Crystal Engineering of Noncentrosymmetric Structures Based on 2-Amino-5-nitropyridine and *n*-Chloroacetic Acid Assemblies

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New noncentrosymmetric crystals including the 2-amino-5-nitropyridinium and 2-amino-5-nitropyridine chromophores have been designed following a strategy first applied to the 2-amino-5-nitropyridinium dihydrogen phosphate. If a counteranion able to self-aggregate in chains or layers as $(H_2PO_4^-)_n$ is associated to the 2-amino-5-nitropyridinium cation, a noncentrosymmetric structure based on herringbone motifs is systematically formed. In the same way it has been observed that a bulky group grafted on the amine radical of the 2-amino-5-nitropyridine induces a noncentrosymmetric structure containing herringbone motifs of molecular entities. The structures of the 2-amino-5-nitropyridinium dichloroacetate ionic crystal and 2-amino-5-nitropyridine/chloroacetic acid cocrystal having respectively the $P2_12_12_1$ and *Cc* symmetries confirm the validity of this strategy. The packings of these assemblies are discussed in terms of steric hindrance and hydrogen bonds. Powder samples of these materials exhibit second harmonic generation signals comparable to that of 3-methyl-4-nitropyridine *N*-oxide under Nd^{3+}:YAG laser (1.06 μm) illumination.

Introduction

Organic crystals for quadratic nonlinear optics have been intensely engineered[1] during the past 15 years. The research of large quadratic susceptibilities $\chi(2)$ depending on the quasi perfect packing of highly polarizable molecules in the crystal network has been the main challenge.[2,3] The structural flexibility of organic chromophores easily modifiable through precise chemical syntheses in view to increase the molecular hyperpolarizability β_{ijk} and the possible grafting of chirality centers are remarkable assets[4,5] compared to the difficulties of the engineering route of inorganic materials in which the requirements of noncentrosymmetry and high susceptibilities $\chi(2)$ have to be accounted at crystal level and cannot be solved in two separated steps: molecular and crystalline ($KTiOPO_4$, $LiNbO_3$, $LiIO_3$). More, the fast optical responses of organic nonlinear chromophores to the laser light have encouraged the research of highly efficient organic materials.[6] The problematic chemical and thermal stabilities and the weak mechanical resistance of organic crystals have at the present time limited their application in nonlinear optical devices. New solutions have been proposed for the design of NLO crystals using organic chromophores as nitroanilines, stilbenes hosted in inorganic or organic matrixes.[7−10] The advantages of such an approach in which the van der Waals interactions are substituted by short hydrogen bonds in the crystal packing should appear in thermal and mechanical properties improved with respect to that of the molecular crystals. This strategy has been applied successfully to the 2-amino-5-nitropyridine chromophore. Numerous very stable noncentrosymmetric structures containing the 2-amino-5-nitropyridinium ($2A5NP^+$) cations anchored onto inorganic or organic host matrixes through hydrogen bond networks have been already engineered.[11] We have observed in this class of materials that a simple geometrical parameter, the intercationic distance $d(NH_2-NH_2)$ between the nonlinear cations, measured through the anionic matrix, reflects the noncentrosymmetric structural organization. So, taking into account a pH specification (pH < 2) allowing the cation formation and its stability, we can deliberately engineer new noncentrosymmetric structures in selecting two-dimensional or chained anionic aggregates able to impose favorable distances $d(NH_2-NH_2) > 4$ Å (Table 1) as already exemplified in the 2-amino-5-nitropyridinium acetophosphonate structure.[12] Then we decided to investigate the behavior of *n*-chloroacetic

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Table 1. Main Intercation Distances in Relation with the Centrosymmetric or Noncentrosymmetric Packings of 2A5NP$^+$ Cations[a]

anions	$d_{NH2\text{-}NH2}$(Å)	$d_{NH2\text{-}NH2}$(Å)	ref.
HSO_4^- (*Pbca*)	3.454		13
$InCl_6^{3-}$ ($P2_1/a$)	3.465		14
BF_4^- ($P2_1/n$)	3.527	5.126(t)	15
HPO_3H^- (*C*2/*c*)	3.809		16
$Cr_2O_7^{2-}$ ($P2_1nb$)	3.896	5.189(t)	17
$CHCl_2-COO^-$ ($P2_12_12_1$)	3.949	6.010(t)	this work
I^- ($P2_1/a$)	3.955	6.660	18
CCl_3-COO^- ($P2_1/n$)	3.956	6.876(t)	this work
Br^- ($P2_1/a$)	4.029	6.390	19
Cl^- ($P2_1$)	4.702	4.813(t)	19
Br^- ($P2_1$)	4.807	4.949(t)	19
$CH_2Cl-COOH$/2A5NP (*Cc*) cocrystal	5.152	4.857(t)	this work
$H_2PO_4^-$ ($Pna2_1$)	6.717	5.675(t)	20
$H_2AsO_4^-$ ($Pna2_1$)	6.941	5.814(t)	13
$(HO_3P-CH_2-COOH)^-$ ($P2_12_12_1$)	7.07	5.05(t)	12
$L-HOOC-CHOH-CHOH-COO^-$ ($P2_1$)	8.248(t)	7.611(t)	21

[a]The second column displays the shortest distance measured on both sides of the anion matrix. (t) corresponds to a cell parameter translation.

acids with increasing acidity toward 2-amino-5-nitropyridine in view to explore the formation of new anionic aggregates. New structures were obtained through the association of 2-amino-5-nitropyridine/2-amino-5-nitropyridinium with the *n*-chloroacetic acids confirming the rule of the optimum distance $d(NH_2-NH_2)$ in relation with the noncentrosymmetry of the crystal packing. Depending on the pH conditions of the chemical reactions involving the 2-amino-5-nitropyridine, two 2-amino-5-nitropyridinium salts were prepared with the trichloroacetic acid ($pK_a = 0.7$ at 25 °C) and dichloroacetic acid ($pK_a = 1.48$ at 25 °C) and a cocrystal was obtained with the chloroacetic acid ($pK_a = 2.85$ at 25 °C). The crystal structure determinations reveal the formation of 2-amino-5-nitropyridinium cations in the former case and the absence of proton transfer on the 2-amino-5-nitropyridine in the latter. The crystal symmetry of such assemblies will be discussed on the base of the hydrogen bond network and the steric hindrance of anionic or neutral entities.

