JOURNAL OF Materials CHEMISTRY

Synthesis, characterisation and structure–property analysis of derivatives of the non-linear optical material 5-nitro-*N*-(1-phenylethyl)pyridin-2-amine†

Philip J. Langley,[a] Ray T. Bailey,[b] Frank R. Cruickshank,[b] Alan R. Kennedy,[b] Stephen Lochran,[b] David Pugh,[b] John N. Sherwood,[b] Anna Viikki[a] and John D. Wallis*[c]

[a]*Centre for Materials Research, Chemical Laboratory, School of Physical Sciences, University of Kent, Canterbury, UK CT2 7NH*
[b]*Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral St., Glasgow, UK G1 1XL*
[c]*Department of Chemistry and Physics, The Nottingham Trent University, Clifton Lane, Nottingham, UK NG11 8NS*

Received 9th October 2000, Accepted 19th December 2000
First published as an Advance Article on the web 27th February 2001

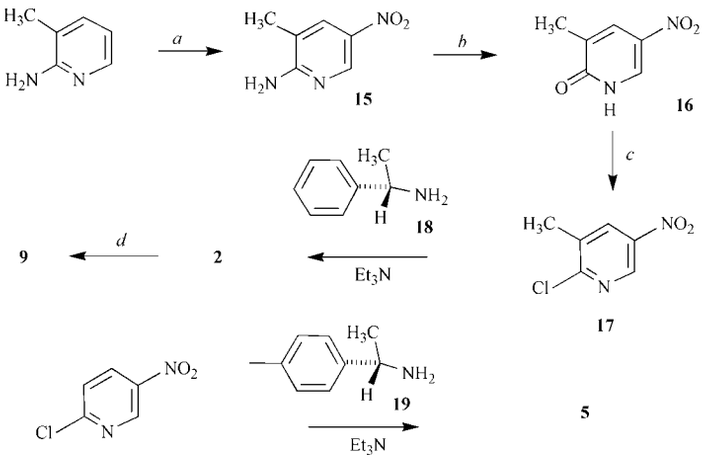
The effects of a series of small structural changes to (*S*)-5-nitro-*N*-(1-phenylethyl)pyridin-2-amine on its solid state non-linear optical properties, including the phenomenon of rotating dielectric axes, have been investigated. Installation of a methyl group in the 3-position of the heterocyclic ring or at the amino nitrogen atom gave the most promising materials, though neither of these materials showed rotating dielectric axes. Details of the crystal structure analyses of a family of these compounds illustrate the delicate interplay between molecular conformation and intermolecular interactions in determining the packing arrangements.

Introduction

The design and synthesis of organic nonlinear optical (NLO) materials is still a very active area of contemporary materials research.[1,2] The development of photonic materials exhibiting technologically useful and accessible second-order ($\chi^{(2)}$) phenomena such as second harmonic generation (SHG), has been particularly prominent. The initial approach to the production of materials with high $\chi^{(2)}$ values—namely the synthesis and powder testing of multitudes of strongly dipolar molecules with high molecular hyperpolarisabilities β—has now been superseded by more rational approaches at the molecular and supramolecular level. These include the maturing concepts of supramolecular chemistry[3] and crystal engineering,[4] which aim to predict how molecules pack or self-assemble in the crystalline state,[4,5] thus providing some clues to the resulting solid-state properties of the materials. Recent theoretical advances in chromophore design,[6] for example the design of octupolar (zero dipole moment) molecules, have opened up new avenues for potential exploration by synthetic chemists.[7–9] These more systematic *modi operandi* have been brought about in part by the minimum requirement for molecular crystals to exhibit measurable NLO activity, namely that they must necessarily belong to a non-centrosymmetric space group.[1] Such packing motifs, however, tend to be avoided by many strongly dipolar molecules with high β values, on electrostatic grounds. Furthermore, strong NLO activity is only achieved in crystal structures in which the orientations of the principal dipolar axes of the chromophores are optimised for the particular NLO effect required. For example, for efficient phase-matched SHG, an angle of *ca.* 55° is required between the charge-transfer (CT) axis of the chromophore and the polar crystal axis; for the electro-optic (EO) effect, the CT axes should lie co-parallel.[1] Many ingenious approaches to satisfy all these criteria have been developed. For the effect of SHG these include: (i) the use of poled polymers, in which the NLO-active component is either a guest in an inert polymer matrix or an intrinsic component of the polymer itself;[10,11] (ii) Langmuir–Blodgett films;[11–13] (iii) molecular co-crystals (organic salts);[14,15] (iv) other acentric solid state arrangements constructed from single-component molecules *via* strong, directional intermolecular interactions (supramolecular synthons), *e.g.* nitrophenylhydrazones;[16] (v) the design of molecules with almost zero ground-state but large first excited-state dipole moments, to encourage non-centrosymmetric packing, *e.g.* POM (3-methyl-4-nitropyridine *N*-oxide);[1] and finally (vi) the reduction in crystal symmetry of centrosymmetric host crystals through the occlusion of tailor-made, SHG-active auxiliaries.[17] Many of these approaches to the rational crystallisation of supramolecular materials have been reviewed recently.[5] All methods have their relative merits and disadvantages; with respect to the latter, the most notable are dilution of the active component in the case of polymers and co-crystals, and the frequent lack of control over supramolecular assembly in one or two dimensions in the case of crystal engineering strategies.

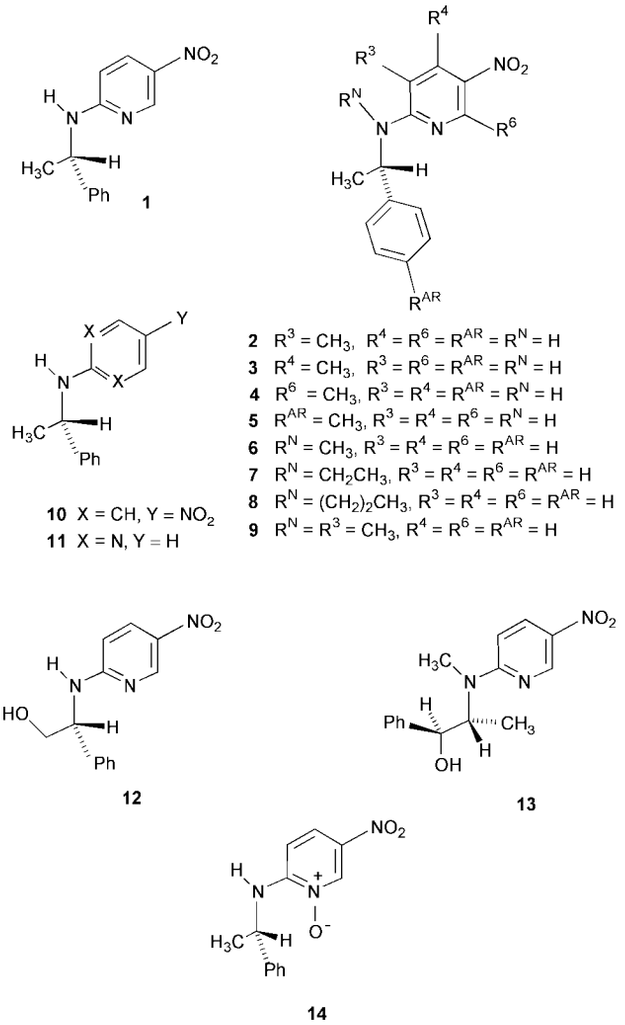
One particular procedure which guarantees non-centrosymmetric packing and very frequently (though not without exceptions[18]) yields measurable SHG activity is the crystallisation of NLO-active molecules in enantiomorphous space groups.[1,2] Even racemic compounds (*e.g.* (±)-*o*-tyrosine) and achiral molecules can crystallise in such space groups (typically $P2_1$ and $P2_12_12_1$, respectively).[19] However, such cases are rather rare and not easily predicted. Clearly, the crystallisation of homochiral compounds with high β values is a more practicable route to the materials under discussion. One such material is the (*S*)-enantiomer of 5-nitro-*N*-(1-phenylethyl)pyridin-2-amine **1**[20] which has been studied in detail by one of our groups.[21] Large crystals of **1** ($P2_1$) can be grown from solution and cut and polished to optical quality. Crystals exhibit Type I, phase-matched SHG with an efficiency of 0.5% at 58.8 MW cm^{-2} (comparable to lithium iodate). The crystals

†Spectroscopic and analytical data for compounds **3,4,7,8,10–14** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/jm/b0/b008124h/



Scheme 1 *Reagents and conditions*: (*a*), HNO_3–H_2SO_4; (*b*), HNO_3, heat; (*c*), $POCl_3$; (*d*), MeI–DMSO–KOH(s).

also exhibit the phenomenon of rotating dielectric axes, the first time this has been observed for an organic material. Whilst **1** has proven to be a considerable success as a commercially viable NLO-active organic material, it suffers during processing from the fact that it decomposes in the melt and is also quite difficult to polish. Here we report on the large-scale synthesis, structural characterisation and crystal growth of derivatives of (*S*)-5-nitro-*N*-(1-phenylethyl)pyridin-2-amine with small additional substituents.[22] The aim was to alter subtly the crystal packing and hence the physical properties of the parent molecule without sacrificing its good NLO characteristics. The first targets were derivatives which carried an extra methyl group.



