Perfect layered arrangement of ion-paired chromophores in a crystalline non-linear optical organic salt: 2-amino-3-nitropyridinium chloride

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2-Amino-3-nitropyridinium chloride is reported as a new crystalline non-linear optical organic salt, built around a two-dimensional hyperpolarisable cationic chromophore. Its crystal structure (space group $P2_1$) reveals a quasi-perfect layered arrangement of the cations and the anions. Within each layer the chromophores are arranged in a herringbone structure and strong hydrogen bonds are present. The first hyperpolarisabilities of ion-paired chromophores calculated for 2-amino-3-nitropyridinium chloride as well as 2-amino-5-nitropyridinium chloride emphasize the favourable contribution of the inorganic anionic sublattice to the enhancement of the molecular β_{ijk} and macroscopic $\chi^{(2)}$ susceptibilities.

In the field of materials for non-linear optics (NLO), there is still an interest in the engineering of crystalline materials with satisfactory quadratic NLO properties. Several efficient inorganic, organic and organomineral NLO crystals have been proposed in recent years; some of these have even reached a high level of development. However, several problems concerning the overall quality of these materials remain to be solved, and more research is needed to improve their optical as well as mechanical properties.[1,2] The engineering of crystalline materials for quadratic non-linear optics is guided by two main requirements:

(i) Ideally, non-linear optical chromophores self-assemble in a non-centrosymmetric structure in such a way that the contribution of hyperpolarisabilities β_{ijk} of individual chromophores results in high macroscopic tensor components $\chi^{(2)}$. This double goal of 'non-centrosymmetry–efficiency' is difficult to obtain. The engineering is often focused on non-centrosymmetric materials from a given hyperpolarisable chromophore. The chromophores are modified or oriented in host matrices in order to improve the efficiency of the $\chi^{(2)}$ tensor.

(ii) A qualified material must also be designed for a precisely targeted application: electrooptical modulation (optimisation of r_{ijk}), frequency doubling, or optical parametric oscillation (optimisation of χ_{ijk} and phase-matching conditions). All the structural modifications which act on the robustness (bond strengths), thermal conductivity (damage threshold) and refractive indices of a non-linear optical crystal can be presently directed by engineering based on the modification of the host matrix of chromophores. Generally, purely organic compounds lack mechanical strength for practical uses, although the electric susceptibility $\chi^{(2)}$ is often quite high relative to that of inorganic materials. In addition, many difficulties are encountered in growing single crystals of sufficient quality.

That is why recently a new crystal engineering strategy, combining mineral and organic moieties, has been proposed with the aim of building more cohesive crystalline structures. The goal of this strategy was to mix the advantages of inorganic ionic structures (cohesion, optical and other damage resistance) with those of organic molecules (structural flexibility, high hyperpolarisability). Thus, numerous 2-amino-5-nitropyridinium ($2A5NP^+$) organic salts, in which the $2A5NP^+$ cation is anchored onto inorganic or organic host matrices, have been reported for their high NLO efficiency.[3a,b] The $2A5NP^+$ cation has two electron-accepting centres, the nitro group in the *para* position and the N^+ pyridinium site in the *ortho* position relative to the amino donor group. This leads to a two-dimensional (2D) hyperpolarisable chromophore. Two-dimensional charge transfer molecules have been receiving greater attention as NLO chromophores, as shown by the recent review paper by Nalwa *et al.*[4] We thought that it might be possible to capitalize on the two-dimensional character of the hyperpolarisable ionic chromophore by using the isomeric 2-amino-3-nitropyridinium cation ($2A3NP^+$) as a non-linear optical chromophore. In this cation the amino donor group is between two different acceptor sites (the nitro group and the N^+ pyridinium site), and charge transfer is possible in two very different directions, as shown in Fig. 1(*b*). To the best of our knowledge, no crystalline NLO material built from this type of chromophore has been previously reported. Before any investigation, the following behaviour might be expected from this new cationic chromophore:

(i) The anchorage of the $2A3NP^+$ cation onto an anionic host matrix will occur through short hydrogen bonds originating from the NH_2 and NH^+ groups as observed experimentally in all the 2-amino-5-nitropyridinium salts.[5]

(ii) Intra-cation hydrogen bonds should be present in such structures because the nitro and amino groups are located *ortho* to one another, as clearly shown by Panunto *et al.* in a study of hydrogen bond patterns of nitroaniline derivatives.[6]

We now report our successful use of this new crystal engineering strategy. 2-Amino-3-nitropyridinium chloride (2A3NPCl), a relatively simple crystalline $2A3NP^+$ salt pre-

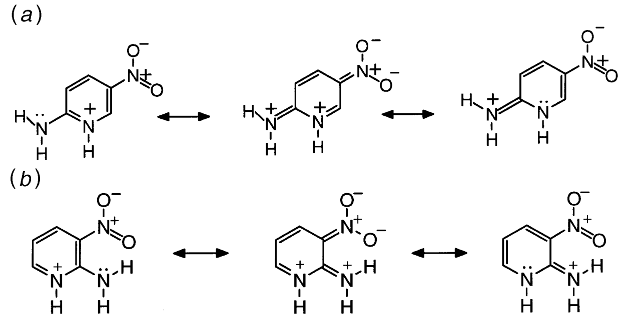


Fig. 1 Mesomeric forms showing the two-dimensional character of the charge transfer in the cationic chromophores (*a*) $2A5NP^+$ and (*b*) $2A3NP^+$

pared from 2-amino-3-nitropyridine, gives an intense second harmonic signal at 530 nm by the powder test of Kurtz and Perry[7] when illuminated by Nd^{3+}–YAG laser light at 1.06 µm [$I_{2\omega}$ observed $> I_{2\omega}$ (POM = 3-methyl-4-nitropyridine-1-oxide)[8]]. In order to elucidate the origin of this strong NLO effect, the crystal structure of 2A3NPCl has been investigated. Since the experimental values of the molecular hyperpolarisabilities for $2A3NP^+$ and $2A5NP^+$ are not yet known, we have also investigated theoretical values for their β_{ijk} tensor components. In addition, we calculated β_{ijk} for the ion pairs $2A3NP^+$ Cl^- and $2A5NP^+$ Cl^- in order to see how the overall hyperpolarisability is affected by the presence of the counterion.

Experimental

Crystal structure

2-Amino-3-nitropyridine (0.01 mol) is easily dissolved in aqueous acidic solution (20 cm^3 containing 0.025 mol HCl) at 20 °C. The solution, slowly evaporated at room temperature, yields pale yellow crystalline platelets up to 3 × 2 × 5 mm in size. The crystallization of 2-amino-3-nitropyridinium chloride occurs when only 2 cm^3 of solvent remains, indicating a high solubility of the salt in HCl solutions. The chemical formula was established from the X-ray crystal structure investigation. The $P2_1$ space group of 2-amino-3-nitropyridinium chloride was confirmed by the unique limiting condition (0k0 with $k = 2n$) and the high second harmonic signal in the Kurtz and Perry powder test.

The cell parameters, space group and crystal structure were determined from single crystal X-ray diffraction data obtained with a four circle diffractometer. Crystal data, experimental conditions, and structural refinement parameters are described in Table 1. No absorption correction was applied; only Lorentz and polarization effects were taken into account. The structure was solved by direct methods using the MULTAN 77 program.[9] Full-matrix least-squares refinements were performed on F: the function minimized was $\Sigma\omega F_o - F_c$ with a unitary weighting scheme. Scattering factors for neutral atoms and f', $\Delta f'$, f'', $\Delta f''$ were taken from *International Tables for X-ray Crystallography*.[10] All calculations were carried out using the Enraf-Nonius SDP program[11] operating on a micro-Vax II computer. The structure was drawn using the MOLVIEW program.[12] The main geometrical features of the 2-amino-3-nitropyridinium cation are described in Table 2, and the hydrogen bonds are described in Table 3.