Experimental Section

Crystals of 2-amino-5-nitropyridinium trichloroacetate were prepared by dissolving 0.01 mol of purified 2-amino-5-nitropyridine (2A5NP) in a 30 cm^3 acidic−water solution containing 0.03 mol of crystallized trichloroacetic acid (Aldrich, 99%) at 40 °C. At room temperature uncombined 2A5NP is separated. Slow evaporation of the filtered solution yields yellow light crystals up to 4 × 3 × 3 mm^3 in size. The same route is followed for the preparation of 2-amino-5-nitropyridinium dichloroacetate crystals, with the ratio 2A5NP/dichloroacetic acid (Aldrich, 99%, $d = 1.563$) = 0.01 mol/0.03 mol. Orthorhombic yellow crystals up to 10 × 5 × 5 mm^3 in size were grown easily. The 2-amino-5-nitropyridine/chloroacetic acid cocrystals are prepared under the well-defined conditions: 2A5NP is purified by sublimation, 0.01 mol of 2A5NP/0.05 mol of crystallized chloroacetic acid (R.P. Prolabo, 99.5%) dissolved in 40 cm^3 water are maintained at 50 °C until the complete dissolution of 2A5NP. Cocrystals (60%) precipitate as very thin needles when the temperature is decreased to ambient. The filtered solution yields yellow light thick rhomboedral prisms of 4 × 4 × 3 mm^3 average size. The chemical formulas of the three compounds were established via crystal structure investigations. The cell parameters and space groups given in Table 2 were determined by X-ray four-circle diffractometry. The noncentrosymmetric space groups $P2_12_12_1$ of 2-amino-5-nitropyridinium dichloroacetate and *Cc* of 2-amino-5-nitropyridine/chloroacetic acid were confirmed by both the last reliability factor (Table 2) and positive second harmonic generation powder tests from a Nd^{3+}:YAG laser fundamental beam (1.06 μm). The X-ray diffracted intensities were corrected for Lorentz and polarization factors. No absorption correction has been applied due to the weak value of absorption coefficient and the favorable crystal geometry in every case. The crystal data, details for the diffracted intensity measurements, and refinement conditions are summarized in Table 2. Crystal structures were solved by direct methods using Multan 77 program[22] and difference Fourier syntheses. Full-matrix least-squares refinements have been performed on *F*, using a unitary weighting scheme. Scattering factors for neutral atoms and *f*′, *f*″ have been taken from the *International Tables for X-ray Crystallography*.[23] The Enraf-Nonius SDP program[24] operating on a micro-Vax II computer was applied for all the calculations. Structures were drawn using Molview program.[25] Refined atomic parameters are given in Tables 3−5. Geometrical features of *n*-chloroacetate anions and molecular chloroacetic acid are pointed out in Table 8.

Structural Description

2-Amino-5-nitropyridinium Trichloroacetate (2A5NPTCA). As clearly indicated in the (**a,c**) projection, the framework of 2A5NPTCA is formed by layers of hydrogen bonded cation−anion clusters, stretching along the **a**+**c** direction (Figure 1). In each layer a first network of short hydrogen bonds N−H- - -O (Table 6)

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Table 2. Crystal Data, Intensity Measurements, and Structural Refinement Parameters

	$2A5NP^+ \cdot CCl_3-COO^-$	$2A5NP^+ \cdot CHCl_2-COO^-$	$2A5NP \cdot CH_2Cl-COOH$
formula wt.	302.50	268.06	233.61
space group	$P2_1/n$	$P2_12_12_1$	Cc
cell parameters			
a, Å	14.136(5)	6.010(8)	4.857(5)
b, Å	6.876(4)	10.841(8)	21.755(8)
c, Å	12.316(5)	17.416(8)	9.428(3)
β, deg	103.49(3)		104.08(6)
diffractometer	CAD4 Nonius	CAD4 Nonius	CAD4 Nonius
radiation, monochr	Ag Kᾱ, graphite	Ag Kᾱ, graphite	Ag Kᾱ, graphite
scan mode	ω scan	ω scan	ω scan
data collection limits	$3 \le \theta° \le 22$	$3 \le \theta° \le 30$	$3 \le \theta° \le 30$
	$-18 \le h \le 18, -9 \le k \le 9,$	$-10 \le h \le 10, 0 \le k \le 19,$	$-8 \le h \le 8, 0 \le k \le 38,$
no. of reflections	$0 \le l \le 16$	$0 \le l \le 31$	$0 \le l \le 16$
total	6108	7099	6073
independent	3105	3792	2855
	with $I \ge 3\sigma(I) = 1040$	with $I \ge 2\sigma(I) = 1092$	with $I \ge 3\sigma(I) = 1048$
number of variables, R, R_w	178, 0.033, 0.034	173, 0.055, 0.053	166, 0.028, 0.029
ρ (e^-/Å^3) in final difference Fourier syntheses	$\rho_{max} = 0.42$, $\rho_{min} = -0.24$	$\rho_{max} = 0.27$, $\rho_{min} = -0.25$	$\rho_{max} = 0.07$, $\rho_{min} = -0.07$
Z	4	4	4
D_x (g cm^{-3})	1.726	1.569	1.606
$F(000)$	608	544	480
T (K)	293	293	293
crystal size (mm)	0.32 × 0.24 × 0.13	0.80 × 0.43 × 0.32	0.64 × 0.40 × 0.32
μ (cm^{-1})	4.110	3.020	2.114