2 $R^3 = CH_3$, $R^4 = R^6 = R^{AR} = R^N = H$
3 $R^4 = CH_3$, $R^3 = R^6 = R^{AR} = R^N = H$
4 $R^6 = CH_3$, $R^3 = R^4 = R^{AR} = R^N = H$
5 $R^{AR} = CH_3$, $R^3 = R^4 = R^6 = R^N = H$
6 $R^N = CH_3$, $R^3 = R^4 = R^6 = R^{AR} = H$
7 $R^N = CH_2CH_3$, $R^3 = R^4 = R^6 = R^{AR} = H$
8 $R^N = (CH_2)_2CH_3$, $R^3 = R^4 = R^6 = R^{AR} = H$
9 $R^N = R^3 = CH_3$, $R^4 = R^6 = R^{AR} = H$

10 X = CH, Y = NO_2
11 X = N, Y = H

12

13

14

Results and discussion

Synthesis of new materials

Molecules **2**–**4**, derivatives of 5-nitro-*N*-(1-phenylethyl)pyridin-2-amine with a methyl group at different positions on the pyridine ring, were prepared by reactions between the corresponding 2-chloro-5-nitropicoline‡ with enantiopure α-methylbenzylamine.[20] 2-Chloro-3-methyl-5-nitropyridine **17** (Scheme 1), required for the synthesis of **2**, was prepared from the corresponding 2-aminopicoline by nitration to give the 5-nitro derivative **15** and immediate hydrolysis to give the 2-pyridone **16** in 55% yield from the aminopicoline.[23] Chlorination with phosphorus oxychloride gave **17** in 93% yield. Treatment of **17** with (*S*)-α-methylbenzylamine **18** in ethanol and triethylamine gave **2** in 83% yield after purification by chromatography on silica. The product was highly crystalline and following encouraging SHG powder test studies (*vide infra*), the synthesis of **2** was carried out successfully on a large scale, preparing typically 100 g material at a time. Retention of the stereochemical configuration was confirmed by comparison of the ^{1}H NMR spectrum of **2** in the presence of a chiral solvating reagent with that of racemic **2**. Analogously, the 4-methyl derivative **3** was synthesized from commercially available 4-methyl-5-nitropyridin-2-amine and 6-methyl-5-nitropyridin-2-amine was converted to the 6-methyl derivative **4**. However, both materials were poorly crystalline. The derivative of **1** with a methyl group on the *para* position of the phenyl ring, **5**, was prepared as a nicely crystalline material from reaction of 2-chloro-5-nitropyridine and the commercially available enantiopure amine **19**. Methylation of the amino nitrogen atom of **1** to give derivative **6** was achieved by alkylation in dimethyl sulfoxide with iodomethane and powdered potassium hydroxide.[24] After purification by chromatography the product was obtained as a highly crystalline product in 87% yield. As a result of promising powder tests, this reaction was scaled up successfully, yielding batches of 50 g of **6**. Using the same procedure, **1** was converted to the *N*-ethyl derivative **7** with iodoethane in 82% yield but the product was a yellow oil. Corresponding reactions using iodopropane or benzyl bromide gave much lower yields. The 3-methyl analogue **2** was *N*-methylated in the same way to give crystalline **9**.

Three further types of structural modifications were made to the 5-nitro-*N*-(1-phenylethyl)pyridin-2-amine structure. The first involved replacement of the nitropyridine ring by a

‡The IUPAC name for picoline is methylpyridine.

Table 1 SHG activity for a range of derivatives of 5-nitro-*N*-(1-phenylethyl)pyridin-2-amine

Compound	SHG(× urea)
1	20
2	18
3	0.75
4	1.5
5	10
6	15
9	0.5
10	8
11	0.2
13	0.3
14	0.18

Table 2 Selected molecular geometry for **1**, **2**, **5**, **6** and racemic **2**

	N(1)–C(2)–N(2)–C(7) Torsion angle/°	C(2)–N(2)–C(7)–C(8) Torsion angle/°	pyridine/ phenyl ring Interplanar angle/°
1	−11(1)	173(1)	84(1)
2	−6.8(6)	175.2(4)	78.4(2)
5A	169.2(3)	150.9(4)	70.9(2)
5B	176.5(3)	169.0(4)	77.2(2)
5C	−8.3(3)	155.3(3)	79.3(2)
6A	1.2(4)	111.9(4)	82.4(1)
6B	−3.9(4)	107.6(4)	86.5(1)
(±)-**2**	−9.6(2)	149.3(1)	77.1(1)

nitrophenyl group or a pyrimidine ring to give **10** and **11**, which were synthesised from chiral amine **18** with 4-fluoronitrobenzene and 2-chloropyrimidine, respectively. A second modification aimed to introduce new hydrogen bonding donors into the molecular structure. Reaction of 2-chloro-5-nitropyridine with (*R*)-2-amino-2-phenylethanol and (1*R*,2*S*)-(−)-ephedrine gave **12** and **13** in very high yields. However, **12** was obtained as a hard glass which softened at 45 °C and not as a crystalline solid. Although solid **13** appeared to be stable it showed a tendency to decompose in solution. The final change involved the synthesis of the pyridine *N*-oxide of parent molecule **1**. The reason for the incorporation of the *N*-oxide group was to explore the effect of the *N*-oxide on the conformation of the 1-phenylethylamino side chain and its subsequent effects on the crystal packing.§ Treatment of **1** with 3-chloroperoxybenzoic acid following a general procedure[25] gave the *N*-oxide **14** in 84% yield but as a sticky oil which slowly solidified over months to a powdery solid.

SHG powder test studies

The SHG powder test results are presented in Table 1. Among the mono-methylated derivatives, compounds **2**, **5** and **6** show the most promising activity, being 10–18 times greater in SHG than urea and nearly as good as **1** itself. The 4- and 6-methyl derivatives showed low activity in the powder test which may be related to their poorer crystallinity. This is probably due to the nitro group not conjugating fully with the amino group *via* the pyridine ring due to steric hindrance from the *ortho* methyl group; for example, in nitrotoluene derivatives the nitro group lies typically at *ca.* 40° to the aromatic plane.[26] This effect would reduce the polarity of the molecule and the strength of its intermolecular interactions. Although inclusion of a 3-methyl group or an *N*-methyl group does not alter the result of the powder test too much, the inclusion of both methyl groups is detrimental with **9** showing just one fortieth of the result for **1** itself. The 5-nitropyridine ring is an essential feature of the SHG effect; replacement with an unsubstituted pyrimidine ring led to a 100 fold reduction. Replacement with a nitrophenyl ring produced a powder test result at 40% of that for **1**, the greater electron attracting power of the pyridine ring is the critical feature. Of the two compounds included to produce more hydrogen bonding, **12** existed as a glass which did not show signs of crystallisation over several months, and crystalline **13** showed a powder result nearly two orders of magnitude less than **1**. The *N*-oxide of **1** also showed an equally disappointing low powder test result. The racemates of **2** and **5** were also tested but found to be inactive. Although this may be due to centrosymmetric crystal structures, and since proven for **2**, it is not always the case that such racemates are inactive. Racemic **1** does generate second harmonic radiation since the space group of the crystals is *Aba*2.[27] For the next step, the solid state structures of the most promising materials **2**, **5** and **6** were examined by X-ray crystallography prior to selection of materials for intensive study.

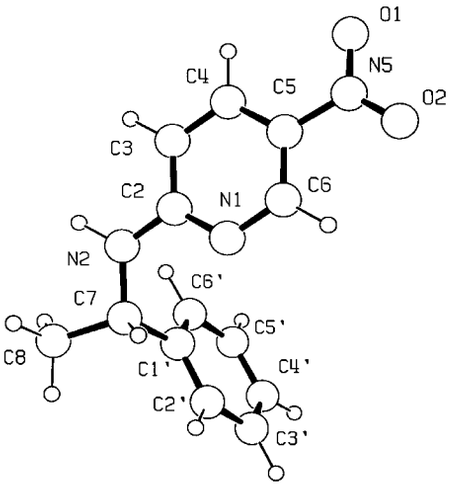


Fig. 1 Molecular conformation of **1**.

