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A structural study of 2-amino-5-nitropyridine and 2-amino-3-nitropyridine: intermolecular forces and polymorphism

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The crystal structures of four compounds from a family of commonly used molecular building blocks of nonlinear optical materials, aminonitropyridines, have been determined. The structures of 2-amino-5-nitropyridine **1**, 2-amino-5-nitropyridine monohydrate **2**, and of two new polymorphs of 2-amino-3-nitropyridine **3,4**, are all stabilised by a combination of hydrogen bonds (including C—H···X interactions) and dispersive and electrostatic interlayer interactions. The balance between these intermolecular forces, and the way in which they influence the packing of these materials, are discussed.

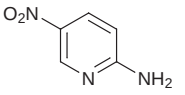
The principles that govern covalent synthesis are generally well understood, and thus an impressive array of molecules with specific molecular properties have been synthesized over the years.[1] From a materials perspective, however, unless individual molecules can be made to 'cooperate' through a favourable spatial arrangement within a 3D crystal, the molecular properties may not express themselves fully in the bulk material. In such cases, the efforts that go into the design and synthesis of the target molecule may be largely unrewarded. Unfortunately, the problems of controlling and predicting structures of molecular and ionic solids are still a long way from being solved. Such issues, which are addressed within the context of crystal engineering,[2] require considerable structural information coupled with a careful analysis of the balance between, and effects of, intermolecular forces.

One area where crystal engineering has an important role to play is in the continuous search for new nonlinear optical materials. A common and often productive route to such materials has been to utilise molecules with electron donating and accepting moieties attached to a conjugated system. The optical response of an SHG-active material is influenced both by the chemical purity and structural composition of the bulk sample. Consequently, the design and preparation of new NLO-materials can therefore be complicated by polymorphism (different crystalline forms of compounds with identical chemical composition). The presence of polymorphic structures is also of crucial importance to the pharmaceutical industry and in areas associated with specialty chemicals, since polymorphs can have significantly different physical properties. Despite this, the possibilities that new materials may appear in several polymorphic forms are often overlooked; a visual inspection of the sample does not always provide conclusive information about the bulk sample, since different polymorphs can display the same crystal habit.[3] However, polymorphic systems can provide excellent opportunities to study a chemical entity in more than one crystalline environment. By comparing thermodynamic quantities and trends displayed by calculated lattice energies for a series of solids, energy differences between molecular conformations can be estimated.[4]

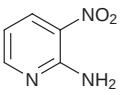
Model systems and objectives

As stated earlier, aromatic amino-nitro systems are potentially useful NLO materials and, typically, cations derived from such molecules have been used within hydrogen-bonded organic anionic networks, or as counterions in organic/inorganic salts.[5] Although several crystal structures of related molecules, *e.g.* 3-methyl-4-nitropyridine *N*-oxide[6] and 4-nitropyridine *N*-oxide,[7] have been published, few structure determinations have been reported on molecular solids containing the amino-nitro 'push–pull' system. In fact, a search of the Cambridge Structural Database[8,9] identified only four such structures,[10] one of them being 2-amino-3-nitropyridine.[11]

In order to study crystal packing and competition/complementarity between different hydrogen-bond interactions in amino-nitro compounds we have initiated a systematic structural study, starting with 2-amino-5-nitropyridine and 2-amino-3-nitropyridine. We have attempted to isolate polymorphic forms of these compounds by recrystallizing each sample from a variety of solvents and under a variety of conditions.[12] To the best of our knowledge, there have been no previous observations of polymorphs of 2-amino-3-nitropyridine.[13] In this paper we report the X-ray single-crystal determination of four structures; 2-amino-5-nitropyridine **1**, 2-amino-5-nitropyridine monohydrate **2**, and two new polymorphs of 2-amino-3-nitropyridine **3** and **4**.[14]



1
2 (monohydrate)



3,4 (polymorphs)

Results

Preparations of **1–4** are described in detail in the Experimental Section, and the relevant X-ray crystallographic information is presented in Table 1. Numbering schemes, molecular geometries and thermal ellipsoids of **1–4** are presented in Fig. 1(*a*)–(*d*). The structure determinations of **1–4** revealed that all four compounds crystallise in centrosymmetric space groups, with intramolecular bond lengths and angles of unremarkable values.