Table 3. 2-Amino-5-nitropyridinium Trichloroacetate[a]

atom	x	y	z	B_{eq}/B_{iso}
Cl1	0.26494(8)	0.4590(2)	0.18654(9)	4.41(2)
Cl2	0.38172(8)	0.2130(2)	0.4380(1)	4.63(2)
Cl3	0.33615(9)	−0.1398(2)	0.5379(1)	5.82(3)
O1	0.8393(2)	−0.0364(4)	0.2344(2)	4.04(7)
O2	0.9679(2)	−0.0329(5)	0.1678(2)	4.97(7)
O3	0.1301(2)	0.0610(4)	0.4836(2)	4.57(7)
O4	0.2288(2)	0.3075(4)	0.5449(2)	4.73(7)
N1	0.9120(2)	0.0430(5)	0.2175(3)	3.32(7)
N2	1.0017(2)	0.7581(5)	0.4138(3)	3.36(8)
N3	0.8959(2)	0.5058(5)	0.3572(2)	2.75(6)
C1	0.9360(3)	0.2364(6)	0.2627(3)	2.67(8)
C2	1.0238(3)	0.3238(6)	0.2578(3)	3.27(9)
C3	1.0476(2)	0.4974(6)	0.3062(3)	3.22(9)
C4	0.9827(3)	0.5928(5)	0.3601(3)	2.43(8)
C5	0.8733(3)	0.3298(6)	0.3120(3)	2.77(8)
C6	0.2067(3)	0.1524(6)	0.4967(3)	3.07(9)
C7	0.2877(3)	0.0525(6)	0.4485(3)	2.90(8)
H(1N2)	0.960(2)	0.810(5)	0.445(3)	1.2(8)
H(2N2)	1.054(3)	0.818(6)	0.419(3)	1.8(9)
H(N3)	0.855(3)	0.570(6)	0.390(3)	2(1)
H(C2)	1.063(2)	0.261(5)	0.225(3)	1.2(8)
H(C3)	1.105(2)	0.562(5)	0.304(3)	1.0(8)
H(C5)	0.818(2)	0.283(5)	0.313(3)	1.3(8)

[a] Atomic coordinates, B_{eq} (Å^2) for non-hydrogen atoms, B_{iso} (Å^2) for hydrogen atoms refined isotropically, esd in parentheses. $B_{eq} = {}^4/_3\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{b}_j$.

Table 4. 2-Amino-5-nitropyridinium Dichloroacetate[a]

atom	x	y	z	B_{eq}/B_{iso}
Cl1	0.9191(3)	0.4374(2)	1.0584(1)	7.70(4
Cl2	0.4987(4)	0.3583(2)	1.1235(1)	7.77(4)
O1	0.6814(9)	0.3338(5)	0.7400(3)	8.9(1)
O2	0.4313(8)	0.4777(5)	0.7395(3)	8.2(1)
O3	0.5204(8)	0.5716(3)	0.9978(3)	6.8(1)
O4	0.4147(7)	0.4069(3)	0.9329(2)	5.53(9)
N1	0.6175(8)	0.4364(6)	0.7566(3)	6.5(1)
N2	1.1950(9)	0.7211(4)	0.9287(3)	5.7(1)
N3	1.0933(8)	0.5399(4)	0.8696(3)	4.23(9)
C1	0.767(1)	0.5180(6)	0.7988(3)	4.9(1)
C2	0.717(1)	0.6424(6)	0.8111(4)	5.8(1)
C3	0.857(1)	0.7163(6)	0.8533(4)	5.6(1)
C4	1.0542(9)	0.6603(5)	0.8851(3)	4.3(1)
C5	0.956(1)	0.4689(5)	0.8276(3)	5.0(1)
C6	0.5176(9)	0.4603(5)	0.9850(3)	4.2(1)
C7	0.651(1)	0.3759(5)	1.0375(3)	4.8(1)
H(1N2)	1.171(8)	0.797(4)	0.938(3)	5(1)
H(2N2)	1.306(9)	0.675(5)	0.952(3)	6(1)
H(N3)	1.205(9)	0.499(5)	0.898(3)	5(1)
H(C2)	0.63(1)	0.688(5)	0.790(3)	7(2)
H(C3)	0.829(9)	0.802(4)	0.864(3)	5(1)
H(C5)	0.986(8)	0.379(4)	0.824(2)	4(1)
H(C7)	0.679(8)	0.292(4)	1.020(2)	4(1)

[a] Atomic coordinates, B_{eq} (Å^2) for non-hydrogen atoms, B_{iso} (Å^2) for hydrogen atoms refined isotropically, esd in parentheses. $B_{eq} = {}^4/_3\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{b}_j$.

maintaining the cation−anion cohesion and building a centrosymmetrical cluster unit is evidenced. Such clusters are assembled through a second network of long hydrogen bonds C−H- - -O having 2_1 symmetry. The formation of C−H- - -O bonds in molecular compounds, now well established,[26−28] has to be taken into account mainly in organic salts in which the charge distribution is very extended on the ionic entities and necessarily balanced through N−H- - -acceptor, C−H- - -acceptor coulombian attractions. The distance $d(NH_2-NH_2)$ = 3.956(6) Å between the two 2-amino-5-nitropyridinium cations centrosymmetrically arranged is located in the part of Table 1 in which the centrosymmetric structures are observed. This situation can be compared to that of the centrosymmetric structural organization of the 2-amino-5-nitropyridinium cations in the bis(2-amino-5-nitropyridinium) dichromate salt (Table 1). This crystal displays a noncentrosymmetric subnetwork of $Cr_2O_7^{2-}$ anions hosting a pseudocentrosymmetric network of $2A5NP^+$ cations[17] with a minimum intercation distance $d(NH_2-NH_2)$ = 3.896 Å. It appears that the distances $d(NH_2-NH_2)$ observed around 4 Å set a boundary between centrosymmetric and noncentrosymmetric structures. The chained clusters of 2A5NPTCA are not connected by C−H- - -Cl bonds. The shortest interchain distances Cl−Cl = 3.840 and 3.962 Å reflect that the chained cluster assemblies are stacked through van der Waals bonds.