Crystal structure analyses

The solid-state structures of **2**, **5** and **6** were determined by single crystal X-ray diffraction to establish the molecular conformations, orientations of the charge-transfer axes and the packing arrangements of the molecules. The study of the crystal structures of this family of closely related molecules may provide some insight into the importance of the intermolecular forces which determine the crystal packing arrangement, and give an example of the scope and limitations to crystal engineering by subtle changes to the molecular structure. The molecular skeleton of these derivatives has two degrees of freedom which determine the molecular conformation. These are the rotations about the N–C bonds from the amino nitrogen atom to the pyridine ring and to the stereogenic centre. Additional degrees of freedom define the orientations of the nitro and phenyl groups with respect to the molecular framework. Since the amino nitrogen atom is likely to have planar bonding geometry only two conformations about the N–C(pyridine) bond are expected: the stereogenic centre can lie either *synperiplanar* or *antiperiplanar* to the pyridine nitrogen atom. The likely orientations about the bond from the amino nitrogen atom to the stereogenic centre are less restricted. Indeed, only direction of the methyl or the phenyl groups into an eclipsing position with the pyridine ring is likely to be especially unfavoured. Selected conformational geometry is given in Table 2.

§The introduction of an *N*-oxide group as an aid to induce a small ground state dipole moment in the pyridine ring (as in the classic case of POM[1]), and therefore encourage non-centrosymmetric packing, is not necessary here because the chiral nature of (*S*)-**1** guarantees a non-centrosymmetric space group.

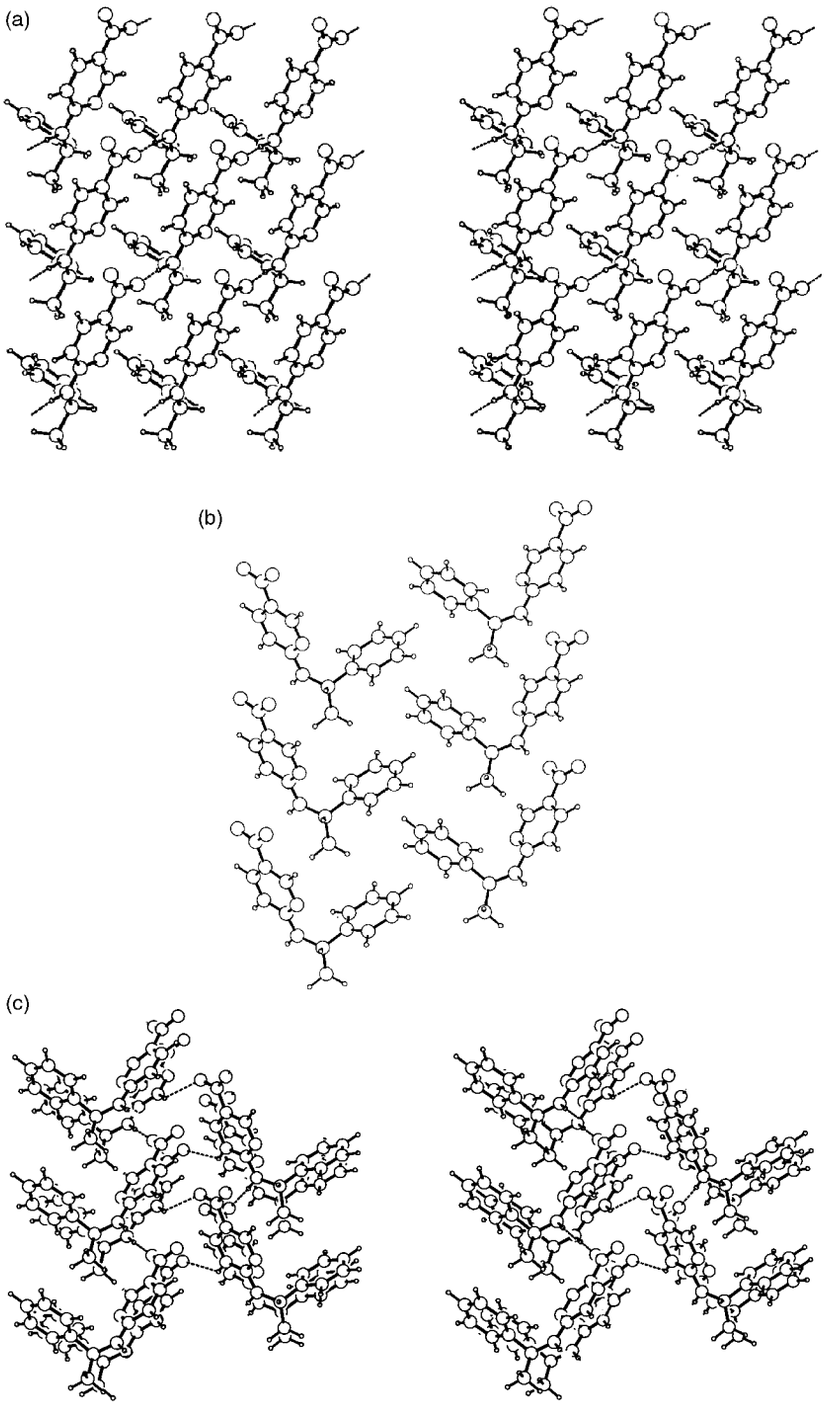


Fig. 2 Details of the crystal packing arrangement[41] of **1**: a) Stereoview of the formation of layers from hydrogen bonded ribbons of molecules. b) Interlocking of phenyl groups at one interface between layers. c) Stereoview of the C–H···O(NO) hydrogen bonding at the second interface between layers.

The molecular conformation and packing arrangement (Figs. 1 and 2) in crystalline enantiopure **1**[28] will be described in some detail as a reference point for the description of the solid state structures of related substances. The same atomic numbering scheme is used for all molecules described subsequently. The stereogenic centre, C(7), lies almost *synperiplanar* to the pyridine nitrogen atom. The side chain is oriented with the methyl group eclipsed by the amino group's hydrogen atom and *antiperiplanar* to the N(2)–C(2) bond. The planes of the phenyl and pyridine rings lie close to perpendicular and the inter-nesting of these V-shaped molecules as well as N–H···O and C–H···O hydrogen bonding are critical in the determination of the mode of solid state packing. In the crystal the molecules are connected into ribbons by hydrogen bonds between the amino group's hydrogen atom and the nitro oxygen atom O(2) which is *synperiplanar* to C(6) (N···O, 3.04(1) Å, N–H···O 1.97(7) Å, angle N–H···O: 170(5)°). These ribbons are aligned to form layers of molecules perpendicular to the *a* axis (Fig. 2a). The space group is $P2_1$ and the three dimensional structure is formed by an ABAB packing arrangement of these layers, with crystallographic 2_1 axes lying between each pair of adjacent layers. In alternate layers, the hydrogen bonded ribbons are oriented along either the [0 1 1] or [0 1 −1] directions, while along the [0 1 0] direction the V-shaped molecules are inter-nested. The two sides of a layer are quite different. All the phenyl groups are directed out from one side of a layer, and in the three dimensional structure two such faces are opposed and interweave their phenyl groups

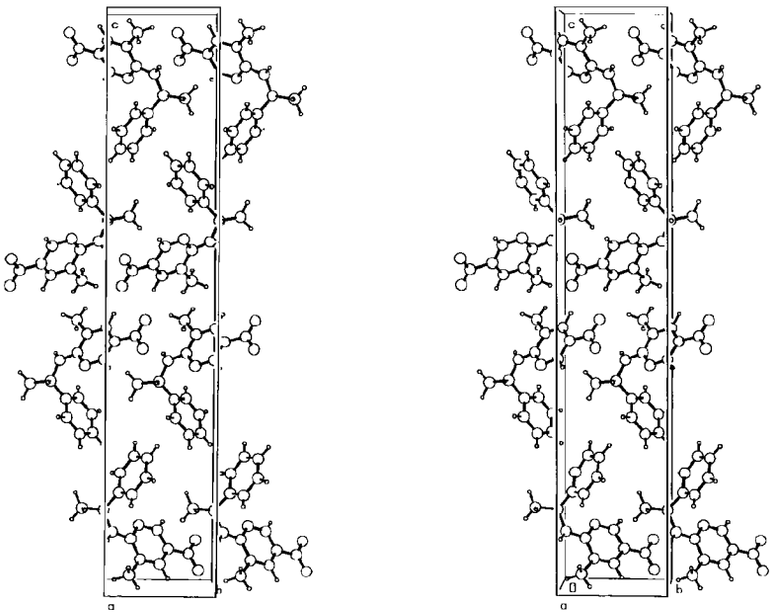


Fig. 3 Stereoview of the crystal packing arrangement[41] in **2**.