The crystal structure of **1** exhibits a flat, layered arrangement with five unique hydrogen-bond interactions within the layer, Table 2. In fact, every possible donor or acceptor is involved in a hydrogen bond (three of these interactions involve —CH moieties as donor functionalities), Fig. 2. Furthermore, since there are two more hydrogen-bond donors than acceptors, each oxygen atom of the nitro group is involved in two hydrogen bonds simultaneously. Somewhat surprisingly, the commonly observed $R_2^2(8)$ motif in 2-aminopyridine moieties involving symmetry related N—H···N hydrogen bonds, is absent in this structure.[15] Nevertheless, the hydrogen bonds in

Table 1 Data collection and refinement for **1**–**4**

crystal data	**1**	**2**	**3**	**4**
empirical formula	$C_5H_5N_3O_2$	$C_5H_7N_3O_3$	$C_5H_5N_3O_2$	$C_5H_5N_3O_2$
M_W	139.12	157.14	139.12	139.12
crystal size/mm	$0.74 \times 0.33 \times 0.09$	$0.58 \times 0.31 \times 0.26$	$0.92 \times 0.38 \times 0.06$	$0.64 \times 0.44 \times 0.12$
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pnma*	*C*2/*c*	$P2_1/c$	$P2_1/n$
a/Å	15.357(3)	16.150(4)	4.917(1)	3.737(2)
b/Å	6.080(2)	11.135(2)	6.940(2)	7.445(2)
c/Å	6.099(2)	7.301(1)	17.507(3)	20.974(6)
β (°)		99.02(2)	95.63(2)	90.52(3)
V/Å^3	569.4(4)	1296.7(4)	594.5(2)	583.4(4)
Z	4	8	4	4
D_c/g cm^{-3}	1.623	1.610	1.554	1.584
F(000)	288	656	288	288
μ(Mo-Kα)/mm^{-1}	0.130	0.135	0.124	0.126
T/K	123	123	153	173
ω scans; θ range (°)	2.65–25.00	2.23–24.99	2.34–25.00	1.94–24.99
range *h*	−18 to 1	−1 to 19	−5 to 5	−1 to 4
range *k*	−7 to 7	−1 to 13	−5 to 8	−1 to 8
range *l*	−7 to 7	−8 to 8	−20 to 20	−24 to 24
reflns. collected	2041	1425	1692	1772
unique/obs. reflns.	552/406	1146/906	1051/568	1032/724
observed data : parameter ratio	6.5	8.2	6.2	7.9
refinement	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares
R/R_w^2 (obs. data)	0.0399/0.0928	0.0554/0.1539	0.0575/0.0987	0.0716/0.1848
R/R_w^2 (all data)	0.0656/0.1061	0.0697/0.1689	0.1352/0.1256	0.1026/0.2052
$\Delta\rho_{max/min}$/e Å^{-3}	0.278/−0.315	0.305/−0.412	0.172/−0.205	0.249/−0.284
S	1.136	1.082	1.030	1.170