2-Amino-5-nitropyridinium Dichloroacetate (2A5NPDCA). The (**b,c**) projection of 2A5NPDCA

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Table 5. 2-Amino-5-nitropyridine/Chloroacetic Acid[a]

atom	*x*	*y*	*z*	B_{eq}/B_{iso}
Cl	0.000	0.43606(4)	1.000	4.92(1)
O1	0.7754(5)	0.7663(1)	0.3214(2)	4.68(5)
O2	0.7094(5)	0.7285(1)	0.5211(3)	4.71(5)
O3	0.2881(5)	0.44569(9)	0.7604(2)	4.23(4)
O4	0.4054(5)	0.34746(9)	0.7607(2)	3.73(4)
N1	0.6594(5)	0.7660(1)	0.4230(3)	3.52(5)
N2	−0.0601(6)	0.9522(1)	0.4749(3)	4.01(5)
N3	0.1599(5)	0.8621(1)	0.5542(2)	2.92(4)
C1	0.4574(6)	0.8139(1)	0.4261(3)	2.95(5)
C2	0.3936(6)	0.8578(1)	0.3173(3)	3.63(5)
C3	0.2197(7)	0.9041(1)	0.3307(3)	3.72(6)
C4	0.1046(6)	0.9068(1)	0.4535(3)	3.14(5)
C5	0.3341(6)	0.8164(1)	0.5415(3)	2.85(5)
C6	0.2965(6)	0.3943(1)	0.8088(3)	2.93(5)
C7	0.1752(7)	0.3761(1)	0.9344(3)	3.79(5)
H(O4)	−0.005(9)	0.854(2)	0.693(5)	8(1)
H(1N2)	−0.114(6)	0.978(1)	0.402(3)	3.8(7)
H(2N2)	−0.123(7)	0.955(2)	0.552(4)	4.9(8)
H(C2)	0.459(6)	0.854(1)	0.226(3)	4.3(7)
H(C3)	0.179(7)	0.933(1)	0.265(3)	4.7(8)
H(C5)	0.370(5)	0.785(1)	0.618(3)	2.7(6)
H(1C7)	0.043(6)	0.342(1)	0.911(3)	4.7(8)
H(2C7)	0.323(7)	0.361(2)	1.014(4)	5.1(8)

[a] Atomic coordinates, B_{eq} (Å^2) for non-hydrogen atoms, B_{iso} (Å^2) for hydrogen atoms refined isotropically, esd in parentheses. $B_{eq} = {}^4/_3\Sigma_i\Sigma_j\beta_{ij}\,\mathbf{a}_i\mathbf{b}_j$.

Table 6. Hydrogen-Bond Distances (Å) and Angles (deg) and Their Esd

	D−H	H- - -A	D- - -A	D−H- - -A (deg)
2-Amino-5-nitropyridinium Trichloroacetate				
N2−H(1N2)- - -O3	0.84(5)	1.94(5)	2.776(5)	178(4)
N2−H(2N2)- - -O3	0.83(4)	2.08(4)	2.768(5)	140(4)
N3−H(N3)- - -O4	0.85(4)	1.83(4)	2.681(5)	176(4)
C5−H(C5)- - -O1	0.86(4)	2.47(4)	3.067(5)	127(3)
2-Amino-5-nitropyridinium Dichloroacetate				
N2−H(1N2)- - -O3	0.85(5)	2.03(5)	2.792(6)	149(4)
N2−H(2N2)- - -O3	0.92(5)	1.89(5)	2.811(7)	176(5)
N3−H(N3)- - -O4	0.95(5)	1.72(5)	2.651(6)	169(5)
C5−H(C5)- - -Cl2	0.99(4)	2.73(4)	3.657(6)	155(3)
C2−H(C2)- - -O1	0.81(6)	2.50(6)	3.291(8)	166(5)
C7−H(C7)- - -O4	0.97(4)	2.70(5)	3.489(7)	155(2)
2-Amino-5-nitropyridine/Chloroacetic Acid				
O4−H(O4)- - -N3	0.87(5)	1.70(5)	2.566(3)	175(4)
N2−H(1N2)- - -O3	0.87(3)	2.12(3)	2.974(3)	168(3)
N2−H(2N2)- - -O3	0.86(4)	2.12(4)	2.962(4)	168(3)
C2−H(C2)- - -Cl	0.99(4)	2.83(3)	3.587(3)	134(2)
C2−H(C2)- - -O2	0.99(4)	2.69(3)	3.303(4)	120(2)
C5−H(C5)- - -O1	0.98(3)	2.36(3)	3.263(4)	153(2)
C7−H(1C7)- - -O1	0.97(3)	2.72(3)	3.675(4)	166(3)
C7−H(1C7)- - -O2	0.97(3)	2.62(3)	3.444(4)	143(3)
C7−H(2C7)- - -O2	0.96(3)	2.69(4)	3.398(4)	131(3)

Table 7. Occupancy Ratio of Nonlinear Optical Chromophores (Oscillators) in Molecular and Ionic Structures Containing the Same Geometrical Entity, 2A5NP or 2A5NP$^+$ ($\tau\% = ZV_{2A5NP^+}/V_{cell}$)

crystal	τ%	ref
2-(cyclooctylamino)-5-nitropyridine	43.9	31, 32
2-(adamantylamino)-5-nitropyridine	42.2	29, 30
(4-nitro-2-pyridinyl)-(*S*)-phenylalaninol	42.4	36, 37
2(*S*)-(phenylethylamino)-5-nitropyridine	47.6	33, 34, 35
2-amino-5-nitropyridinium dichloroacetate	51.7	this work
2-amino-5-nitropyridinium acetophosphonate	52.3	12
2-amino-5-nitropyridine/chloroacetic acid	60.7	this work
2-amino-5-nitropyridinium dihydrogen phosphate	64.7	20
2-amino-5-nitropyridinium bromide	75.7	19
2-amino-5-nitropyridinium chloride	79.5	19

reveals chained dichloroacetate anions on which the 2A5NP$^+$ cations are grafted by N−H- - -O and C−H- - -Cl hydrogen bonds (Figure 2). The cations bridge two