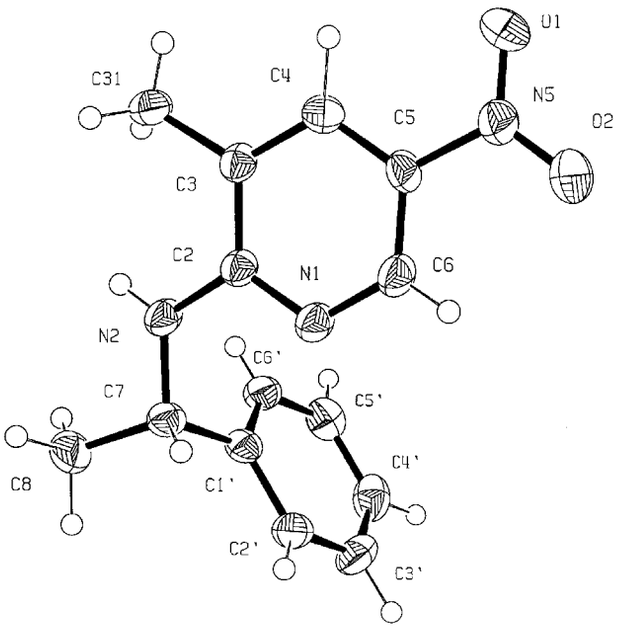


Fig. 4 Molecular conformation[40] of **2** with atomic displacement parameters drawn at the 50% probability level.

as shown (Fig. 2b). The shortest contacts between these faces are C···H contacts in the 2.9–3.0 Å range. The other face of the layer is formed by two pyridine ring hydrogen atoms (3- and 4-H) and a nitro oxygen atom (O(1)) from each constituent molecule. In the solid state structure two such faces are opposed. The critical contacts are weak hydrogen bonding interactions between H(3) atoms of one plane with protruding nitro O(1) atoms of the second plane (Fig. 2c). The C–H···O distance is 2.51(6) Å, the C–H···O angle is 129(3)°, and the N–O···H angle is 135(1)°. Short interactions between aromatic C–H and the oxygen atoms have been widely observed and are accepted as indications of weak hydrogen bonding.[29,30] A search of the Cambridge Crystallographic Database[26] reveals many examples of contacts between nitro O atoms and aryl H atoms in the 2.3–2.4 Å range, and neutron diffraction measurements of *p*-dinitrobenzene[31] and *s*-trinitrobenzene[32] have shown contacts in the range 2.20–2.37 Å.

Initial crystallisation experiments on enantiopure **2**, the 3-methyl derivative of **1**, indicated that it readily formed clear yellow block and rod-like crystals, with identical unit cell dimensions. The melting point was 67 °C higher than that of **1**. The small structural change compared with **1** has a quite notable consequence on the size of the unit cell. Two cell lengths are very similar to those in **1** but the third one is doubled to 35.88 Å, and this corresponds to the direction perpendicular to the layers in crystalline **1**. The layer packing is now of an ABCDABCD type (Fig. 3). The crystal system has

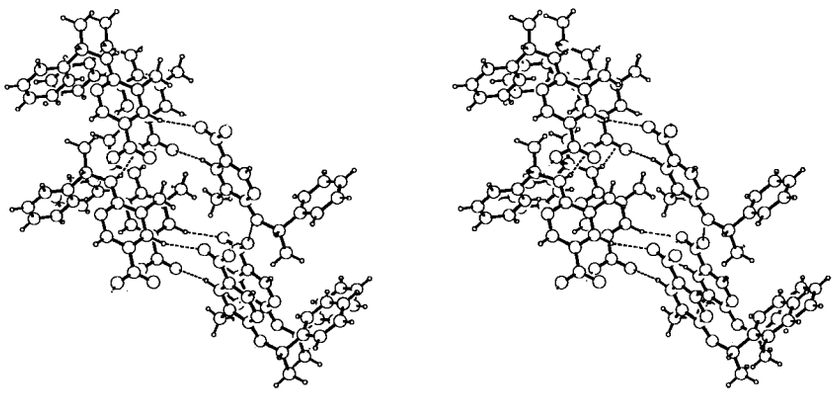


Fig. 5 Stereoview of the C–H···O(NO) hydrogen bonding at one interface between layers for crystalline **2**.[41]

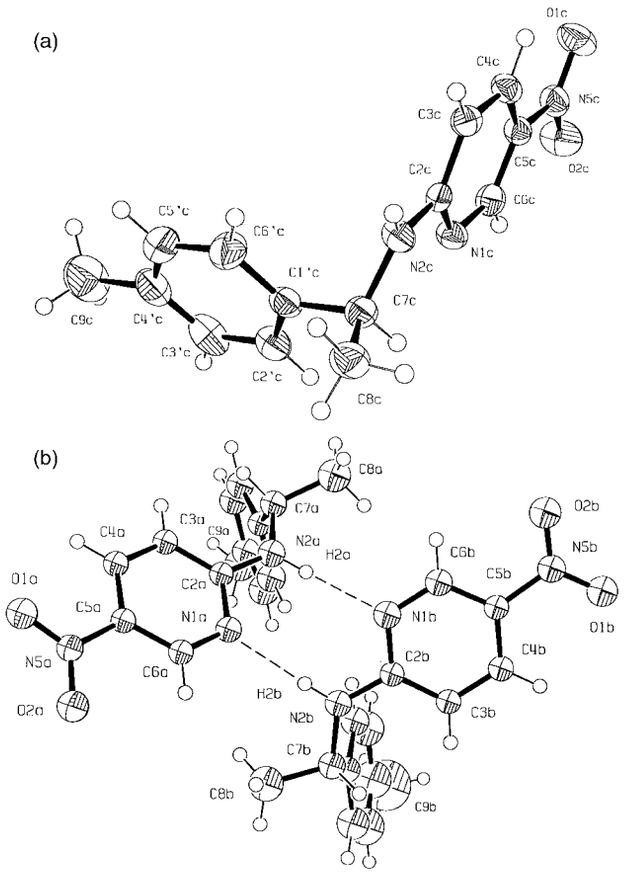


Fig. 6 Molecular conformations[40] of three unique molecules of **5** with atomic displacement parameters drawn at the 50% probability level: a) molecule C, with conformation similar to that in crystalline **1**; b) molecules A and B linked by a pair of N–H···N hydrogen bonds.

changed to orthorhombic, and the space group is $P2_12_12_1$. The molecular conformation of **2** (Fig. 4) is similar to that of **1** (Table 2). The short bond from the amino nitrogen atom to the pyridine ring (1.360(5) Å) is indicative of electron delocalisation from nitrogen into the pyridine ring. The plane of the nitro group is almost coplanar with the pyridine ring (interplanar angle: 4.2(5)°). The structure of the ring shows some 'quinoid' character with the N(1)–C(6) (1.337(5) Å) and C(3)–C(4) bonds (1.380(4) Å) being shorter than the other N–C (1.350(5) Å) and C–C bonds (1.384(6)–1.428(6) Å).

In the crystal structure the arrangement of molecules within a layer is very similar to that in **1** with N(2)–H(2)···O(2) hydrogen bonding linking the molecules into ribbons (NH···O 2.20(4) Å, N···O 3.014(5) Å, angle N–H···O 161(3)°). The ribbons lie side by side to form layers with phenyl groups protruding from one face of the layer only. There is internesting of V-shaped molecules along the [0 1 0] direction, and the charge transfer axis of the molecule lies at 30.8° to this direction. The layers pack with like faces together. The packing between the faces containing protruding phenyl rings is similar to that in **1**, and involves interlocking of these groups. This pair of layers is related by crystallographic 2_1 axes parallel to the *b* axis. However, compared with **1** there is a change where the other faces meet. The critical difference is that installation of a methyl group at the 3-position blocks the interplanar C–H···O hydrogen bonding which was observed for **1**. The crystal packing pattern at this interface thus changes to allow C–H···O bonding between the same nitro oxygen atom, O(1), and the 4-hydrogen atom (H···O 2.40(4) Å, C(4)···O(1) 3.395(5) Å, angle C(4)–H(4)···O(1) 160(3)°) (Fig. 5). These two layers are related by two fold screw axes parallel to the *a* axis, and perpendicular to the 2_1 axes at the other interface. This generates an ABCD packing arrangement before the cycle can be repeated (Fig. 3). The two sets of 2_1 axes generate a third set of 2_1 axes parallel to the *c* axis, which relate the first and third, second and fourth layers *etc.* In **2** the interlayer C–H···O contacts are much nearer to the preferred linear arrangement (angle at H: **2**, 160 *cf.* **1**, 129°) and, furthermore, the *ortho*-nitro group in **2** withdraws electron density from the 4-H atom enhancing its potential for hydrogen bonding while in **1** the equivalent hydrogen atom is *ortho* to an electron donating nitrogen atom. The recently reported[33] crystal structure of the closely related derivative (*R*)-3,5-dinitro-*N*-(1-phenylethyl)pyridin-2-amine, shows an alternative molecular conformation and packing arrangement. There is an intramolecular N–H···O hydrogen bond between the amino group and the *ortho*-nitro group, which weakens the role of an additional intermolecular hydrogen bond from the amino hydrogen atom to a 5-nitro group.