Table 1 Crystal data, intensity measurements and structural refinement parameters for 2-amino-3-nitropyridinium chloride

formula	$C_5H_6ClN_3O_2$
molecular weight	175.58
space group	$P2_1$
a/Å	6.496(1)
b/Å	9.040(4)
c/Å	7.263(1)
β (°)	116.6(9)
V/Å^3	381.3(3)
Z, D_x/g cm^{-3}	2, 1.529
unit-cell refinement	25 reflect ($10 < \theta < 12.8°$)
F(000)	180
μ/cm^{-1}	2.417 (λ Ag-Kα)
crystal size/mm	0.25 × 0.30 × 0.40
temperature/K	293
apparatus	Nonius CAD4
monochromator	graphite (220)
radiation/Å	0.5608 (Ag-Kα)
Bragg angle limits (°)	3–30
h,k,l, limits	(−11,11; 0,16; 0,12)
scan technique	ω scan
background/s	5–22
scan speed/deg s^{-1}	0.025 to 0.111
scan width (°)	1.10
control reflections	(0 4 3), (0 −4 3)
period between intensity measurements/s	7200
reflections between orientations	400
reflections collected	2518
unique data	1150
data used in refinement	754 [$I > 2\sigma(I)$]
refined parameters	123
R (R_w)	0.027 (0.026)
weighting scheme	unitary
goodness-of-fit	0.262
largest shift/error	0.30
max residual density/e Å^{-3}	0.18

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/18.

NLO Chromophores

The UV–VIS spectrum of a low concentration solution of the organic salt 2A3NPCl in ethanol shows an intense characteristic charge transfer absorption band with $\lambda_{max} = 385$ nm. This absorption, due to the charge transfer shown in Fig. 1, is responsible for the yellow colour of the 2A3NPCl material and is similar to that observed for classic 4-nitroaniline derivatives. In order to understand better the highly efficient second harmonic signal in the new crystalline material and compare with the already known 2A5NPCl material, we calculated the first hyperpolarisabilities for several species. The calculation

Table 2 Selected interatomic distances and bond angles in the $2A3NP^+$ chromophore

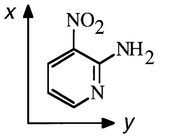
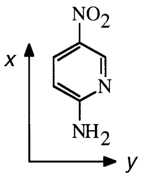
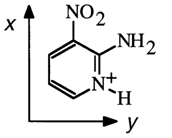
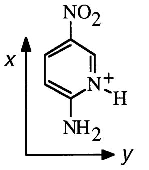
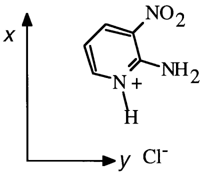
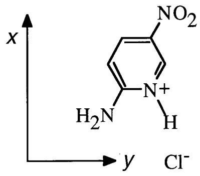
bond distances/Å	
N(1)–C(1)	1.357(3)
N(1)–C(5)	1.338(4)
N(1)–H(1)	0.86(4)
N(2)–C(1)	1.324(4)
N(2)–H(2)	0.79(2)
N(2)–H(3)	0.89(4)
N(3)–C(2)	1.459(3)
O(1)–N(3)	1.233(3)
O(2)–N(3)	1.209(4)
C(1)–C(2)	1.407(4)
C(2)–C(3)	1.360(4)
C(3)–C(4)	1.380(4)
C(3)–H(4)	0.96(4)
C(4)–C(5)	1.366(5)
C(4)–H(5)	0.80(3)
C(5)–H(6)	1.03(4)
bond angles/degrees	
C(1)–N(1)–C(5)	124.3(3)
C(1)–N(1)–H(1)	107(2)
C(5)–N(1)–H(1)	128(2)
C(1)–N(2)–H(2)	127(2)
C(1)–N(2)–H(3)	114(2)
H(2)–N(2)–H(3)	119(3)
O(1)–N(3)–O(2)	123.6(3)
O(1)–N(3)–C(2)	119.0(3)
O(2)–N(3)–C(2)	117.3(2)
N(1)–C(1)–N(2)	116.4(2)
N(1)–C(1)–C(2)	114.8(2)
N(2)–C(1)–C(2)	128.7(2)
N(3)–C(2)–C(1)	119.8(2)
N(3)–C(2)–C(3)	117.9(2)
C(1)–C(2)–C(3)	122.3(2)
C(2)–C(3)–C(4)	119.5(3)
C(2)–C(3)–H(4)	116(2)
C(4)–C(3)–H(4)	124(2)
C(3)–C(4)–C(5)	118.7(3)
C(3)–C(4)–H(5)	122.3(3)
C(5)–C(4)–H(5)	118.4(3)
N(1)–C(5)–C(4)	120.2(3)
N(1)–C(5)–H(6)	110.8(3)
C(4)–C(5)–H(6)	128.7(3)