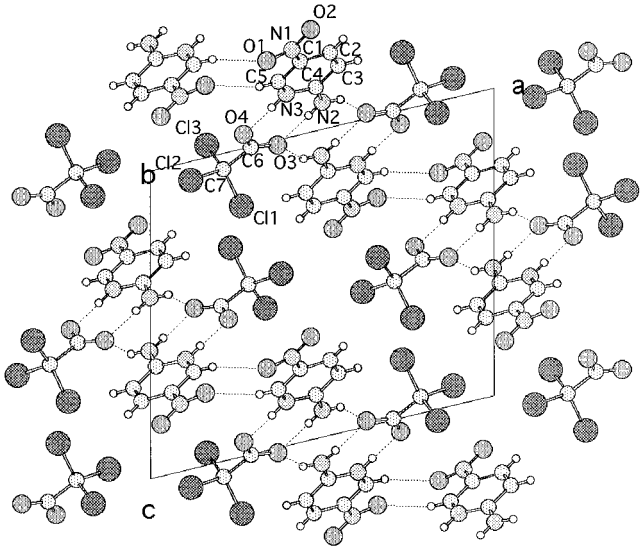

Figure 1. Centrosymmetric H-bonded cation−anion clusters stretching along the **a**+**c** direction in the 2-amino-5-nitropyridinium trichloroacetate crystal.

Table 8. Geometrical Features of Counteranions and Molecule (Distances (Å) and Angles (deg) and Their Esd)

2-Amino-5-nitropyridinium Trichloroacetate			
C6−O3	1.235(5)	O3−C6−O4	129.0(5)
C6−O4	1.222(6)	O3−C6−C7	114.6(4)
C6−C7	1.567(6)	O4−C6−C7	116.3(4)
C7−Cl1	1.778(4)	C6−C7−Cl1	109.4(3)
C7−Cl2	1.756(5)	C6−C7−Cl2	112.5(3)
C7−Cl3	1.753(5)	C6−C7−Cl3	108.1(3)
O3−O4	2.217(4)	Cl1−C7−Cl2	108.3(2)
Cl1−Cl2	2.865(2)	Cl2−C7−Cl3	109.2(2)
Cl2−Cl3	2.860(2)	Cl1−C7−Cl3	109.3(2)
Cl1−Cl3	2.880(2)		
2-Amino-5-nitropyridinium Dichloroacetate			
C6−O3	1.227(6)	O3−C6−O4	126.7(5)
C6−O4	1.241(7)	O3−C6−C7	118.3(5)
C6−C7	1.523(8)	O4−C6−C7	115.0(4)
C7−Cl1	1.780(6)	C6−C7−Cl1	112.0(4)
C7−Cl2	1.765(6)	C6−C7−Cl2	107.5(4)
C7−H(C7)	0.97(4)	C6−C7−H(C7)	118(3)
O3−O4	2.206(6)	Cl1−C7−H(C7)	105(3)
Cl1−Cl2	2.899(3)	Cl2−C7−H(C7)	104(3)
		Cl1−C7−Cl2	109.7(3)
2-Amino-5-nitropyridine/Chloroacetic Acid			
C6−O3	1.205(3)	O3−C6−O4	125.7(3)
C6−O4	1.280(4)	O3−C6−C7	124.0(3)
C6−C7	1.499(4)	O4−C6−C7	110.3(2)
C7−Cl	1.750(3)	C6−C7−Cl	113.7(2)
C7−H(1C7)	0.97(3)	C6−C7−H(1C7)	113(2)
C7−H(2C7)	0.96(5)	C6−C7−H(2C7)	110(2)
O4−H(O4)	0.87(5)	Cl−C7−H(1C7)	108(2)
O3−O4	2.211(3)	Cl−C7−H(2C7)	108(2)
		H(1C7)−C7−H(2C7)	104(3)

anion chains via N−H- - -O contacts, so building infinite thick layers of cation-anions running parallel to the (**a,b**) plane at $c = 0$ and $^1/_2$. Such layers are interconnected through C2−H(C2)- - -O1 bonds in a three-dimensional framework. Compared to the previous structure in which the anions are not interconnected due to the absence of H-bonds, this framework reveals the formation of chained anionic aggregates through C7−H(C7)- - -O4 contacts (Figure 3) building herringbone motifs of nonlinear cations (Figure 4). Between the anionic chains the cations are brought close to the distance $d(NH_2-NH_2) = 3.949$ Å. This distance is critical regarding to the part of the Table 1 in which centrosymmetric or pseudocentrosymmetric organization of cations

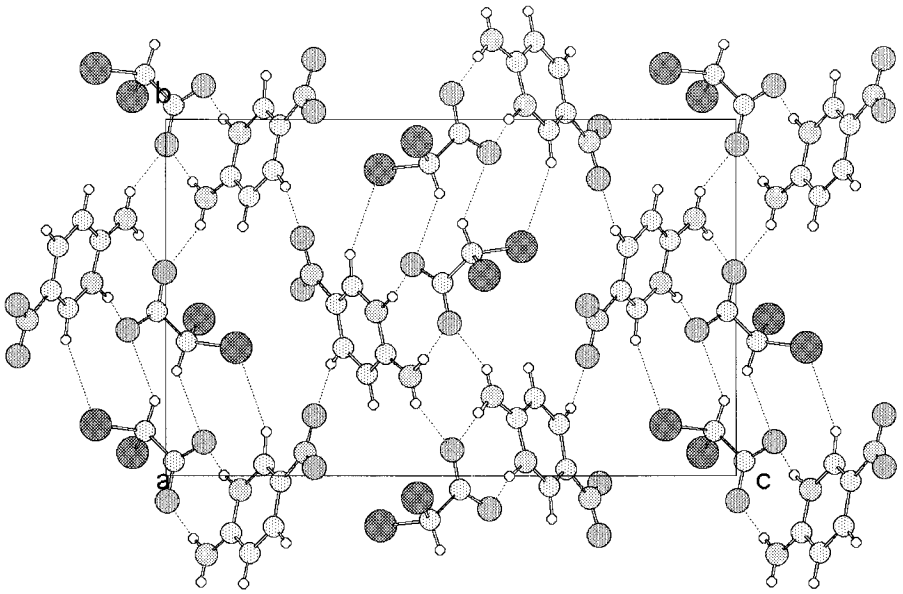

Figure 2. (**b,c**) projection of 2-amino-5-nitropyridinium dichloroacetate. H-bond network in dotted lines.