Despite the simple relationship between the crystal packings of **1** and **2**, even small changes can result in complex changes to the crystal packing, as can be seen in the structure of **5** which differs from **1** by the addition of a methyl group to the *para*-position of the phenyl ring. Now there are three independent molecules (A, B, and C) in the asymmetric unit, which exhibit two different conformational types! Molecule C adopts a conformation similar to that of **1** (Fig. 6a), the main difference is a rotation of *ca.* 16° about the N(2)–C(7) bond which leaves the methyl group displaced significantly out of the pyridine plane. In contrast, the conformations of molecules A and B are quite different. The stereogenic carbon centres in these molecules are nearly *antiperiplanar* to their pyridine nitrogen atoms, and not *synperiplanar* as in molecule C. The conformations about the N(2)–C(7) bonds put the methyl groups nearly

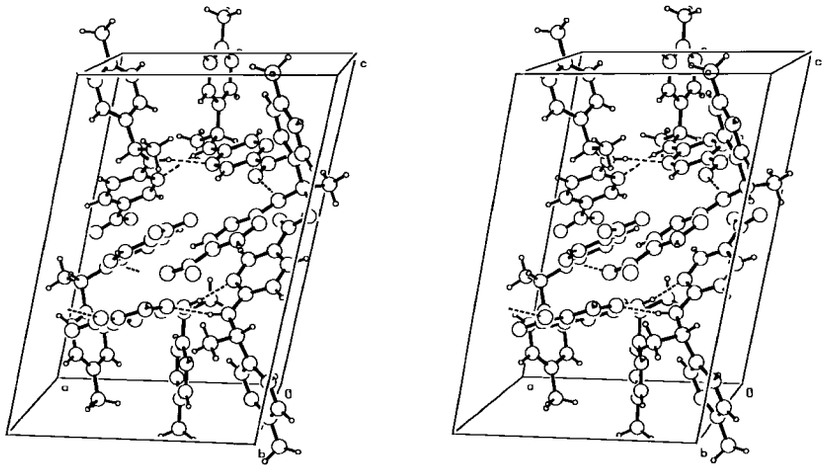


Fig. 7 Stereoview of the crystal packing arrangement[41] of **5**.

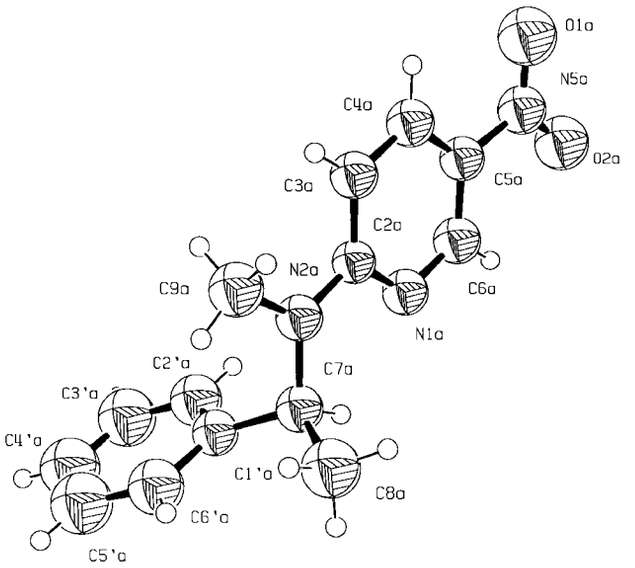


Fig. 8 Molecular conformation[40] of one of the two unique molecules in crystalline **6** with atomic displacement parameters drawn at the 50% probability level.

antiperiplanar to the N(2)–C(2) bonds. The two molecules are linked to each other by two N–H···N(pyridine) bonds (Fig. 6b). The distances between pyridine and amino nitrogen atoms are 2.998(5) and 3.010(5) Å. In this dimeric unit, the charge transfer axes are disposed in almost opposite directions. The crystal packing pattern of these two motifs is shown in Fig. 7. Molecule C is linked to the A/B dimer by a hydrogen bond between the N–H bond of molecule C and a nitro oxygen atom of molecule B (O(2B)···H(2C): 2.22 Å, O(2B)···H(2C)–N(2C): 146°, N(2B)–O(2B)···H(2C) 124°), so that the axes of the three 4-methylphenyl groups are all directed to the same side. This motif is packed into layers in the *ab* plane, with adjacent layers related by the two fold axes along *b*. One interface between the layers involves primarily π–π stacking between the nitropyridine rings, and the second interface is formed by interlocking of the 4-methylphenyl rings.

Initial crystallisation experiments on the *N*-methyl derivative **6** indicated ready formation of crystalline material. The space group is $P2_1$ and the asymmetric unit contains two crystallographically independent molecules which have similar conformations (Fig. 8). The stereogenic centre lies *synperiplanar* to the pyridine nitrogen atom as observed in **1**, **2** and one molecule of **5**. Addition of the *N*-methyl group alters the conformational preference about the N(2)–C(7) bond. The methyl and phenyl groups attached to C(7) now stagger the N–Me bond (C(9)–N(2)–C(7)–C(8): 67.4(4) and 69.7(3)°; C(9)–N(2)–C(7)–C(1′): 60.9(4) and 58.0(4)°), and leave the hydrogen atom attached to C(7) lying near to the heterocyclic plane and directed towards the pyridine nitrogen atom (C(2)–N(2)–C(7)–H(7): 8.8(3) and 4.3(3)°). The planes of the phenyl and pyridine groups lie close to perpendicular, however, their mutual orientation is quite different from those in crystalline **1** and **2**, due to the conformational change about N(2)–C(7) and a rotation about the phenyl ring's axis, so that inter-nesting of molecules is no longer possible. The nitro groups are coplanar with their attached pyridine rings (interplanar angles 2.9(6) and 3.8(3)°), and the short bonds between the pyridine ring and the amino nitrogen atom (1.362(4) and 1.357(3) Å) are in accord with the presence of the dipolar axis. The crystal packing arrangement (Fig. 9) bears no resemblance to those of **1** and **2** since there is now no possibility of N–H···O hydrogen bonding. There is some evidence for C–H···O interactions between nitro oxygen atoms and the hydrogens of the electron deficient pyridine rings (O(1B)···H(6A): 2.45 Å).

The crystal structure of racemic **2** was determined, since

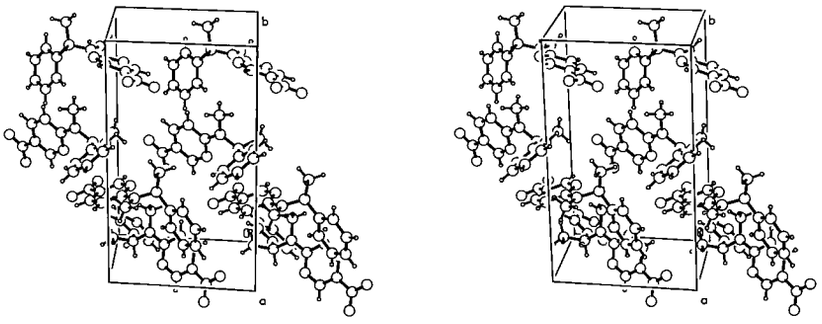


Fig. 9 Stereoview of the crystal packing arrangement[41] of **6**.

