Sarma & Desiraju, 1985), scheme *ii*, proton disorder may be absent, but protons were not located for confirmation. In **1**, the two-fold symmetry accommodates proton disorder.



5 **6**

Heterodimer 4

ii

Differences were found in the amino-nitro hydrogen-bond distances and angles upon a change in temperature. To compare the amino-nitro hydrogen-bond geometry in the two structures, atom H(4A) in the X-ray structure was corrected for apparent shortening of the N(1A)-H(4A) bond. Atom H(4A) was repositioned to extend the N(1A)-H(4A) bond from 0.95 Å to 1.09 Å. The N···O distances increase at 298 K, N(1A)···O(2B) = 3.227 (3) Å, N(1A)···O(3B) = 3.330 (3) Å, as seen by comparison with the length at 15 K, N(1A)···O(2B) = 3.156 (5), N(1A)···O(3B) = 3.198 (4) Å. Errors in the differences reveal significant changes, Δ(N(1A)···O(2B)) = 0.071 (4) Å and Δ(N(1A)···O(3B)) = 0.132 (6) Å. The increasing N···O distance is manifested as a separation of the heterodimers along the *a* axis contributing to a 1.7% increase in the *a* axis length at 298 K. A change of similar magnitude is noted in the H···O distance, 298 K: H(4A)···O(2B) = 2.39 Å, H(4A)···O(3B) = 2.55 Å; 15 K: H(4A)···O(2B) = 2.275 (9) Å, H(4A)···O(3B) = 2.37 (1) Å, with Δ(H(4A)···O(2B)) = 0.12 Å and Δ(H(4A)···O(3B)) = 0.18 Å. There is a corresponding change in the hydrogen-bond angles, 298 K: N(1A)-H(N)···O(2B) = 140.8°, N(1A)-H(4A)···O(3B) = 131.9° and 15 K: N(1A)-H(4A)···O(2B) = 146.2 (8)°, N(1A)-H(4A)···O(3B) = 139.1 (7)°, with Δ(N(1A)-H(4A)···O(2B)) = 5.4° and Δ(N(1A)-H(4A)···O(3B)) = 7.2°.

Analysis of temperature dependent changes in the acid hydrogen-bond geometry must rely on the oxygen positions which were accurately located at both temperatures. The O···O distances were found to be nearly identical, 298 K: O(1A)···O(1B) = 2.62 (1) Å and 15 K: O(1A)···O(1B) = 2.600 (5) Å.

Comparative analysis of the two structures of **1** suggest that the amino-nitro hydrogen bonds are weaker than the acid hydrogen bonds. At both temperatures, the amino-nitro hydrogen bonds are longer than the acid hydrogen bonds. Also, the amino-nitro hydrogen-bond lengths are easily deformed as the temperature changes, while the acid hydrogen-bond lengths remain essentially the same.

Conclusions: Neutron diffraction reveals that the cocrystal **1** has a two-fold rotation axis coincident with the long molecular axis of the acid heterodimer. Proton disorder is permitted as a result of this two-fold axis which is analogous to disorder permitted in homodimers as a result of the inversion center

Comparative analysis of the structures of **1** at 298 K and 15 K revealed that the amino-nitro hydrogen bonds are easily altered as a function of temperature. The N···O and H···O distances increase significantly with increasing temperature with a corresponding change in the N-H···O hydrogen-bond angle. These results are consistent with ranking the amino-nitro hydrogen bonds as weak in comparison to the carboxylic acid hydrogen bonds which do not change at all over this temperature range.