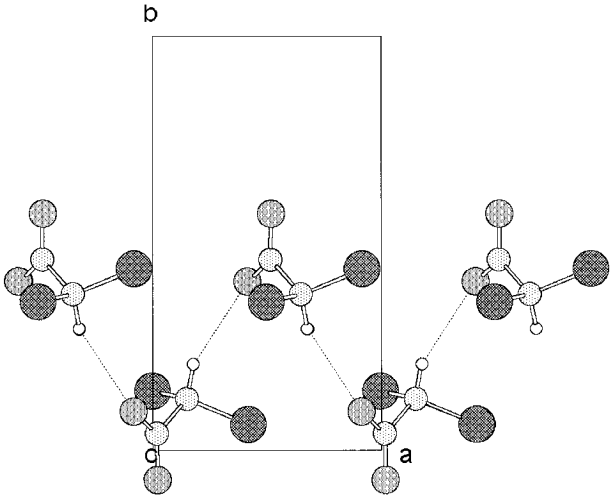

Figure 3. Chain of dichloroacetate anions aggregated through long C−H- - -O contacts.

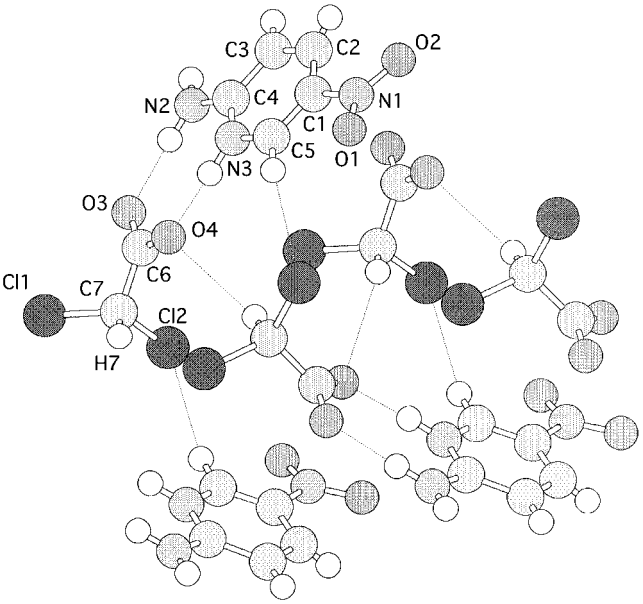

Figure 4. Sketch of herringbone motif displaying the anchorage of chromophores onto the anion chain.

appears as the most frequent. In fact, if a two-dimensional aggregation of these chains had been possible as in the phosphate,[20] arsenate,[13] acetophosphonate,[12] and tartrate[21] anionic layers, a less critical distance $d(NH_2-NH_2)$ (>4 Å) could have been obtained. The formation of anionic walls between the $2A5NP^+$ cations has been observed on the base of several crystal structure determinations as the main requirement in view to engineer noncentrosymmetric structures showing herringbone motifs. Molecular crystals as 2-(adamantylamino)-5-nitropyridine[29,30] ($Pna2_1$) and 2-(cyclooctylamino)-5-nitropyridine[31,32] ($Pca2_1$) designed from the 2-amino-5-nitropyridine chromophore exhibit noncentrosymmetric structures due to the steric hindrance of adamantyl and cyclooctyl grafted groups: herringbone motifs of chromophores are formed as in noncentrosymmetric 2-amino-5-nitropyridinium crystals. The crystal structure of 2-amino-5-nitropyridinium dichloroacetate ($P2_12_12_1$) is close to that of 2-amino-5-nitropyridinium acetophosphonate[12] ($P2_12_12_1$), the difference appearing in the chained anionic aggregate in the former case compared to the two-dimensional anionic aggregate in the latter (Figures 2 and 5). The dichloroacetate anion has one hydrogen donor group CH and four acceptors. The acetophosphonate anion is potentially richer with four hydrogen donors 2 × OH, 2 × CH and three effective acceptor groups which are the oxygen atoms, OH groups being not concerned presently as H-acceptors. A two-dimensional polymeric anion can be formed when two H-donor groups are at least present in the anionic unit: for instance, $H_2PO_4^-$ anion aggregates as one-dimensional or two-dimensional layered polymeric anion[8] $(H_2PO_4^-)_n$. More than two H-donor groups should be present in the anion structure for building a dense layered anionic aggregate able to induce noncentrosymmetric structures. A powder sample of 2A5NPDCA exhibits a second harmonic generation

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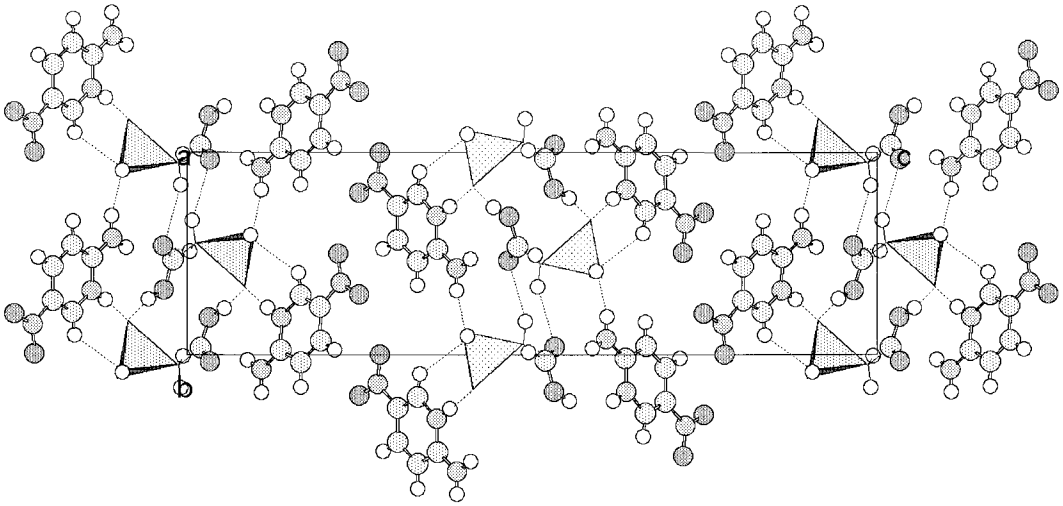

