Nonlinearity Enhancement by Solid-State Proton Transfer: A New Strategy for the Design of Nonlinear Optical Materials

Cara C. Evans,† M. Bagieu-Beucher,‡ René Masse,‡ and Jean-François Nicoud*,†

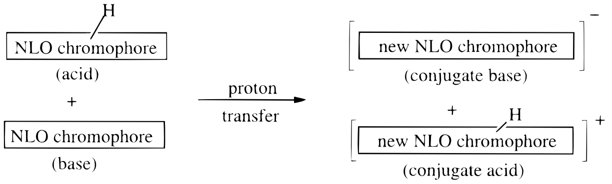
Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur et CNRS (UMR 7504), 23 rue du Loess, 67037 Strasbourg Cedex, France, and Laboratoire de Cristallographie, associé á l'Université Joseph Fourier, CNRS, BP 166, 38042, Grenoble-Cedex 09, France

Received September 10, 1997. Revised Manuscript Received December 19, 1997

Theoretical considerations of the molecular hyperpolarizabilities (β) of donor−acceptor substituted aromatic molecules show that the transfer of a proton from the electron-donor group of an acid to the electron acceptor group of a base could increase β for both resulting ionic species relative to the corresponding neutral molecules. To take advantage of this, the cocrystallization of 4-nitrophenol with various organic bases was studied. Cocrystallization of 4-nitrophenol with 4-(dimethylamino)pyridine gives yellow crystals that display a strong second harmonic signal by the Kurtz and Perry powder test. The material crystallizes in the orthorhombic space group $P2_12_12_1$ and is composed of 4-(dimethylamino)pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP2). Theoretical calculations of the hyperpolarizabilities predict that the values of β are greater for the 4-(dimethylamino)pyridinium and 4-nitrophenolate ions than for the corresponding neutral molecules. A second noncentrosymmetric material has been grown from an equimolar melt of 4-hydroxypyridine and 4-nitrophenol. In this cocrystal, which forms in the noncentrosymmetric orthorhombic space group $Pna2_1$, the pyridine derivative is present as the 4-pyridone tautomer. Though proton transfer occurs for only one of the two crystals presented here, the work with DMAPNP2 illustrates that new, highly efficient NLO materials can be designed by using acid/base chemistry.

Introduction

Over the past three decades organic materials have been the subject of much investigation for application in nonlinear optics (NLO). The advantages offered by organic over inorganic systems include high electronic susceptibility ($\chi^{(2)}$) through high molecular hyperpolarizability (β), fast response time, facile modification through standard synthetic methods, and relative ease of device processing. However, these molecular materials are limited by poor thermal and chemical stability. To provide increased stability and a framework for a noncentrosymmetric arrangement of chromophores, another approach involves the growth of crystals that contain inorganic and organic ions.[1] Other examples of noncentrosymmetric crystals have been reported in which both cation and anion are organic materials.[2] Acid/base interactions in the solid state provide further opportunity to investigate such systems. If we consider two separate NLO organic chromophores, one being an acid and the second being a base, we anticipate that proton transfer between these two partners could increase the hyperpolarizabilities of both species as shown below:



If the resulting organic salt has a noncentrosymmetric structure, this new crystal engineering strategy could lead to highly efficient NLO materials. Here we report the first example of this route to organic materials for second harmonic generation.

The argument that proton transfer, under certain conditions, tends to increase molecular hyperpolarizability (β) is based on the two-level model for β.[3] According to this model, the tensor component of β along the charge-transfer axis (β_{ct}) is described in terms of the ground and first excited states of a conjugated molecule substituted with electron-donating and -accepting groups.

---

* Author to whom correspondence should be sent. E-mail: nicoud@michelangelo.u-strasbg.fr.

† Groupe des Matériaux Organiques.

‡ Laboratoire de Cristallographie.

(1) (a) Pécaut, J.; Le Fur, Y.; Masse, R. *Acta Crystallogr.* **1993**, *B49*, 535. (b) Pécaut, J.; Masse, R. *Acta Crystallogr.* **1993**, *B49*, 277. (c) Pécaut, J.; Levy, J.-P.; Masse, R. *J. Mater. Chem.* **1993**, *3*, 999.

(2) (a) Le Fur, Y.; Bagieu-Beucher, M.; Masse, R.; Nicoud, J.-F.; Lévy, J.-P. *Chem. Mater.* **1996**, *8*, 68. (b) Pécaut, J.; Masse, R. *J. Mater. Chem.* **1994**, *4*, 1851. (c) Pécaut, J. *Z. Kristallogr.* **1993**, *208*, 238. (d) Zyss, J.; Masse, R.; Bagieu-Beucher, M.; Levy, J. P. *Adv. Mater.* **1993**, *5*, 120.