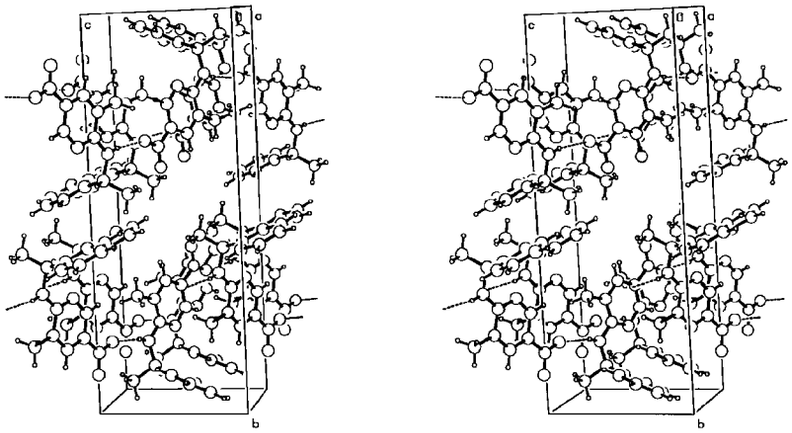


Fig. 10 Stereoview of the crystal packing arrangement[41] of racemic **2**.

racemic **1** retained some nonlinear optical activity by crystallising in a non-centrosymmetric space group *Aba*2,[26] however the space group was centrosymmetric and the molecular conformation and packing (Fig. 10) were quite different. Compared to enantiopure **2** there is a rotation of *ca.* 25° about the N(2)–C(7) bond which puts the axis of the phenyl group almost perpendicular to the pyridine plane and moves the methyl group out of this plane. N–H···O hydrogen bonding between amino and nitro groups produces ribbons of molecules, but in this racemic case the enantiomers are arranged alternately along the ribbon (NH···O 2.29(2) Å, N···O 3.140(2) Å, angle N–H···O 169(2)°). Neighbouring ribbons are arranged with pyridine rings parallel to form sheets perpendicular to the *b* axis, but nearest neighbours between ribbons are of opposite stereochemical configuration so that there can be no inter-nesting of molecules as was observed in the enantiopure substance. In contrast to the enantiopure crystal, where the two faces of the sheet were quite different, in the racemic case they are related by a glide plane. There are no especially close contacts between the layers.

Choice of new materials for intensive study

Of the three materials which looked most promising in the powder tests, **2**, **5** and **6**, the compounds **2** and **6** were chosen for large scale synthesis and crystal growth studies. All three substances had higher melting points than **1**, indeed that of **2** was almost 70 °C higher which would widen the temperature range over which crystals could be grown. Compound **5** has not been examined further as yet primarily because it showed a lower SHG activity which may be related to the fact that the asymmetric unit contained three independent molecules, two of which had their dipolar axes aligned more or less *anti*-parallel. Both **2** and **6** have been synthesized in large quantities and purified by chromatographic methods. Both materials could be grown into large crystals (typical size $40 \times 40 \times 15$ mm^3) from saturated warm acetone solutions. Crystalline material of **2** can also be obtained from the vapour and the melt. Prisms have been cut and polished from both materials, and full details of their crystal growth and non-linear optical properties will be reported elsewhere.[34] Compound **2** crystallises in the orthorhombic space group $P2_12_12_1$. It follows from the crystallographic symmetry that the dielectric axes coincide with the crystallographic axes and cannot rotate about the *b* axis in this material as they do in **1** despite the fact that the two molecules only differ by replacement of a hydrogen atom with a methyl group. This latter feature was unique for **1** among organic optical materials. No evidence for rotating dielectric axes has been found in optical experiments on **6**. Compound **2** possesses a well defined cleavage plane (001), but compound **6** has no well defined cleavage plane. This latter property is an advantage when polishing samples where easy cleavage leads to considerable difficulty in achieving optical quality faces. Compound **6** is also harder than **1** and **2** and is easier to polish for this reason. In **2** the molecular charge transfer axis lies closest to the *b* axis with which it makes an angle of 30.8°, while the angles to the *a* and *c* axes are 66.1° and 71.8°. The $\chi^{(2)}$ tensor for crystalline **2** contains only cross terms *i.e.* applied fields in the directions *x* and *y* induce a polarisation in the *z* direction and this field mixing does not require the presence of a well defined 'charge transfer' direction throughout the crystal. The closer alignment of the molecular charge transfer axis with the *y* dielectric axis (coincident with the crystallographic *b* axis) is supported by the largest refractive index being in the *y* direction. In crystalline **6** observing the *ac* plane (Fig. 9) the charge transfer axes of one set of molecules make an angle of *ca.* 50° with the *c*-axis, and the second (crystallographically independent) set of molecules have their pyridine rings roughly edge-on to the *ac* plane and their charge transfer axes make an angle of *ca.* 30° with the *c*-axis. The resultant charge transfer axis lies at 40.1° to the *c* axis. As expected, the largest refractive index is in the *z* direction.

Experimental

General

High resolution ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 FT NMR spectrometer, operating at 270.05 and 67.80 MHz respectively. The solvent employed was $CDCl_3$ unless stated otherwise and contained tetramethylsilane (1% v/v) as an internal reference ($\delta_{TMS} = 0.00$ ppm). Coupling constants *J* are measured in Hz. Infra-red samples were prepared as Nujol mulls. Optical rotations were measured at 589 nm and are given in 10^{-1} deg cm^2 g^{-1}. Anhydrous THF was obtained by distillation over sodium–benzophenone; Et_3N was purified by reflux and distillation over CaH_2. Flash column chromatography was performed on Sorbsil C 40/60-H silica gel (40–60 microns).

2-Chloro-5-nitropyridines

2-Chloro-3-methyl-5-nitropyridine **17**[35] and 2-chloro-6-methyl-5-nitropyridine[36,37] were synthesized by literature methods, and 2-chloro-4-methyl-5-nitropyridine was purchased from Aldrich.

Reactions of 2-chloro-5-nitropyridines with chiral amines

Typically, the 2-chloro-5-nitropyridine derivative (1.0 mol. eq.) was dissolved in absolute ethanol (5–10 ml per 1 g of chloronitropyridine) and the enantiopure amine **18** or **19** (1.5–2.0 mol. eq.) and distilled Et_3N (1.5–2.0 mol. eq.) were added and the solution refluxed with stirring under a nitrogen atmosphere for 24–72 h. The solvent was removed by rotary evaporation under reduced pressure and the residue taken up in water and ethyl acetate. The organics were extracted with ethyl acetate ($\times 3$) and washed with brine solution. Drying over anhydrous sodium sulfate followed by filtration and removal of solvent, yielded an orange-yellow solid. Purification by flash column chromatography on silica, using ethyl acetate–hexane (normally 3 : 7) as eluent, yielded the desired product as a yellow crystalline solid or as a viscous oil which crystallised slowly on cooling. Residual solvent was removed by drying *in vacuo* over P_2O_5.

(*S*)-3-Methyl-5-nitro-*N*-(1-phenylethyl)pyridin-2-amine 2

Yellow cubes and rods (from aqueous ethanol) (83.2%); mp 145–146 °C; found: C, 65.4; H, 5.8; N, 16.4%. $C_{14}H_{15}N_3O_2$ requires: C, 65.4; H, 5.9; N, 16.3%; δ_H: 8.91 (d, $J_{6,4}$ 2.6, 6-*H*), 7.99 (dd, $J_{4,6}$ 2.6 and $J_{4,Me}$ 0.8, 4-*H*), 7.32 (m, C_6H_5), 5.51 (quin, $J_{H,Me}$ 6.9 and $J_{H,NH}$ 6.6, C*H*Me), 5.11 (br d, $J_{H,NH}$ 6.6, N-*H*), 2.17 (s, 3-CH_3) and 1.63 (d, $J_{H,Me}$ 6.9, CHCH_3); δ_C: 158.84 (2-*C*), 144.47 (1′-*C*), 143.53 (6-*C*), 135.86, 131.48 (4-,5-*C*), 128.78 (3′-,5′-*C*), 127.51 (4′-*C*), 126.16 (2′-,6′-*C*), 115.79 (3-*C*), 50.81 (*C*HMe), 22.28 (CH*C*H$_3$) and 16.75 (3-*C*H$_3$); ν_{max}: 3398, 3394, 1597, 1520, 1124 and 702; *m*/*z* (CI): 258 ([M+H]$^+$, 100%), (228); $[\alpha] = -201$ ($c = 0.48$, dichloromethane). Subsequently this material was prepared on a large scale yielding 80 g of product after chromatography and recrystallisation. Further purification, before crystal growing experiments were started, was made by continuous chromatography[2] on silica using dichloromethane as eluent.