Table 3 Hydrogen bonds and angles in the 2A3NPCl crystal structure and angles around the Cl^- anion

bond lengths/Å	
N(1)–H(1)	0.86(4)
Cl–H(1)	2.15(4)
Cl–N(1)	3.016(2)
N(2)–H(2)	0.79(2)
O(1)–H(2)	2.19(2)
O(2)–H(2)	2.27(2)
N(2)–O(1)	2.658(3)
N(2)–O(2)	3.038(4)
N(2)–H(3)	0.89(4)
H(3)–Cl	2.55(3)
Cl–N(2)	3.364(2)
C(3)–H(4)	0.96(4)
H(4)–Cl	2.70(4)
H(4)–O(2)	2.28(4)
C(3)–O(2)	2.654(4)
C(3)–Cl	3.492(3)
C(4)–H(5)	0.80(3)
C(5)–H(6)	1.03(4)
H(6)–Cl	2.74(4)
Cl–C(5)	3.485(3)
bond angles/degrees	
Cl–H(1)–N(1)	177(4)
O(1)–H(2)–N(2)	119(2)
O(2)–H(2)–N(2)	162(2)
Cl–H(3)–N(2)	151(3)
Cl–H(4)–C(3)	139(3)
O(2)–H(4)–C(3)	102(3)
Cl–H(6)–C(5)	128(3)
adjacent angles around the Cl anion/degrees	
H(1)–Cl–H(3)	47.8
H(3)–Cl–H(4)	101.7
H(4)–Cl–H(6)	91.4
H(6)–Cl–H(1)	119

was performed for the neutral pyridines (2A3NP and 2A5NP), the protonated pyridines ($2A3NP^+$ and $2A5NP^+$) and the ion pairs corresponding to the organic salts ($2A3NP^+Cl^-$ and $2A5NP^+Cl^-$), as they are positioned in the crystals. The geometries of the pyridines and the pyridiniums, with a C_s imposed symmetry, were optimized by *ab initio* DFT methods in DMOL ver. 3.00 software from BIOSYM. The β tensor components were then computed on these optimized structures by using the semi-empirical AM1 parameters and the finite field method available in MOPAC 6.[13] The results for the most significant values of β (in 10^{-30} esu units) are summarized in Table 4. All the chromophores are planar, so the z axis is not drawn. The orientation of each calculated species in the xy plane is given in Table 4.

Table 4 Static β_{ijk} components (in 10^{-30} esu) calculated by the finite-field method using AM1 parameters, based on the optimized geometries for neutral molecules and isolated cations and on the actual conformations in the crystals for the ion pairs

	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}
	4.1	2.0	1.4	1,8
	13.3	2.3	0	0.5
	1.2	1.7	0.5	1.1
	3.4	1.6	0.5	0.7
	24.4	2.6	3.4	4.7
	24.2	4.4	4.5	7.2