(3) (a) Oudar, J.-L.; Zyss, J. *Phys. Rev. A* **1982**, *26*, 2016. (b) Oudar, J.-L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

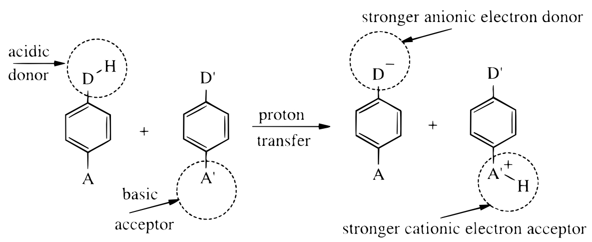
S0897-4756(97)00618-2 CCC: $15.00

Mathematically, the expressions are

$$\beta_{ct} = C\frac{\omega_{eg}}{({\omega_{eg}}^2 - \omega^2)({\omega_{eg}}^2 - 4\omega^2)} f\Delta\mu_{g,e} \qquad (1)$$

$$\beta_{ct} \propto \Delta\mu_{g,e}\frac{{\mu_{g,e}}^2}{{E_{g,e}}^2} \qquad (2)$$

In (1), C is a constant, ω_{eg} is the frequency of the charge-transfer transition, ω is the fundamental frequency, f is the oscillator strength, and $\Delta\mu_{g,e}$ is the difference between the ground and excited-state dipole moments. In (2), $E_{g,e}$ is the energy difference between the ground- and charge-transfer states, and ${\mu_{g,e}}^2$, the square of the transition matrix element, is proportional to the oscillator strength. An increase in the donor or acceptor capability for a given position of substitution lowers the $E_{g,e}$ and increases the oscillator strength, tending to result in greater hyperpolarizability. Such a change is observed when a proton is transferred from the electron-donor group of an acid to the electron-acceptor group of a base. Assuming two 1-donor-4-acceptor benzene derivatives as starting materials, the change is illustrated in the the following scheme:



The cocrystallization of two chromophores, in this case an acid and a base, is a common approach to the design of materials for NLO. This method was investigated extensively by Etter and co-workers, who examined the growth of acentric cocrystals through hydrogen bonding.[4] Another group, Pan, Bosshard, and co-workers, reported proton transfer between merocyanine dyes and phenol derivatives.[5] In the literature there are many such examples of noncentrosymmetric cocrystals grown through hydrogen bonding, and in some cases, ionic interactions. Here we present the first purposeful utilization of proton transfer to increase the hyperpolarizabilities of the chromophores.

The acid chosen for study in this work was 4-nitrophenol, and the base was one of several derivatives of pyridine substituted in the para position by an electron-donating functional group. For the acid and its conjugate base, the nitrophenolate anion, the electron acceptor (NO_2) is the same, but the donor groups differ. For para substitution, the Hammett σ coefficients[6] predict that O^- ($\sigma = -0.81$)[7] is a better electron donor than OH ($\sigma = -0.38$).[8] On the basis of consideration of only $\mu_{g,e}$ and $E_{g,e}$ in the two-level model, therefore, the 4-nitrophenolate anion is anticipated to have a greater molecular hyperpolarizability than 4-nitrophenol. As for the base, protonation and the resulting positive charge on the ring nitrogen of the pyridine derivative are predicted to make the heteroatom a stronger electron acceptor.

In this work, the pyridine derivatives were substituted in the para position by five functional groups of varying donor strengths: CH_3, NH_2, $N(CH_3)_2$, OH, or pyrrolidine. Of these, cocrystals of the last three with 4-nitrophenol were effective for second harmonic generation (SHG) by the Kurtz and Perry powder test with Nd^{3+}:YAG laser radiation ($\lambda = 1.06\ \mu m$).[9] In contrast to the work with 4-pyrrolidinopyridine, noncentrosymmetric single cocrystals could be grown from nitrophenol with the dimethylamino or hydroxyl derivative of pyridine. These two materials also resulted in the strongest second harmonic signals, which had intensities between those of POM [3-methyl-4-nitropyridine-1-oxide][10] and NPP [*N*-(4-nitrophenyl)-(*S*)-prolinol].[11] Therefore, here we will focus on the cocrystals of 4-nitrophenol (NP) with 4-(dimethylamino)pyridine (DMAP) and 4-nitrophenol with 4-hydroxypyridine (Py). We present the structure of a 4-(dimethylamino)pyridinium 4-nitrophenolate 4-nitrophenol ionic crystal (DMAPNP2), in which the 4-nitrophenolate anion and the 4-(dimethylamino)-pyridinium cation result from proton transfer and neutral 4-nitrophenol stands as a third partner. Additionally, we describe a 4-pyridone 4-nitrophenol cocrystal (PyNP) formed from the melt. No proton transfer is observed in this material, in which 4-hydroxypyridine exists as the 4-pyridone tautomer.[12]