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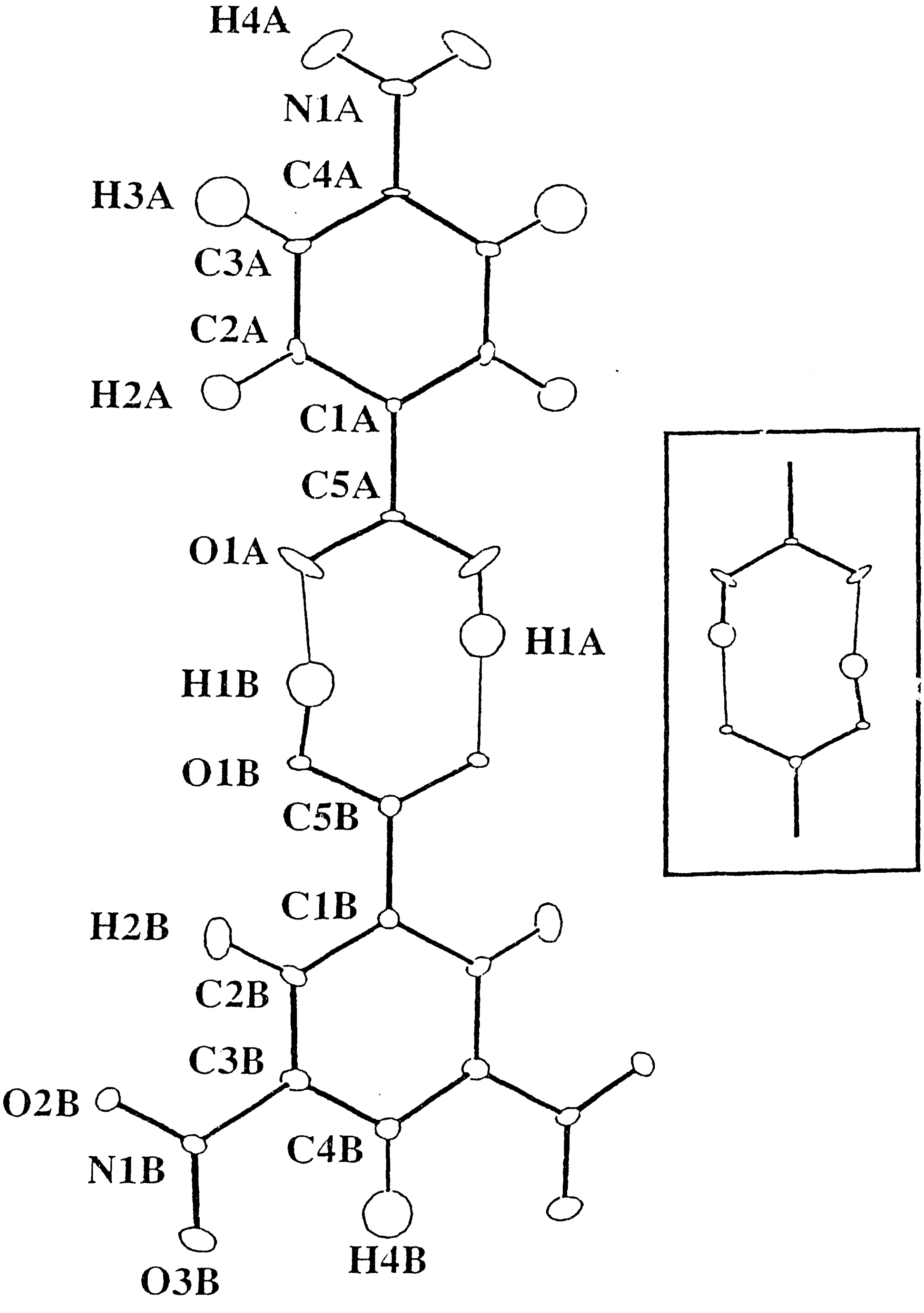
Figure Legends

Figure 1. ORTEP drawing of the heterodimer (**1**) of 4-aminobenzoic acid (**2**) and 3,5-dinitrobenzoic acid (**3**) from neutron diffraction data. The acid hydrogens occupy disorder positions with an occupancy factor of 0.44 (2) for H(1A) and 0.56 H(1B). This disorder in the hydrogen positions is illustrated by the ORTEP drawing and the inset.

Figure 2. ORTEP drawing of the (101) plane of the cocrystal (**1**) of 4-aminobenzoic acid (**2**) and 3,5-dinitrobenzoic acid (**3**).

Figure 1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N1A
C4A
H3A
C3A
C2A
H2A
C1A
C5A
O1A
H1A
H1B
O1B
C5B
C1B
H2B
C2B
C3B
O2B
N1B
C4B
O3B
H4B