Figure 5. (**b,c**) projection of the 2-amino-5-nitropyridinium acetophosphonate structure showing the anion aggregation along the (**a,b**) plane.

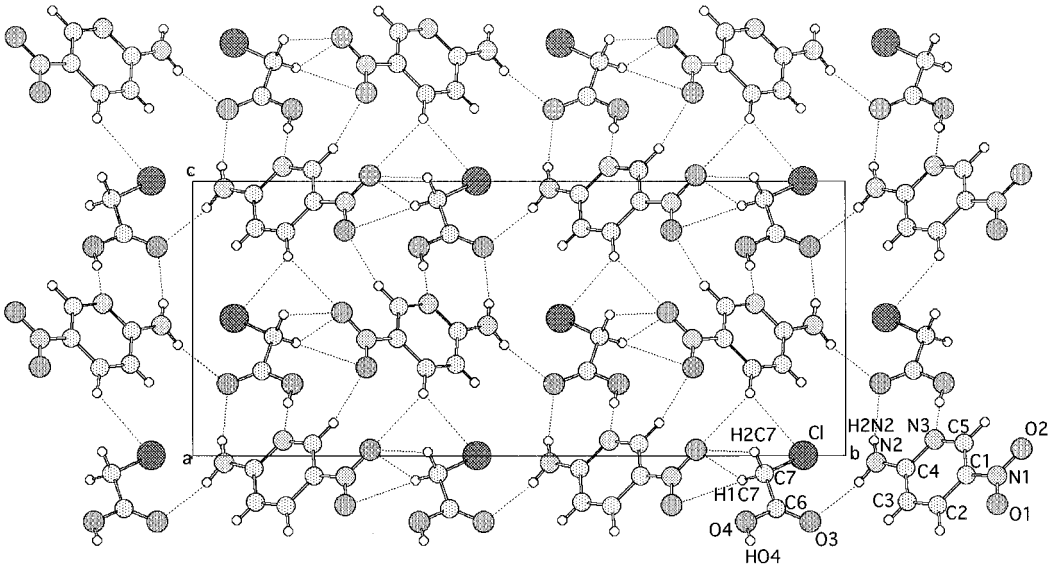

Figure 6. View along the **a** direction of the 2-amino-5-nitropyridine/chloroacetic acid cocrystal. The three-dimensional H-bonding scheme is indicated in dotted lines.

signal lower in magnitude than that of 3-methyl-4-nitropyridine *N*-oxide sample and upper than that of KH_2PO_4, by using a Nd^{3+}:YAG laser light at 1.06 μm.

2-Amino-5-nitropyridine/Chloroacetic Acid (2A5NPCA). As revealed by the crystal structure investigation (Figure 6), the proton transfer from the carboxylic group to the nitrogen atom of the pyridine ring does not occur like in the previous compounds. The chloroacetic acid is weakly dissociated (pK = 2.85, 25 °C) and despite the drastic conditions of the chemical reaction (see Experimental Section) the proton transfer on the 2-amino-5-nitropyridine, a weak base, is not possible. However, the formation of a noncentrosymmetric cocrystal can be explained in relation with the molecular structures containing the same chromophore. It appears relatively short H bonds between the 2A5NP molecule and the carboxylic radical of the chloroacetic acid: H(O4)- - -N3, H(2N2)- - -O3, and H(1N2)- - -O3 (Table 6) pointing out that the organic acid molecule acts as a steric group grafted on the 2A5NP molecule. This situation is similar to that observed in the noncentrosymmetric molecular crystals as 2-(adamantylamino)-5-nitropyridine[29,30] (AANP), 2-(cyclooctylamino)-5-nitropyridine[31,32] (COANP), 2(*S*)-(phenylethylamino)-5-nitropyridine[33−35] (MBANP), (4-nitro-2-pyridinyl)-(*S*)-phenylalaninol[36,37] (NPPA) and *N*-(5-nitro-2-pyridyl)-leucinol[38] (NPLO) in which the large steric groups, adamantyl, cyclooctyl, phenylethyl, phenylalaninol, and leucinol grafted on the NH^- group of the pyridine ring induce herringbone motifs of chromophores. A second network of longer H contacts C−H- - -O, C−H- - -Cl ensures the three-dimensional cohesion of pairs 2A5NP/chloroacetic acid in the network. The H(C2) atom is engaged in a three-center H bond between C2, Cl, and O2 atoms. The same situation is realized with H1(C7)