Both the 4-(dimethylamino)pyridinium and 4-nitrophenolate ions have been examined previously in solid-state studies. Centrosymmetric crystals that contain the 4-(dimethylamino)pyridinium cation have been grown with both organic[13] and inorganic[14] anions. Nitrophenolate, on the other hand, is SHG active as the hydrate of the sodium salt in noncentrosymmetric space group *Ima*2.[15] Koshima et al. cite powder X-ray diffraction, differential scanning calorimetry, and spectroscopic data as evidence for the formation of a 1:1 molecular compound between 4-nitrophenol and several derivatives of

---

[4] (a) Huang, K.-S.; Britton, D.; Etter, M. C.; Byrn, S. R. *J. Mater. Chem.* **1997**, *7*, 713. (b) Russell, V. A.; Etter, M. C.; Ward, M. D. *Chem. Mater.* **1994**, *6*, 1206. (c) Frankenbach, G. M.; Etter, M. C. *Chem. Mater.* **1992**, *4*, 272. (d) Etter, M. C.; Huang, K.-S. *Chem. Mater.* **1992**, *4*, 824. (e) Etter, M. C.; Huang, K. S.; Frankenbach, G. M.; Adsmond, D. A. *Am. Chem. Soc., Symp. Ser.* **1991**, *455*, 446. (f) Etter, M. C.; Frankenbach, G. M.; Adsmond, D. A. *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 25.

[5] (a) Wong, M. S.; Pan, F.; Gramlich, V.; Bosshard, C.; Günter, P. *Adv. Mater.* **1997**, *9*, 554. (b) Pan, F.; Wong, M. S.; Gramlich, V.; Bosshard, C.; Günter, P. *Chem. Commun.* **1996**, 1557. (c) Pan, F.; Wong, M. S.; Gramlich, V.; Bosshard, C.; Günter, P. *J. Am. Chem. Soc.* **1996**, *118*, 6315.

[6] Hammett σ coefficients are usually defined in terms of the difference in acidity between benzoic acid and a meta- or para-substituted benzoic acid. In this case, for $X-C_6H_4CO_2H$, σ corresponds to $pK_a(X=H) - pK_a(X\neq H)$. σ is positive for electron-withdrawing groups and negative for electron-donating groups.

[7] Hine, J. *J. Am. Chem. Soc.* **1960**, *82*, 4877.

[8] Matsui, T.; Ke, H. C.; Hepler, L. G. *Can. J. Chem.* **1974**, *52*, 2906.

[9] Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

[10] Zyss, J.; Chemla, D. S.; Nicoud, J.-F. *J. Chem. Phys.* **1981**, *74*, 4800.

[11] Zyss, J.; Nicoud, J.-F.; Coquillay, M. *J. Chem. Phys.* **1984**, *81*, 4160.

[12] 4-Pyridone stands for 4(1*H*)-pyridinone.

[13] (a) Bossa, M.; Colapietro, M.; Morpurgo, G. O.; Morpurgo, S.; Portalone, G. *J. Phys. Chem.* **1996**, *100*, 9302. (b) Biradha, K.; Edwards, R. E.; Foulds, G. J.; Robinson, W. T.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1705.

[14] Chao, M.; Schempp, E.; Rosenstein, R. D. *Acta Crystallogr.* **1977**, *B33*, 1820.

[15] (a) Minemoto, H.; Ozaki, Y.; Sonoda, N.; Sasaki, T. *J. Appl. Phys.* **1994**, *76*, 3975. (b) Minemoto, H.; Ozaki, Y.; Sonoda, N.; Sasaki, T. *Appl. Phys. Lett.* **1993**, *63*, 3565. (c) Minemoto, H.; Sonoda, N. *Acta Crystallogr.* **1992**, *C48*, 737.