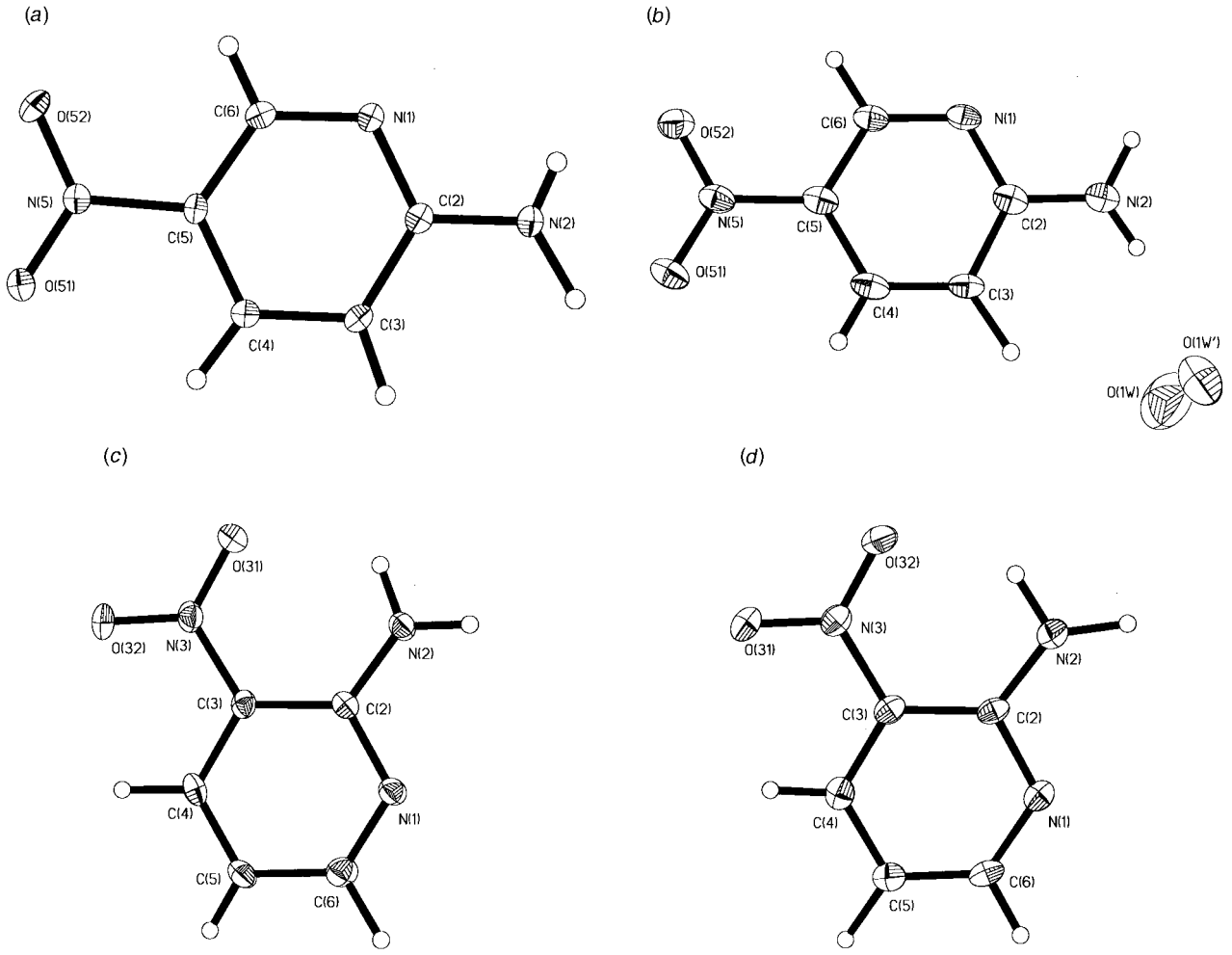


Fig. 1 Molecular geometry and numbering schemes for (*a*) **1**, (*b*) **2**, (*c*) **3** and (*d*) **4**. Thermal ellipsoids at 30% probability.

Table 2 Geometry of the hydrogen bonds in **1**[a]

D—H···A	r(H···A)/Å	r(D···A)/Å	∠(D—H···A) (°)
N(2)—H(21)···O(52)′	2.454(4)	3.035(4)	132.42(9)
N(2)—H(22)···O(51)″	1.906(2)	2.982(3)	177.8(1)
C(3)—H(3)···O(52)″	2.577(4)	3.497(4)	157.59(8)
C(6)—H(6)···O(51)‴	2.639(4)	3.463(4)	151.36(8)
C(4)—H(4)···N(1)‴	2.426(4)	3.346(4)	157.0(1)

[a]Symmetry code: (′) $-1/2+x$, y, $-z+1/2$; (″) $-1/2+x$, y, $-z+11/2$; (‴) x, y, $z+1$; (⁗) x, y, $z-1$.