Discussion

Crystal structure

The cations and anions of 2A3NPCl are packed in layers parallel to the crystallographic plane defined by the ***b*** and ***a***+2***c*** vectors (Fig. 2). These planes of ions are perpendicular to the direction defined by the ***a*** vector and intersect the unit cell at $a/4$ and $3a/4$. The strongest hydrogen bonds form within the layer; no long H-bonds are detected between adjacent planes separated by 3.25 Å. The screw axes located at ($a/2$,0,$c/2$) and (0,0,$c/2$) act on the crystallographic motif so that the chromophores arrange in a herringbone structure (Fig. 3). The anion charge is balanced through N–H···Cl and C–H···Cl hydrogen bonds (Table 3). The unique intercation contact N(2)–H(2)···O(2) induces the aggregation of chromophores in zigzag chains. The three-centre hydrogen bonds C(3)–H(4)···O(2), Cl and N(2)–H(2)···O(1), O(2) involve two intra-cation links. This situation, observed in nitroaniline derivatives in which nitro and amino groups are *ortho* to one another,[6] precludes the rotation of the nitro group with respect to the pyridinium ring. The dihedral angle between the planes of the NO_2 group and the heterocycle is 0.3°, indicating a coplanar geometry. Only an approximate figure can be given for the dihedral angle between the plane of the NH_2 group and the pyridinium plane because the H atoms are located less accurately than C, N, O, or Cl atoms by X-ray diffraction; the value is *ca.* 4.2° for 2A3NPCl. Distortion or twisting of the NH_2 and NO_2 groups modifies the efficiency of the intramolecular charge transfer and consequently the values of β_{ijk} and χ_{ijk}. In structures built with the 2-amino-5-nitropyridinium cations a twisting of the NO_2 group under the influence of C–H···O bonds of neighbouring cations has always been observed. For instance, the twisting angle of the nitro group is 3.6° in 2-amino-5-nitropyridinium acetophosphonate,[14] 7(1)° in 2-amino-5-nitropyridinium monohydrogenphosphite,[15] and as large as 16.7° in 3-methyl-4-nitropyridine 1-oxide.[16] The second harmonic generation (SHG) signal at 530 nm is strong, which implies that phase-matching conditions occur for at least some χ_{ijk}. Furthermore, because of the layered structure, high electrooptical coefficients r_{ijk} are expected in the (−1 0 2) plane. If ***X***, ***Y*** and ***Z*** are the dielectric axes with ***X*** along ***a***, ***Y*** along ***b***, and ***Z*** belonging to the (−1 0 2) plane perpendicular

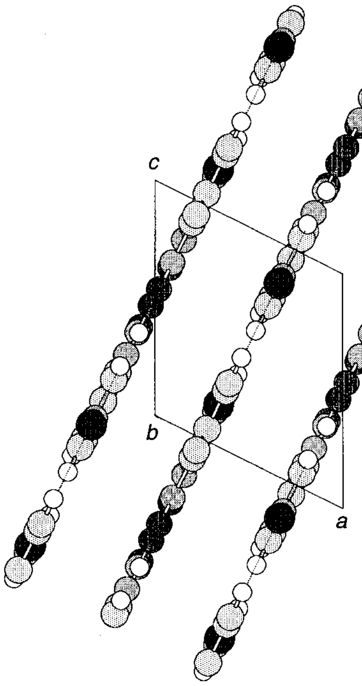


Fig. 2 Perfect layered arrangement of ion pairs $2A3NP^+Cl^-$ in planes parallel to the crystallographic plane $(-1\ 0\ 2)$

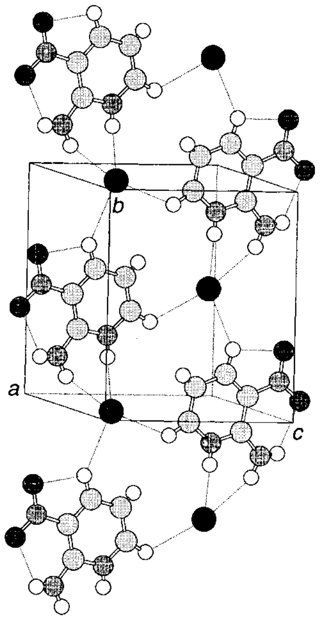


Fig. 3 Herringbone structure of cations viewed in a plane intersecting the ***a*** direction at $a/4$. Hydrogen bonds, except the N(2)–H(2)···O(2) contact which induces the cation aggregation, are shown.

to ***a***, the indices of refraction are expected to rank as $n_Y \cong n_Z \gg n_X$.