Table 1. Crystal Data, Intensity Measurements, and Structural Refinement Parameters

formula	$C_7H_{11}N_2^+\cdot C_6H_4NO_3^-\cdot C_6H_5NO_3$	$C_5H_5NO\cdot C_6H_5NO_3$
molecular wt	400.39	234.21
space group	$P2_12_12_1$	$Pna2_1$
a (Å)	6.355(1)	22.930(4)
b (Å)	11.927(2)	11.696(2)
c (Å)	24.942(4)	4.061(1)
β (deg)		
V (Å^3)	1891(1)	1089.1(6)
Z, D_x (g cm^{-3})	4, 1.407	4, 1.428
unit-cell refinement	25 reflect ($12 < \theta < 16°$)	25 reflect ($12 < \theta < 14°$)
F(000)	840	488
μ (cm^{-1})	1.153 (λ Mo Kα)	1.198 (λ Mo Kα)
crystal size (mm)	0.70 × 0.25 × 0.25	0.80 × 0.32 × 0.32
temp (K)	293	293
apparatus	Nonius CAD4	Nonius CAD4
radiation (Å), monochromator	0.7107 (Mo Kα), graphite (220)	0.7107 (Mo Kα), graphite (220)
bragg angle limits (deg)	3−30	3−30
scan technique	ω scan	ω scan
background (s)	6−20	5−55
scan speed (deg s^{-1})	0.03−0.11	0.011−0.11
scan width (deg)	1.20	1.20
control reflections		
intensity every	7200 s (no decay)	7200 s (no decay)
orientation every	400 reflns	400 reflns
reflections collected	3739	3639
unique data	2045 ($R_{\mathrm{int}} = 0.023$)	1781 ($R_{\mathrm{int}} = 0.014$)
data used in refinement	1912 ($I > 3\sigma(I)$)	1112 ($I > 1\sigma(I)$)
refined parameters	342	193
R (R_{w})	0.056 (0.054)	0.056 (0.052)
weighting scheme	unitary	unitary
goodness of fit	0.817	0.648
largest shift/error	0.04	0.03
max.residual density (e Å^{-3})	0.205	0.192
min residual density (e Å^{-3})	−0.171	−0.198

nitroaniline.[16] The two materials that are noncentrosymmetric are complexes of 3-nitrophenol with 3-nitroaniline[16a] and of 4-nitrophenol with 3-nitroaniline.[16b] In the work of Pan, Bosshard, and co-workers, cocrystallization of 2-amino-4-nitrophenol with merocyanine dye, the proton transfer that occurs does not increase the hyperpolarizability of the merocyanine basic chromophore.[5]

To our knowledge, no crystal structure has been published of 4-pyridone, the tautomer of 4-hydroxypyridine which is probably the form of the pure solid.[17] However, 4-pyridone has been reported to crystallize with nitric acid in space group $I2/a$; the proton from the nitric acid links dimers of 4-pyridone.[18] In other crystals, substituted 4-hydroxypyridines exist as either the 4-pyridone[19] or the 4-hydroxypyridine[20] tautomer.

Experimental Section

Crystal Growth. *(a) 4-(Dimethylamino)pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP2):* A crystal suitable for single-crystal X-ray diffraction was grown by dissolving equimolar quantities of 4-(dimethylamino)pyridine (Lancaster, 99%) and 4-nitrophenol (Aldrich, 98%) in boiling 1:1 (v:v) distilled water and acetonitrile (SDS, 99.5%). Yellow needles formed by slow cooling. ^{1}H NMR (200 MHz; acetone-d_6) indicated that the composition of the crystals was 1 4-(dimethylamino)pyridine:2 nitrophenol, which was confirmed by elemental analysis (MHW Laboratories, Phoenix, AZ). ^{1}H NMR δ 8.17−8.12 (dd, 6H, $J = 2.1$, 7.0 Hz), 7.04−6.98 (dd, 4H, $J = 2.1$, 9.2 Hz), 6.66−6.63 (dd, 2H, $J = 1.6$, 5.0 Hz), 3.73 (br s), 3.05 (s, 6H). Calcd for $C_{19}H_{20}N_4O_6$: C, 59.76; H, 5.79; N, 16.08%. Found: C, 57.36; H, 5.17; N, 14.33%. Mp 128−131 °C.