Figure 2

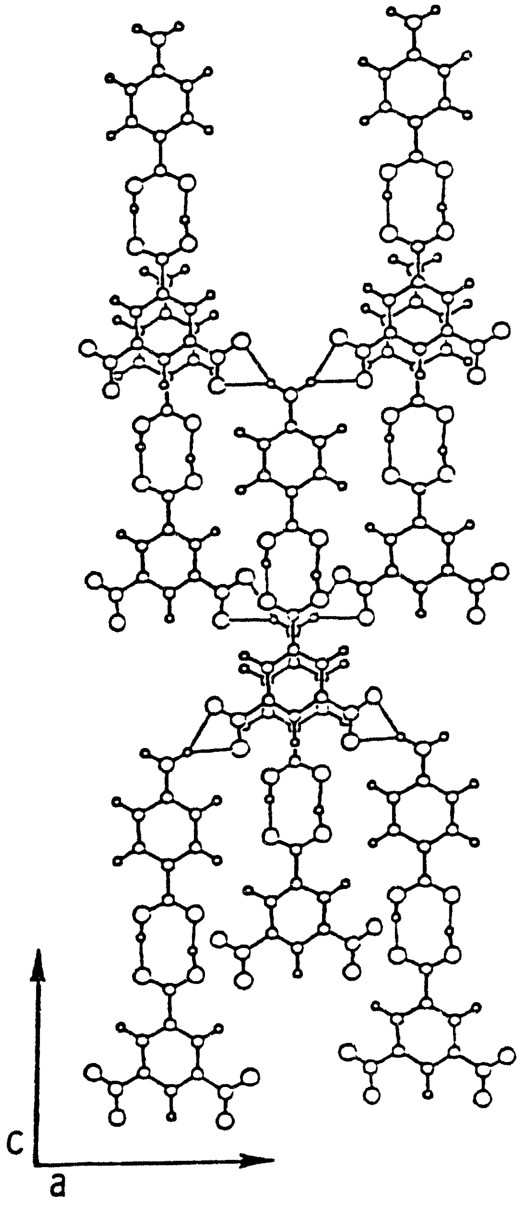

Table 1. *Unit cell parameters and least-squares results for the X-ray and neutron diffraction analysis.*

	298 K X-ray	15 K neutron
	A. unit cell parameters	
space group	Fdd2	Fdd2
a (Å)	21.49 (3)	21.135 (3)
b (Å)	7.041 (7)	6.8567 (7)
c (Å)	20.65 (2)	20.602 (2)
$\alpha = \beta = \gamma$ (°)	90	90
Volume (Å^3)	3120 (1)	2985.6 (6)
Z	8	8
D_c (g•cm^{-3})	1.48	1.5541
	B. measurement of intensity data	
λ (Å)	0.71073	0.7-4.2
total reflections	5204	3827
μ_c (cm^{-1})	1.17	0.968 (λ = 0.7 Å) 2.896 (λ = 4.2 Å)
cutoff	$I > \sigma(I)$	$I > 3\sigma(I)$
scan technique	$\omega - 2\theta$	TOF

Table 1 Continued. *Unit cell parameters and least-squares results for the X-ray and neutron diffraction analysis.*

	298 K X-ray	15 K neutron
	<u>C. least-squares results</u>	
no. variables (*n*)	117	161
reflections used in refinement (*m*)	618	1667
m/*n*	5	10
function minimized	$\Sigma w(F_{obs} - F_{calc})^2$ $w = 1/\sigma^2 (F)$ $\sigma^2(I) = \sigma^2(I)_c + (0.05I)^2$	$\Sigma w(F_{obs}^2 - F_{calc}^2)^2$ $w = 1/\sigma^2 (F^2)$ $\sigma^2 = \sigma^2(F^2) + (0.04F^2)^2 + 500$
$R(F_o)$	0.032	0.061
$R_w(F_o)$	0.029	-
$R(F_o^2)$	-	0.106
$R_w(F_o^2)$	-	0.118
S	1.065	1.313
max shift/e.s.d.	0.03	0.002
Greatest +/-ρ	0.13 e•Å^{-3}	-0.298 x 10^{-12} cm•Å^{-3}

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses for the 15 K neutron diffraction structure.*

$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_j^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$

Atom	x	y	z	U_{eq} 10^4
N(1A)	0.0	0.0	0.0	130 (10)
C(1A)	0.0	0.0	0.2024 (3)	23 (6)
C(2A)	-0.0553 (2)	0.0423 (3)	0.1679 (2)	53 (8)
C(3A)	-0.0556 (2)	0.0410 (4)	0.1012 (2)	69 (9)
C(4A)	0.0	0.0	0.0663 (3)	50 (10)
C(5A)	0.0	0.0	0.2736 (2)	50 (10)
O(1A)	-0.0520 (2)	0.0373 (5)	0.3029 (3)	140 (1)
O(1B)	-0.0525 (2)	0.0173 (4)	0.4289 (2)	65 (8)
C(1B)	0.0	0.0	0.5295 (3)	41 (6)
C(2B)	-0.0543 (2)	0.0532 (3)	0.5633 (2)	52 (8)
C(3B)	-0.0527 (2)	0.0533 (3)	0.6301 (2)	49 (8)
C(4B)	0.0	0.0	0.6652 (3)	50 (10)
C(5B)	0.0	0.0	0.4578 (3)	46 (6)
N(1B)	-0.1090 (1)	0.1179 (2)	0.6662 (2)	51 (5)
O(2B)	-0.1549 (2)	0.1731 (4)	0.6347 (2)	79 (8)
O(3B)	-0.1070 (2)	0.1164 (4)	0.7255 (2)	92 (9)
H(1A)	-0.054 (1)	0.043 (2)	0.350 (1)	190 (20)
H(2A)	-0.0984 (4)	0.0745 (8)	0.1945 (4)	170 (20)
H(3A)	-0.0991 (5)	0.072 (1)	0.0744 (4)	250 (10)
H(4A)	0.0408 (5)	-0.010 (1)	-0.0245 (4)	270 (30)
H(1B)	-0.0462 (8)	0.019 (2)	0.3791 (8)	190
H(2B)	-0.0966 (4)	0.0961 (9)	0.5368 (4)	190 (20)
H(4B)	0.0	0.0	0.7193 (7)	220 (20)