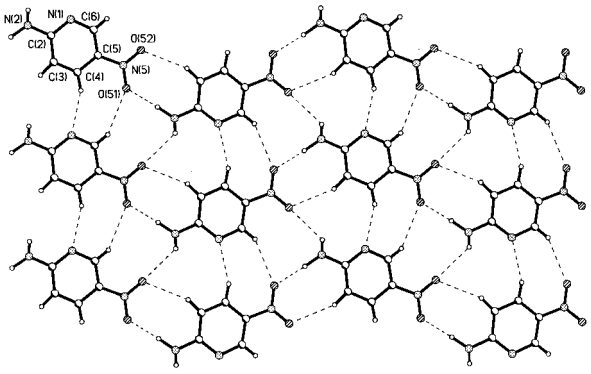


Fig. 2 Hydrogen-bond interactions within layers in **1**

1 (including C—H···A, where A is an acceptor), are working in concert to produce a lamellar 2D structure. The interlayer separation is exceptionally short, approximately 3.035 Å (as a comparison, the interlayer separation in graphite is 3.35 Å). A recent theoretical study[16] of the intermolecular forces present in these crystal structures shows that this intralayer arrangement can be understood in terms of electrostatics and simple packing effects. Intermolecular interaction energies were calculated using ORIENT 3.2[17] and the distributed multipoles were obtained from the HF/6–31G* wave function of the single molecules using CADPAC.[18] The experimental interplanar distance in **1** is reproduced quite well (2.98 *vs.* 3.04 Å exp.), and the change in electrostatic energy as a function of interplanar distance is small, indicating that the separation results from a balance between repulsion and dispersion. Translational motion has a larger effect on the repulsive forces which means that the optimum packing is achieved when electrostatic forces are maximized, and when the layers are as close as possible (to maximize dispersion) without incurring a prohibitive repulsive energy penalty.[16] This balance can be achieved if the aromatic rings in one layer fit over nitrogen and oxygen atoms, which are smaller, in the neighbouring layer.

The water molecule in **2** is disordered and as a consequence, the 3D packing in this compound is rather more complex than in **1**, and it is also influenced by several hydrogen bonds involving the water molecule, Table 3. However, even in the presence of one molecule of water, the 2-amino-5-nitropyridine molecules are arranged in a 2D network, Fig. 3, with three unique hydrogen bonds within each sheet (including two

Table 3 Geometry of the hydrogen bonds in **2**[a]

D—H···A	r(H···A)/Å	r(D···A/Å	∠(D—H···A) (°)
N(2)—H(21)···N(1)′	2.087(3)	3.037(3)	171.50(8)
N(2)—H(22···O(1W)	2.203(9)	3.010(9)	153.8(2)
N(2)—H(22)···O(1W)′	2.20(2)	2.96(1)	145.6(6)
C(3)—H(3)···O(1W)	2.340(6)	3.266(6)	140.0(2)
C(3)—H(3)···O(1W)″	2.34(1)	3.37(1)	155.2(4)
C(4)—H(4)···O(52)‴	2.458(3)	3.208(3)	143.24(8)
C(6)—H(6)···O(51)⁗	2.618(3)	3.477(3)	147.05(7)

[a]Symmetry code: (′) $-x$, $-y$, $-z$; (″) $-x$, $1-y$, $-z$; (‴) $1/2-x$, $1/2+y$, $-1/2-z$; (⁗) $1/2-x$, $y-1/2$, $-1/2-z$.

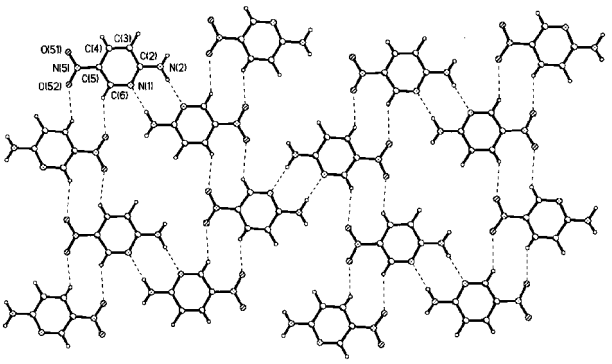


Fig. 3 Hydrogen-bond interactions within layers in **2**. Water molecules not shown for clarity.

hydrogen bonds involving —CH donor functionalities), Table 3. These hydrogen bonds generate two different 'dimeric' interactions: an $R_2^2(8)$ motif *via* symmetry-related N—H···N interactions and two $R_2^2(10)$ motifs involving C—H···O hydrogen bonds. The water molecules are located within the 'holes' in the organic layer, and there is virtually no overlap between aromatic moieties in adjacent layers, indicating the absence of significant attractive π–π interactions.