(*S*)-5-Nitro-*N*-(1-(4′-methylphenyl)ethyl)pyridin-2-amine 5

Flat needles (from aqueous ethanol) (84.2%); mp 106–108 °C; found: C, 65.5; H, 5.9; N, 16.3%. $C_{14}H_{15}N_3O_2$ requires: C, 65.4; H, 5.9; N, 16.3%; δ_H: 8.95 (d, $J_{6,4}$ 2.7, 6-*H*), 8.09 (dd, $J_{4,3}$ 9.3, $J_{4,6}$ 2.7, 4-*H*), 7.23 (d, *J* 8.1, 2′-,6′-*H*), 7.16 (d, *J* 8.1, 3′-,5′-*H*), 6.23 (d, $J_{3,4}$ 9.3, 3-*H*), 6.00 (br s, N-*H*), 4.87 (m, br s, C*H*Me),

2.33 (s, 4′-CH_3) and 1.59 (d, $J_{H,Me}$ 6.7, CHCH_3); δ_C: 160.51 (2-*C*), 146.77 (6-*C*), 139.75 (1′-*C*), 137.36 (4-*C* or 5-*C*), 135.90 (4′-*C*), 133.00 (4-*C* or 5-*C*), 129.58 (3′-,5′-*C*), 125.68 (2′-,6′-*C*), 105.49 (3-*C*), 51.86 (*C*HMe), 23.51 (CH*C*H_3) and 21.04 (4′-*C*H_3); ν_{max}: 3369, 3220, 3051, 1603, 1585, 1577, 1525, 1493, 1329 and 1290; *m*/*z*: (CI) 258 ($[M+H]^+$), 243 ($[M+H-Me]^+$), 119 (100%) and 91; $[\alpha] = -189$ (*c* = 1.0, dichloromethane).

General procedure for *N*-alkylation of 1

Powdered potassium hydroxide (4 mol. eq.) was added to DMSO (10 ml per 1 g KOH) and stirred for 5 min. **1** (1 mol. eq.) was added in one portion and the resulting orange-red solution stirred for another 10 min. The appropriate alkyl iodide (1.2 mol. eq.) was added and stirring continued for another 1–4 hours. The resulting darker, blood-red solution was added to water (1.2 L per 0.1 mol product) and extracted with dichloromethane (4 × 500 ml per 0.1 mol product). The combined organics were washed with water (3 × 500 ml per 0.1 mol product), dried over anhydrous sodium sulfate, filtered and the solvent removed to yield a viscous brown oil which, depending on the product, crystallised slowly on cooling. Chromatography on silica eluting typically with hexane–ethyl acetate 7 : 3 gave the purified product with a characteristic yellow-orange colour which was dried *in vacuo* over P_2O_5.

(*S*)-*N*-Methyl-5-nitro-*N*-(1-phenylethyl)pyridin-2-amine 6

Thick yellow needles (from methanol) (87.0%); mp 98–100 °C; found: C, 65.1; H, 5.9; N, 16.4%. $C_{14}H_{15}N_3O_2$ requires: C, 65.4; H, 5.9; N, 16.3%; δ_H: 9.09 (d, $J_{6,4}$ 2.7, 6-*H*), 8.21 (dd, $J_{4,3}$ 9.3, $J_{4,6}$ 2.7, 4-*H*), 7.31 (m, C_6H_5), 6.48 (d, $J_{3,4}$ 9.3, 3-*H*), 6.35 (br quartet, C*H*Me), 2.83 (s, N-CH_3), 1.61 (d, $J_{H,Me}$ 7.1, CHCH_3); δ_C: 160.67 (2-*C*), 146.51 (6-*C*), 140.43 (1′-*C*), 134.90 and 132.94 (4-,5-*C*), 128.61 (3′-,5′-*C*), 127.46 (4′-*C*), 126.86 (2′-,6′-*C*), 104.23 (3-*C*), 53.10 (*C*HMe), 30.91 (N-*C*H_3) and 16.16 (CH*C*H_3); ν_{max}: 1595, 1568, 1109, 766, 698; *m*/*z* (CI): 258 ($[M+H]^+$, 100) and 228 (45); $[\alpha]$ −504 (*c* = 0.47, dichloromethane). Subsequently this material was prepared on a large scale yielding 30–50 g of product after chromatography and recrystallisation. Continuous chromatography on silica was not so successful in this case.

(*S*)-*N*,3-Dimethyl-5-nitro-*N*-(1-phenylethyl)pyridin-2-amine 9

Yellow needles (ethanol), mp 60–61 °C (88%); found: C, 66.7; H, 6.6; N, 15.7%. $C_{15}H_{17}N_3O_2$ requires: C, 66.4; H, 6.3; N, 15.5%; δ_H: 8.95 (d, $J_{4,6}$ 2.8, 6-*H*), 8.10 (dd, $J_{4,6}$ 2.8, $J_{4,Me}$ 0.7, 4-*H*), 7.32 (m, C_6H_5), 5.71 (q, *J* 6.9, C*H*Me), 2.81 (s, N-CH_3), 2.39 (s, 3-CH_3), 1.65 (d, *J* 6.9, CHCH_3); δ_C: 164.0 (2-*C*), 142.5 (6-*C*), 141.0 (1′-*C*), 136.7 and 135.0 (4-,5-*C*), 128.5 (3′-,5′-*C*), 127.2 (4′-*C*), 127.1 (2′-,6′-*C*), 119.4 (3-*C*), 56.6 (*C*HMe), 33.2 (N-*C*H_3), 21.0 (3-*C*H_3), 16.3 (CH*C*H_3); ν_{max}: 1592, 1412, 1332, 1190, 1102, 1048, 1026; *m*/*z* (CI): 272 ($[M+1]^+$, 100%), 242, 168, 138; $[\alpha] = -341$ (*c* = 0.29, dichloromethane).

Compounds 3, 4, 7, 8, 10–14

Details are given in the Supplementary Information.†

Powder testing

The powder testing for second order harmonic generation was carried out by an in-house procedure at Strathclyde which has been described.[39]

¶CCDC reference number 1145/258. See http://www.rsc.org/suppdata/jm/b0/b008124h/ for crystallographic files in .cif format.

X-Ray crystallography¶

2: Crystal data. $C_{14}H_{15}N_3O_2$, $M_r = 257.29$, orthorhombic, $a = 5.481(4)$, $b = 6.791(8)$, $c = 35.88(3)$ Å, $V = 1335(2)$ Å^3, $P2_12_12_1$, $Z = 4$, $D_c = 1.28$ g cm^{-3}, $\mu(MoK\alpha) = 0.88$ cm^{-1}, $T = 150$ K, R(int) 0.12, 1842 independent reflections, final $R1 = 0.057$, $wR2 = 0.172$ for 1562 reflections with $F > 4\sigma(F)$. All hydrogen atoms were located in difference Fourier maps and their positions and isotropic displacement parameters included in the refinement. The absolute configuration was based on the known chirality of the precursor amine.

5: Crystal data. $C_{14}H_{15}N_3O_2$, $M_r = 257.29$, monoclinic, $a = 11.415(7)$, $b = 10.6973(5)$, $c = 16.935(2)$ Å, $\beta = 102.638(9)°$, $V = 2017.8(3)$ Å^3, $P2_1$, $Z = 6$, $D_c = 1.27$ g cm^{-3}, $\mu(MoK\alpha) = 0.87$ cm^{-1}, $T = 150$ K, R(int) 0.07, 5847 independent reflections, final $R1 = 0.050$, $wR2 = 0.119$ for 4322 reflections with $F > 4\sigma(F)$. Hydrogen atoms were positioned by calculation and assigned isotropic displacement parameters of 1.2 times the equivalent isotropic displacement parameter of the attached non-hydrogen atom (or 1.5 times for methyl groups) and allowed to 'ride' on the attached atom. The absolute configuration was based on the known chirality of the precursor amine.

6: Crystal data. $C_{14}H_{15}N_3O_2$, $M_r = 257.29$, monoclinic, $a = 8.979(1)$, $b = 15.977(2)$, $c = 9.410(2)$ Å, $\beta = 96.52(1)°$, $V = 1341.2(4)$ Å^3, $P2_1$, $Z = 4$, $D_c = 1.27$ g cm^{-3}, $\mu(MoK\alpha) = 0.9$ cm^{-1}, $T = 293$ K, R(int) 0.10, 3752 independent reflections, final $R1 = 0.048$, $wR2 = 0.111$ for 2870 reflections with $F > 4\sigma(F)$. Hydrogen atoms were treated in the same way as for **5**. The absolute configuration was based on the known chirality of the precursor amine.

(±)-2: Crystal data. $C_{14}H_{15}N_3O_2$, $M_r = 257.29$, monoclinic, $a = 6.978(1)$, $b = 22.337(4)$, $c = 8.390(1)$ Å, $\beta = 91.15(1)°$, $V = 1307.5(4)$ Å^3, $P2_1/c$, $Z = 4$, $D_c = 1.31$ g cm^{-3}, $\mu(MoK\alpha) = 0.90$ cm^{-1}, $T = 293$ K, R(int) 0.01, 3159 unique reflections, final $R1 = 0.0398$ for 2253 reflections with $F > 4\sigma(F)$, $wR2 = 0.1188$. Hydrogen atom positions were allowed to refine independently with isotropic displacement parameters.