(b) 4-Pyridone 4-nitrophenol (PyNP): A mixture of 0.01 mol of 4-hydroxypyridine (ACROS, 98%) and 0.01 mol of 4-nitrophenol (Aldrich, 98%) was ground and placed in a glass ampule and sealed under vacuum. After the sample had been heated to 160 °C, the melt was cooled slowly at rates of 5 °C h^{-1} from 160 to 100 °C and 10 °C h^{-1} from 100 to 20 °C. Yellow crystalline needles up to 0.5 × 0.5 × 4 mm^3 in size were prepared by this method (mp 148−154 °C). The formula of this compound was determined via the crystal structure investigation and ^{1}H NMR (300 MHz; acetone-d_6). The classification of the crystal in noncentrosymmetric space group $Pna2_1$ was confirmed by both the last reliability factor (Table 1) and a positive second harmonic generation powder test. ^{1}H NMR δ 8.20−8.15 (m, 2H), 7.88 (d, 2H, $J = 4.6$ Hz), 7.08−7.02 (m, 2H), 6.42 (d, 2H, $J = 4.8$ Hz), 2.95 (br s).

---

(16) (a) Koshima, H.; Wang, Y.; Matsuura, T.; Mizutani, H.; Isako, H.; Miyahara, I.; Hirotsu, K. *Mol. Cryst. Liq. Cryst.* **1996**, *279*, 265. (b) Koshima, H.; Wang, Y.; Matsuura, T. *Mol. Cryst. Liq. Cryst.* **1996**, *277*, 63. (c) Koshima, H.; Wang, Y.; Matsuura, T.; Mibuka, N.; Imahashi, S. *Mol. Cryst. Liq. Cryst.* **1996**, *275*, 233.

(17) (a) 2-Hydroxypyridine exists in the solid state as the 2-pyridone tautomer: Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 591. (b) In polar solvents such as water, the tautomeric equilibrium of 4-hydroxypyridine tautomeric equilibrium is shifted far to the lactam form: Karelson, M. M.; Katritzky, A. R.; Szafran, M.; Zerner, M. C. *J. Org. Chem.* **1989**, *54*, 6030. Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, 1985; pp 47−50.

(18) Goodgame, D. M. L.; Lalia-Kantouri, M.; Williams, D. J. *J. Cryst. Spec. Res.* **1993**, *23*, 373.

(19) (a) Le Fur, Y.; Masse, R.; Cherkaoui, M. Z.; Nicoud, J.-F. *Z. Kristallogr.* **1995**, *210*, 856. (b) Toledo, L. M.; Laugyer, J. W.; Fowler, F. W. *Chem. Mater.* **1994**, *6*, 1222. (c) Hine, J.; Ahn, K.; Gallucci, J. C.; Linden, S. M. *Acta Crystallogr.* **1990**, *C46*, 2136. (d) Larson, S. B.; Sanghvi, Y. S.; Revankar, G. R.; Robins, R. K. *Acta Crystallogr.* **1990**, *C46*, 791. (e) Nakatsuji, Y.; Bradshaw, J. S.; Tse, P.-K.; Arena, G.; Wilson, B. E.; Dalley, N. K.; Izatt, R. M. *J. Chem. Soc., Chem. Commun.* **1985**, 749. (f) Boer, F. P. *Acta Crystallogr.* **1972**, *B28*, 3200.

(20) (a) Burgess, J.; Fawcett, J.; Patel, M. S.; Russell, D. R. *J. Chem. Res.* **1993**, *50*, 214. (b) Breitenback, J.; Nieger, M.; Vögtle, F. *Chem. Ber.* **1991**, *124*, 2583. (c) Schmitz, F. J.; DeGuzman, F. S.; Hossain, M. B.; van der Helm, D. *J. Org. Chem.* **1991**, *56*, 804. (d) Nakatsuji, Y.; Bradshaw, J. S.; Tse, P.-K.; Arena, G.; Wilson, B.; Dalley, N. K.; Izatt, R. M. *J. Chem. Soc., Chem. Commun.* **1985**, 749. (e) Boer, F. P.; Turley, J. W.; van Remoortere, F. P. *J. Chem. Soc., Chem. Commun.* **1972**, 573.