Table 3. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses.*

	298 K X-ray	15K neutron
N(1A)-C(4A)	1.362 (5)	1.366 (5)
C(1A)-C(2A)	1.403 (3)	1.398 (4)
C(1A)-C(5A)	1.459 (6)	1.465 (6)
C(2A)-C(3A)	1.372 (4)	1.374 (5)
C(3A)-C(4A)	1.405 (4)	1.406 (4)
O(1A)-C(5A)	1.264 (3)	1.280 (5)
N(1B)-C(3B)	1.472 (4)	1.473 (4)
N(1B)-O(2B)	1.220 (3)	1.226 (4)
N(1B)-O(3B)	1.221 (3)	1.221 (4)
C(1B)-C(2B)	1.390 (3)	1.391 (4)
C(1B)-C(5B)	1.487 (6)	1.476 (6)
C(2B)-C(3B)	1.380 (4)	1.376 (4)
C(3B)-C(4B)	1.376 (3)	1.378 (4)
O(1B)-C(5B)	1.261 (3)	1.266 (4)
N(1A)-C(4A)-C(3A)	120.7 (2)	120.7 (2)
O(1A)-C(5A)-O(1A')	122.5 (4)	123.6 (5)
O(1A)-C(5A)-C(1A)	118.7 (2)	118.2 (3)
C(1A)-C(2A)-C(3A)	121.1 (3)	120.8 (3)
C(2A)-C(1A)-C(2A')	118.2 (3)	118.8 (4)
C(2A)-C(1A)-C(5A)	120.9 (2)	120.6 (2)
C(2A)-C(3A)-C(4A)	120.6 (3)	120.5 (3)

Table 3 Continued. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses.*

	298 K X-ray	15 K neutron
C(3A)-C(4A)-C(3A')	118.5 (4)	118.5 (4)
O(1B)-C(5B)-O(1B')	123.9 (4)	123.8 (4)
O(1B)-C(5B)-C(1B)	118.0 (2)	118.1 (2)
N(1B)-C(3B)-C(2B)	118.6 (3)	119.0 (3)
N(1B)-C(3B)-C(4B)	118.2 (3)	117.8 (3)
C(1B)-C(2B)-C(3B)	118.1 (2)	118.7 (3)
C(2B)-C(1B)-C(2B')	120.7 (3)	119.9 (4)
C(2B)-C(1B)-C(5B)	119.7 (2)	120.0 (2)
C(2B)-C(3B)-C(4B)	123.2 (2)	123.1 (3)
C(3B)-C(4B)-C(3B')	116.6 (3)	116.5 (4)
C(3B)-N(1B)-O(2B)	118.2 (3)	117.7 (2)
C(3B)-N(1B)-O(3B)	117.9 (3)	118.3 (3)
O(2B)-N(1B)-O(3B)	123.9 (3)	124.0 (4)

Table 4. *Bond distances (Å) and angles (°) for hydrogen-bonded atoms with e.s.d.'s in parentheses.*

	298 K X-ray	15K neutron
O(1A)···O(1B)	2.62 (1)	2.600 (5)
O(1A)-H(1A)	*	0.97 (2)
O(1B)-H(1B)	*	1.04 (2)
H(1A)···O(1B)	*	1.63 (2)
H(1B)···O(1A)	*	1.58 (1)
N(1A)···O(2B)	3.227 (3)	3.156 (5)
N(1A)···O(3B)	3.330 (3)	3.198 (4)
N(1A)-H(4A)	*	1.000 (9)
H(4A)···O(2B)	2.43 (1)	2.275 (9)
H(4A)···O(3B)	2.58 (1)	2.37 (1)
O(1A)-H(1A)···O(1B)	*	170 (1)
O(1B)-H(1B)···O(1A)	*	167 (2)
N(1A)-H(4A)···O(2B)	142 (3)	146.2 (8)
N(1A)-H(4A)···O(3B)	133 (3)	139.1 (7)

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*In the X-ray structure, the hydrogens were placed in idealized positions and so the values for these hydrogen-bond parameters were not included.

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