Non-linear optical properties

Calculations on the 2A3NP neutral molecule indicate that a more pronounced two-dimensional character of the hyperpolarisability exists for this species than for 2A5NP. The latter has a high value of β_{xxx} corresponding to the 2-amino–5-nitro charge transfer along the x axis, as shown in Fig. 1(*a*). The calculated value of β_{xxx} corresponds well to the already reported static $\beta(0)$ value of $(13.9 \pm 0.5) \times 10^{-30}$ esu, extrapolated to zero frequency from the electric field induced second harmonic generation (EFISHG) measurement at 1.06 µm.[17] When the amino donor group is placed between the nitro group and the pyridine nitrogen atom, the charge transfer described in Fig. 1(*b*) leads to off-diagonal components of β that can reach nearly 50% of the β_{xxx} value. This is in accordance with the results recently reported for the diagonal and off-diagonal components of hyperpolarisability, β_{xxx} and β_{xyy} respectively, of tri- and tetra-substituted benzene with C_{2V} symmetry.[18] For molecules with the π-conjugation extended by three substituents, β_{xyy} is enhanced when one donor is present with two acceptors located in *ortho* rather than *meta* positions.

As for the protonated molecules, the calculations gave relatively low values for their hyperpolarisabilities. We notice, however, a value of the off-diagonal component β_{xyy} for $2A3NP^+$ which is higher than β_{xxx}. For crystalline materials built with such chromophores, we cannot easily deduce their NLO efficiency from the orientation of the molecules in the lattice. The classical one-dimensional analysis is no longer valid, and optimum values of the NLO coefficients as a function of the orientation of molecules with respect to the two-fold axis is now dependent on the ratio β_{xyy}/β_{xxx}, as was discussed by J. Zyss *et al.* in their work concerning 2-amino-5-nitropyridinium hydrogen L-tartrate.[19] The low values which we calculated appeared inconsistent with the high second harmonic signal of 2A3NPCl crystalline powder. We then investigated the actual contribution of the anionic sublattice to the NLO properties of the material, since the anions and the cations lie in the same plane. We calculated the hyperpolarisabilities of the ion pairs $2A3NP^+Cl^-$ and $2A5NP^+Cl^-$, keeping the same conformations and positions of the ions as in the crystals.[20] Both the ion pairs have higher theoretical β_{xxx} values (24.4 and 24.2×10^{-30} esu, respectively) than $2A3NP^+$ and $2A5NP^+$, the x axis being the chloride–nitro axis. According to our calculations it appears that, in this type of non-linear organic salt, the chloride anion may make a significant contribution to the hyperpolarisability of the cationic chromophore and hence to the $\chi^{(2)}$ of the material. In our case we should consider the actual chromophore to be the ion pair $2A3NP^+Cl^-$, for which the Cl^-–NO_2 axis is nearly coincident with the NH_2–NO_2 axis.

Conclusion

We have investigated the 2-amino-3-nitropyridinium cation and other two-dimensional charge transfer chromophores as a new family of non-linear optical organic salts. 2-amino-3-nitropyridinium chloride (2A3NPCl) crystals are highly efficient for the second harmonic generation of laser light at 1.06 µm. The analysis of the crystal structure reveals a perfect layered arrangement of the chromophores in layers parallel to the crystallographic plane $(-1\ 0\ 2)$. As shown by theoretical calculations, within the layer each chloride anion forms an ion pair with a neighbouring pyridinium cation, leading to an enhanced hyperpolarisability of the whole. The possible mutual interaction between organic and inorganic sublattices in non-linear organic salts deserves further attention and could lead to a new crystal engineering strategy for the design of new efficient organic NLO materials.

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