An X-ray powder diffractogram was recorded for a bulk sample of 2-amino-5-nitropyridine recrystallized from water and compared with powder patterns simulated from single-crystal data for the two structures **1** and **2**. All significant diffraction peaks present in the experimental pattern could be accounted for by combining the two simulated patterns. This, however, does not rule out the possibility of obtaining polymorphs of 2-amino-5-nitropyridine or its hydrated analogue through sublimation or recrystallization from other solvents or under different conditions.

Similarly, an experimental X-ray powder pattern of a bulk sample of 2-amino-3-nitropyridine was recorded and compared with the simulated pattern based on single crystal data for the previously reported crystal structure,[11] Fig. 4. The experimental pattern does show the presence of Form I, but there is also a number of peaks that are unaccounted for.

Since the chemical purity of the sample had been established by solution ^{1}H NMR, the additional peaks in the experimental powder pattern were thought to belong to a hitherto unknown polymorph of 2-amino-3-nitropyridine, and several recrystallization experiments were subsequently carried out. Upon recrystallisation from acetone, only the previously reported polymorph, Form I, was obtained (as determined by powder X-ray diffraction), but when the sample was recrystallised from ethanol, the recorded powder pattern displayed no similarities with the pattern expected for Form I, and thus indicated the presence of at least one new polymorph. We were able to isolate diamond-shaped crystals of 2-amino-3-nitropyridine

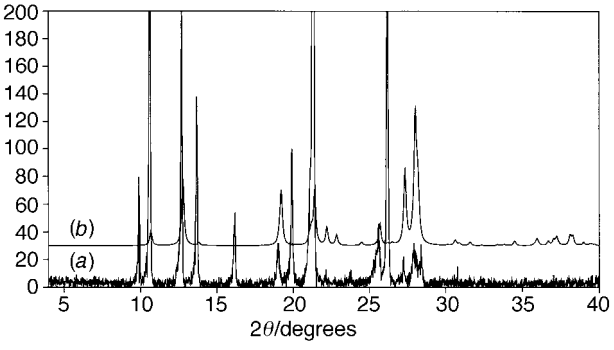


Fig. 4 (*a*) The experimental X-ray powder diffraction pattern of bulk 2-amino-3-nitropyridine and (*b*) the diffraction pattern simulated from the single-crystal data of Form I (ref. 11) of 2-amino-3-nitropyridine

through slow recrystallization from ethanol and the subsequent structure determination confirmed the existence of a new polymorph, **3** (Form II) of 2-amino-3-nitropyridine.

The molecule itself is planar with the two substituents coplanar with the aromatic ring. This is likely to be a result of the intramolecular N—H···O hydrogen bond that exists between the two functionalities, thereby restricting their torsional flexibility, Table 4. The structure contains infinite, staggered ribbons held together by two unique hydrogen bonds, N—H···N and N—H···O, each of which gives rise to ring-like dimeric interactions, $R_2^2(8)$ and $R_2^2(12)$, respectively, Fig. 5. Neighbouring ribbons are tilted, *ca.* 45° with respect to each other. As a comparison, Form 1 of 2-amino-3-nitropyridine also contains ribbon-like motifs, held together by two unique hydrogen bonds, but in this case the ribbon is generated *via* C—H···O, $R_2^2(10)$, and N—H···N, $R_2^2(8)$ dimeric interactions, resulting in a linear topology, Fig. 6.[11] Preliminary thermal microscopy data indicate that Form I undergoes a phase transformation at 120 °C. The melting point of the modification that appears after the phase transition is 166 °C, and these phases are probably enantiotropically related.[19]

We then made a serendipitous discovery of a third polymorph of 2-amino-3-nitropyridine during an attempt to cocrystallize 2-amino-3-nitroypyridine with maleic acid. We recovered pale yellow cuboid crystals which were suitable for X-ray single-crystal diffraction. The experiment revealed another monoclinic polymorph of 2-amino-3-nitropyridine, Form III. The structure is very similar to that observed for Form II and, indeed, all hydrogen-bond interactions show the same connectivity, Table 5, with identical graph-sets. The difference between the two polymorphs is most easily observed by comparing the topology of the infinite 1D ribbons in the two forms. Whereas the ribbon is flat in Form II, Fig. 7(*a*), it has a distinctive 'step' in Form III, Fig. 7(*b*). In all three polymorphs, the molecule is planar with an intramolecular N—H···O hydrogen bond between amino-nitro moieties.