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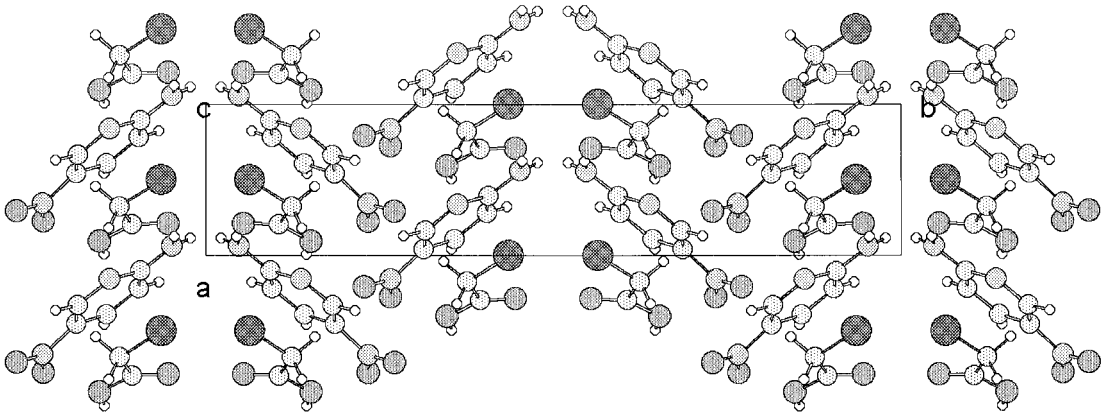

Figure 7. View along the **c** direction evidencing the herringbone motifs of chromophores which frame the cocrystal.

and C7, O1, O2 atoms. The homogeneity of long H bonds and the three-dimensional distribution of all H bonds provide a better stability to the structure compared to the molecular structures built with the same chromophore. Crystals are growing as thick rhombohedral prisms. The structure viewed in the **c** direction (Figure 7) displays layers of herringbone motifs parallel to the (**a**,**c**) plane located at $b = 0$ and 0.5. The shortest distance $d(NH_2-NH_2)$ except the **a** translation is 5.152 Å. This value is situated in the region of the Table 1 where the noncentrosymmetric structures are the most frequently observed. In the non-centrosymmetric molecular structures as COANP, MBANP, and NPPA designed with the 2A5NP chromophore the equivalent distances are respectively $d(NH-NH) = 6.321$, 6.371, and 6.031 Å, suggesting the same correlation between the noncentrosymmetry of the framework and the optimum interspacing $d(NH-NH)$ as that evidenced in ionic structures. A parameter to be taken into account in this family of materials is the density of chromophores per unit volume of matter. The intensity of nonlinear optical polarization is proportional to the number of oscillators per unit volume of matter. The average volume of $2A5NP^+$ cation is defined by its molecular volume calculated from ionic structures in which it is involved and for which the anion volumes are known. $V2A5NP^+ = 146.6$ Å^3. We estimate that the volume of the 2A5NP molecule is the same. $\tau = ZV_{2A5NP^+}/V_{cell}$ indicates the proportion of volume occupied by the chromophores. Since the efficiency of a nonlinear crystal is related both to the molecular hyperpolarizability of the chromophores and their optimum orientation with respect to the main symmetry elements of the point group,[39] the Table 7 cannot establish a scale of NLO efficiencies. However, we observe in the cocrystal a high density of chromophores compared to the bulky molecular compounds, probably responsible of the high SHG signal.[40] Among the ionic compounds the 2-amino-5-nitropyridinium chloride appears as the most efficient following the τ value, confirmed by the SHG comparative intensities. The second harmonic generation signal observed from a powder sample of 2A5NPCA, illuminated by a Nd^{3+}:YAG laser light at 1.06 μm, is higher than that of a 3-methyl-4-nitropyridine *N*-oxide reference. As first approximation the compromise between nonlinear efficiency, transparency, and stability would be better in 2A5NPCA than in 3-methyl-4-nitropyridine *N*-oxide so indicating the ingeneering route of nonlinear optical cocrystals as an attractive direction of research.

Conclusion

The subnetworks of nonlinear chromophores revealed by these structures are similar to that observed in molecular and ionic structures previously referenced. Chains of chromophores in COANP, AANP, and MBANP are induced via intermolecular hydrogen bonds involving donor amino groups and acceptor nitro groups.[41] In COANP and AANP the unique hydrogen donor amino group connects an oxygen atom of the nitro group belonging to a close molecule, the second oxygen atom being involved in a C−H- - -O bond from the cyclooctyl or adamantyl grafted group of an adjacent molecule, so building a zigzag chain of chromophores. The interpenetration of zigzag arrays frames herringbone motifs. In MBANP the unique N−H- - -O bond directs the formation of half-herringbone motifs: herringbone motifs result from the association of such submotifs through van der Waals bonds. In NPPA the hydroxyl radical of the phenylalaninol bulky group is the key of the molecular packing: both H acceptor from the NH group and H donor toward the nitro group, the hydroxyl group induces the formation of two half-herringbone motifs. Complete herringbone motifs are obtained through van der Waals connections. In ionic structures the 2-amino-5-nitropyridinium chromophores anchored onto host matrixes through three N−H- - -A(acceptor) bonds are always organized in half herringbone motifs. The structures are noncentrosymmetric when herringbone motifs are formed. It has been established that the formation of herringbone motifs is favored if the cations are removed to an optimum distance $d(NH_2-NH_2) > 4$ Å. This condition is realized when chained or layered polymeric aggregates are selected as counteranions. These packings are cohesive via van der Waals and H bonds in molecular crystals and multiple and short H bonds in ionic crystals. The chemical stability and thermal and mechanical resistances of nonlinear optical crystals are essential qualities in view to their industrial development. Our engineering route is justified by the research of highly cohesive packings of nonlinear organic chromophores. It appears that ionic crystals are more stable than molecular crystals,

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especially if three-dimensional, homogeneous and short hydrogen-bond networks are formed. The structure of the 2A5NPDCA confirms as previously referenced in Table 1 the role played by the polymeric counteranion in view to gain a noncentrosymmetric packing of cations. The structure of the 2A5NPCA cocrystal shows that the bulky group induces a noncentrosymmetric structure as in 2-amino-5-nitropyridine molecular derivatives. Although the design of nonlinear optical crystals based on intermolecular H contacts seems to show some predictive character,[4b,5,41,42] future engineering routes able to improve the crystal stability should be based on the use of mixed covalent (ionic) and hydrogen bond networks as exemplified in the crystal structure of bis-(4-nitropyridine *N*-oxide) cadmium chloride.[43]

Supporting Information Available: Tables of crystal data (23 pages); tables of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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