All molecular illustrations were made with the ORTEPIII[40] and PLUTON97[41] graphics computer programs. Molecular geometry calculations were made with the SHELXL93[42] and the PLATON97[41] program suites.

Acknowledgements

We thank the EPSRC for financial support (GR/J/38581). We thank Professor M. B. Hursthouse and Dr D. Hibbs of the EPSRC X-ray Service for several datasets, Dr J. A. Ballantine of the EPSRC Mass Spectrometry Service for many mass spectra and Dr D. O. Smith and Mrs M. Williamson for NMR data. We thank the European Credit Transfer System for support (AV).

References

1 *Molecular Nonlinear Optics: Materials, Physics and Devices*, ed. J. Zyss, Academic Press Ltd., London, 1994; C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz and P. Günter, *Organic Nonlinear Optical Materials*, Gordon and Breach, Basel, 1995.
2 J. D. Wright, *Molecular Crystals, 2nd Edition*, Cambridge University Press, Cambridge, 1995.
3 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.
4 G. R. Desiraju, *Crystal Engineering*, Elsevier, Amsterdam, 1989; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
5 H.-B. Bürgi, J. Hulliger and P. J. Langley, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 425.
6 T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays and

A. Persoons, *J. Mater. Chem.*, 1997, **7**, 2175; I. D. L. Albert, T. J. Marks and M. A. Ratner, *J. Am. Chem. Soc.*, 1997, **119**, 6575; J. O. Morley, P. Pavlides and D. Pugh, *Int. J. Quantum Chem.*, 1992, **43**, 7.
7 J. Zyss, *Nonlinear Opt.*, 1991, **1**, 3.
8 V. R. Thalladi, S. Brasselet, H.-C. Weiss, D. Bläser, A. K. Katz, H. L. Carrell, R. Boese, J. Zyss, A. Nanagia and G. R. Desiraju, *J. Am. Chem. Soc.*, 1998, **120**, 2563, and references therein.
9 R. Wortmann, C. Glania, P. Krämer, R. Matschiner, J. J. Wolff, S. Kraft, B. Treptow, E. Barbu, D. Längle and G. Görlitz, *Chem. Eur. J.*, 1997, **3**, 1765.
10 T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 155.
11 S. Miyata and X. T. Tao, *Functionalised Monomers for Polymerisation, 2nd Edition*, Ed. K. Takemoto, R. M. Ottenbrite, M. Kamachi, Dekker, New York, 1997, pp. 309–385.
12 H. Nakanishi and S. Okada, *Organic Molecular Solids*, Ed. W. Jones, CRC, Boca Raton, FL, USA, 1997, pp. 243–266.
13 C. Bosshard and M. Kupfer, *Adv. Nonlinear Opt.*, 1996, **3**, 163.
14 M. S. Wong, F. Pan, M. Bösch, R. Spreiter, C. Bosshard, P. Günter and V. Gramlich, *J. Opt. Soc. Am. B*, 1998, **15**, 426.
15 Y. Le Fur, M. Bagieu-Beucher, R. Masse, J.-F. Nicoud and J.-P. Lévy, *Chem. Mater.*, 1996, **8**, 68.
16 M. S. Wong, V. Gramlich, C. Bosshard and P. Günter, *J. Mater. Chem.*, 1997, **7**, 2021.
17 I. Weissbuch, R. Popovitz-Biro, M. Lahav and L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1995, **51**, 115.
18 A. Togni and G. Rihs, *Organometallics*, 1993, **12**, 3368.
19 J. Jaques, A. Collet and S. H. Wilen, *Enantiomers, Racemates, and Resolutions*, Krieger Publishing Company, Florida, 1991, pp. 14–18.
20 R. Twieg, A. Azema, K. Jain and Y. Y. Cheng, *Chem. Phys. Lett.*, 1982, **92**, 208.
21 R. T. Bailey, F. R. Cruickshank, P. Kerkoc, D. Pugh and J. N. Sherwood, *J. Appl. Phys.*, 1995, **79**, 602; R. T. Bailey, G. H. Bourhill, F. R. Cruickshank, D. Pugh, G. S. Simpson and J. N. Sherwood, *J. Appl. Phys.*, 1993, **73**, 1591; R. T. Bailey, F. R. Cruickshank, D. Pugh and J. N. Sherwood, *J. Phys. D: Appl. Phys.*, 1993, **26**, 208; R. T. Bailey, F. R. Cruickshank, P. Kerkoc, D. Pugh and J. N. Sherwood, *J. Appl. Phys.*, 1993, **74**, 3047; B. K. Nayar, R. Kashyap, K. I. White, R. T. Bailey, F. R. Cruickshank, S. M. G. Guthrie, B. J. McArdle, H. Morrison, D. Pugh, E. A. Shepherd, J. N. Sherwood and C. S. Yoon, *J. Mod. Opt.*, 1988, **35**, 511; R. T. Bailey, F. R. Cruickshank, S. M. G. Guthrie, B. J. McArdle, H. Morrison, D. Pugh, E. A. Shepherd, J. N. Sherwood and C. S. Yoon, *Opt. Commun.*, 1988, **65**, 229.
22 P. J. Langley, J. D. Wallis, R. T. Bailey, F. R. Cruickshank, D. Pugh and J. N. Sherwood, UK Patent Application No. 9809118.4.
23 G. F. Hawkins and A. Roe, *J. Org. Chem.*, 1949, **14**, 328.
24 R. A. W. Johnstone and M. E. Rose, *Tetrahedron*, 1979, **35**, 2169.
25 L. W. Deaddy, *Synth. Commun.*, 1977, **7**, 509.
26 F. A. Allen and O. Kennard, Cambridge Structural Database, *Chem. Des. Autom. News*, 1993, **8**, 1.
27 T. Kondo, F. Akase, M. Kumagai and R. Ito, *Opt. Rev.*, 1995, **2**, 128.
28 T. Kondo, N. Ogasawara, R. Ito, K. Ishida, T. Tanase, T. Murata and M. Hidai, *Acta Crystallogr., Sect. C*, 1988, **44**, 102.
29 J. Bernstein, M. C. Etter and L. Leiserowitz, in *Structure Correlation*, Ed. H.-B. Bürgi and J. D. Dunitz, VCH, Weinheim, Vol. 2, p. 436.
30 G. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290; G. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, 1999, Oxford University Press, Oxford.
31 M. Tonogaki, T. Kawata, S. Ohba, Y. Iwata and I. Shibuya, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1993, **49**, 1031.
32 C. S. Choi and J. E. Abel, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 193.
33 J. M. Cole, J. A. K. Howard and J. A. H. MacBride, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1331.
34 R. T. Bailey, F. R. Cruickshank, P. J. Langley, S. Lochran, D. Pugh, J. N. Sherwood, G. S. Simpson and J. D. Wallis, *J. Phys. Chem. A*, 1998, **102**, 8520; R. T. Bailey, F. R. Cruickshank, S. Lochran, D. Pugh, J. N. Sherwood, D. Pugh, P. J. Langley and J. D. Wallis, *Bull. Mater. Sci.*, 1999, **22**, 421; S. Lochran, R. T. Bailey, F. R. Cruickshank, D. Pugh, J. N. Sherwood, G. S. Simpson, P. J. Langley and J. D. Wallis, *J. Phys. Chem. B*, 2000, **104**, 6710.
35 G. F. Hawkins and A. Roe, *J. Org. Chem.*, 1949, **14**, 328.
36 H. E. Baumgarten and H. C.-F. Su, *J. Am. Chem. Soc.*, 1952, **74**, 3828.
37 E. D. Parker and W. Shive, *J. Am. Chem. Soc.*, 1947, **69**, 63.
38 H. E. Smith, W. I. Cozart, T. de Paulis and F.-M. Chen, *J. Am. Chem. Soc.*, 1979, **101**, 5186.
39 R. T. Bailey, S. Blaney, F. R. Cruickshank, S. M. G. Guthrie, D. Pugh and J. N. Sherwood, *Appl. Phys. B: Photophys. Laser Chem.*, 1988, **47**, 83.
40 C. K. Johnson and M. N. Burnett, *ORTEPIII, Report ORNL-6895*, Oak Ridge National Laboratory, Tennessee, USA, 1996.
41 A. L. Spek, PLATON97 and PLUTON97, Program Suites for the Display and Analysis of Crystal and Molecular Structures, University of Utrecht, The Netherlands, initially described in: A. L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, C34.
42 G. Sheldrick, *SHELXL93, Computer program for crystal structure refinement*, University of Göttingen, Germany.