Table 4 Geometry of the hydrogen bonds in **3**[a]

D—H···A	*r*(H···A)/Å	*r*(D···A/Å	∠(D—H···A) (°)
N(2)—H(21)···N(1)′	2.071(5)	2.972(4)	166.5(4)
N(2)—H(22)···O(31)″	2.198(4)	3.044(4)	147.6(1)
N(2)—H(22)···O(31)	2.087(4)	2.663(4)	117.5(1)
C(4)—H(4)···O(32)‴	2.413(4)	3.177(4)	129.4(1)

Symmetry code: (′) 2−*x*, 1−*y*, 2−*z*; (″) 1−*x*,−*y*, 2−*z*; (‴) −*x*, 1/2+*y*, 11/2−*z*; (⁗) 1+*x*, 1+*y*, *z*.

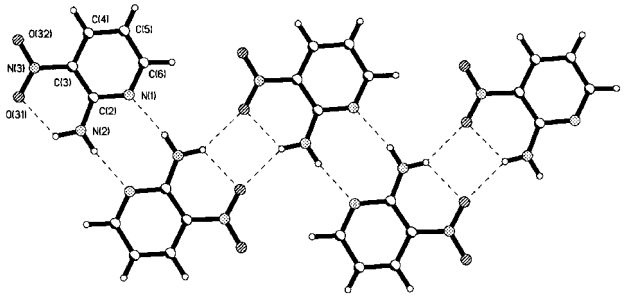


Fig. 5 Hydrogen-bonded molecular ribbon in **3**

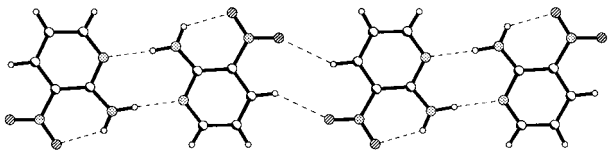


Fig. 6 Molecular ribbon in the first reported polymorph of 2-amino-3-nitropyridine (ref. 11)

Table 5 Geometry of the hydrogen bonds in **4**[a]

D—H···A	*r*(H···A)/Å	*r*(D···A/Å	∠(D—H···A) (°)
N(2)—H(21)···O(32)	1.907(5)	2.672(5)	135.8(1)
N(2)—H(21)···O(32)‴	2.484(5)	3.055(5)	118.6(1)
N(1)—H(22)···N(2)′	1.970(5)	2.965(5)	156.9(1)
C(5)—H(5)···O(31)″	2.450(6)	3.278(6)	125.9(1)

Symmetry code: (′) −*x*+1, −*y*+2, −*z*+1; (″) −*x*−1/2, *y*−1/2, −*z*+11/2 (‴) −*x*, 1−*y*, 1−*z*.

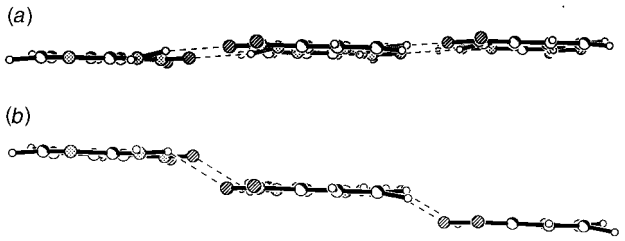


Fig. 7 Edge-on view of the molecular ribbons in (*a*) **3** and (*b*) **4**

Discussion

The fact that all four crystal structures presented here are centrosymmetric obviously means that these aromatic amino-nitro compounds will not display second harmonic generation. It is tempting to conclude that these molecules crystallise in centrosymmetric structures simply to accommodate an antiparallel alignment of neighbouring dipoles, which in turn translates into an overall symmetric space group for the resulting 3D solid. However, such explanations have been contested based upon studies that have failed to find a correlation between high molecular dipole moments and centrosymmetric structures.[10] It is clear that the precise nature of the effects of a high molecular dipole moment upon the resulting crystal structure has yet to be fully understood, especially when stronger intermolecular forces, *e.g.* hydrogen bonding, are present.

From a practical point of view, it is important to note that there are at least three polymorphs of 2-amino-3-nitropyridine and a hydrated and non-hydrated structure of 2-amino-5-nitropyridine. Is it therefore possible to obtain non-centrosymmetric structures of these compounds by varying some of the experimental conditions? In the case of 2-amino-3-nitropyridine this would seem unlikely, as all three contain a dimeric N—H···N motif where participating molecules are related by an inversion centre. Such a dimer precludes packing in a non-centrosymmetric space group, and it would certainly seem that the odds are against obtaining an NLO-active polymorph of 2-amino-3-nitropyridine, based upon extant structural data. However, if the foundation for this dimer is destroyed, *i.e.* by replacing $-NH_2$ with $-N(Me)_2$ or $-NH(Me)$, then the chances of promoting a non-centrosymmetric packing arrangement should be enhanced, although there are several other ways in which neighbouring molecules or adjacent sheets can be aligned in an antiparallel manner. We are unaware of any reported structure determinations of such molecular solids, and are currently examining their crystal structures.

As for 2-amino-5-nitropyridine, there are no recurring 'dimeric' interactions between neighbouring molecules in **1** and **2**, which may indicate a larger degree of flexibility in terms of the intermolecular motifs that are likely to appear in hitherto undiscovered polymorphs. Nevertheless, this molecule can also form the dimeric motif generated by symmetry related N—H···N hydrogen bonds which will preclude SHG-activity in the resulting material. However, it is possible to lower the symmetry and thereby increase the chances of obtaining non-centrosymmetric structures by cocrystallization reactions of molecules with complementary hydrogen-bond functionalities.

Experimental section

Preparation of single crystals of 1

2-Amino-5-nitropyridine was slowly recrystallized from ethanol to yield pale yellow, thin, plate-like crystals. Found: C, 43.0; H, 3.7; N, 30.1%. Calc. for $C_5H_5N_3O_2$: C, 43.18; H, 3.63; N, 30.20%. Mp 187–189 °C.

Preparation of single crystals of 2

2-Amino-5-nitropyridine was slowly recrystallized from water to yield yellow, needle-like crystals. Found: C, 38.4; H, 4.7; N, 26.5%. Calc. for $C_5H_7N_3O_3$: C, 38.22; H, 4.40; N, 26.75%. Mp 186–188 °C.

Preparation of single crystals of 3 (Form II)

2-Amino-3-nitropyridine was slowly recrystallized from ethanol to produce yellow, diamond-like crystals. Found: C, 43.1; H, 3.7; N, 30.0%. Calc. for $C_5H_5N_3O_2$: C, 43.18; H, 3.63; N, 30.20%. Mp 165–167 °C.

Preparation of single crystals of 4 (Form III)

2-Amino-3-nitropyridine was dissolved in water and added to an aqueous solution of maleic acid. Five drops of conc. HCl were then added, and the mixture was heated under reflux for 2 h. The solution was then left to cool to ambient temperature and left to stand. After two weeks crystals of two distinct morphologies appeared; yellow, elongated crystals (Form II, **3**, as determined by single-crystal X-ray diffraction), and irregular, cuboid yellow–brown crystals. Found: C, 42.9; H, 3.7; N, 29.9%. Calc. for $C_5H_5N_3O_2$: C, 43.18; H, 3.63; N, 30.20%. Mp 162–163 °C.

X-Ray crystallography

Crystal data were collected using a Siemens P4 four-circle diffractometer with graphite monochromated Mo-Kα radiation. Crystal stabilities were monitored by measuring standard reflections every 100 reflections, and there were no significant variations ($< \pm 1\%$). Cell parameters were obtained from 35 accurately centred reflections in the 2θ range 10–25°. ω scans were employed for data collection ($\theta/2\theta$ for **4**) and Lorentz and polarization corrections were applied. The structures were solved by direct methods and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were located from difference Fourier maps and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded) was used for subsequent refinements. The function minimized was $\Sigma[\omega(|F_o|^2 - |F_c|^2)]$ with reflection weights $\omega^{-1} = [\sigma^2 |F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max |F_p|^2 + 2|F_c|^2]/3$. The SHELXTL PC and SHELXL-93 packages were used for data reduction and structure solution and refinement.[21]

Hydrogen atoms could not be located for the disordered water molecules in **2**. Each water molecule is disordered over two sites and this disorder was refined to an occupancy of 80:20. It was also noted that crystals of **2** become opaque over a few days when removed from the solvent, which is presumably due to loss of water from the lattice.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/89.

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