Table 2. Spectroscopic Data for 4-(Dimethylamino)pyridine, 4-Nitrophenol, and Their Conjugate Acid and Base

species	solvent	λ_{max} (nm)	ϵ_{max} ($mol^{-1}\ L\ cm^{-1}$)
4-(dimethylamino)pyridine	$CHCl_3$	262	14 000
4-(dimethylamino)pyridine	H_2O	280	18 600
4-(dimethylamino)pyridinium ion	1 M HCl in H_2O	280	19 500
4-nitrophenol	$CHCl_3$	308	9 900
4-nitrophenol	H_2O	318	9 000
4-nitrophenolate ion	1 M KOH in H_2O	402	19 400

Table 3. Calculated Values of Molecular Hyperpolarizabilities for 4-Nitrophenol, 4-(Dimethylamino)pyridine, and Their Conjugate Base and Acid, Respectively

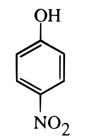
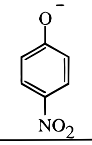
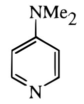
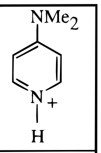
NLO Chromophore				
β_{zzz} (10^{-30} esu)	5.25	18.2	5.1	10.8

Table 4. Hydrogen-Bond Distances (Å) and Angles (deg) and Their Esd's

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
4-(Dimethylamino)pyridinium 4-Nitrophenolate 4-Nitrophenol				
O3−H(O3)···O6	0.94(4)	1.61(4)	2.515(4)	160(5)
N4−H(N4)···O6	0.93(4)	1.72(4)	2.642(4)	174(4)
C9−H(C9)···O3	1.02(4)	2.60(5)	3.245(5)	121(3)
C11−H(C11)···O2	0.98(4)	2.47(4)	3.221(5)	133(3)
C14−H(C14)···O4	0.93(5)	2.60(5)	3.506(5)	165(4)
C15−H(C15)···O5	1.07(4)	2.34(4)	3.141(5)	130(3)
4-Pyridone 4-Nitrophenol				
O3−HO3···O4	0.99(4)	1.61(4)	2.591(4)	173(4)
N2−HN2···O4	0.99(5)	1.71(5)	2.692(5)	171(5)
C5−HC5···O2	0.99(4)	2.67(4)	3.259(5)	118(3)
C6−HC6···O2	0.94(4)	2.69(4)	3.261(5)	120(4)
C9−HC9···O1	0.97(5)	2.64(5)	3.296(6)	168(4)
C9−HC9···O2	0.97(5)	2.63(5)	3.354(6)	131(3)
C11−HC11···O1	1.01(5)	2.67(5)	3.250(5)	162(4)
C15−HC15···O5	1.07(4)	2.34(4)	3.141(5)	130(3)

(c) Cocrystallization of other pyridine derivatives with 4-nitrophenol: Other pyridine derivatives considered were 4-aminopyridine (Lancaster, 98%), 4-methylpyridine (Aldrich, 98%), and 4-pyrrolidinopyridine (Lancaster, 98%). Equimolar quantities of each base and 4-nitrophenol were dissolved in acetonitrile (SDS, reagent grade), distilled methanol, distilled water, or combinations of these solvents. Crystals were allowed to form through slow evaporation of solvent and were characterized for NLO activity by the Kurtz and Perry powder test.

Kurtz and Perry Powder Test. A pulsed Nd^{3+}:YAG laser ($\lambda = 1.06\ \mu m$) was used to qualitatively determine the efficiency of the crystals for frequency doubling. The references used were urea, POM [3-methyl-4-nitropyridine-1-oxide],[10] and NPP [*N*-(4-nitrophenyl)-(*S*)-prolinol].[11] DMAPNP2 and PyNP give strong SHG signals that are comprised between the ones of POM and NPP. Compound with 4-pyrrolidinopyridine is moderately SHG active (>urea, <POM). Compounds with 4-aminopyridine and 4-methylpyridine are not SHG active whatever the crystallization conditions.

X-ray Diffraction. The space groups and cell parameters in Table 1 were determined using an Enraf-Nonius CAD-4 four-circle diffractometer with Mo $K\alpha$ radiation. Diffracted intensities were corrected for Lorentz and polarization factors. No absorption correction was applied because the absorption coefficient was low and the crystal geometry was favorable in each case. The crystal data, details of the diffracted intensity measurements, and refinement conditions are summarized in Table 1. Crystal structures were solved by direct methods using the Multan 77 program[21] and difference Fourier syntheses. Full-matrix least-squares refinements were performed on F using a unitary weighting scheme. Scattering factors for neutral atoms and f', f'' were taken from the *International Tables for X-ray Crystallography*.[22] The Enraf-Nonius SDP program[23] operating on a micro-Vax II computer was used for all calculations, and structures were drawn in the Molview program.[24] Geometric features of hydrogen bonds and chromophores are presented in Tables 4 and 5.

Spectroscopy. *(a) UV−Visible spectroscopy:* 0.01 mM solutions were prepared by dissolving 4-nitrophenol (Aldrich, 98%) or 4-(dimethylamino)pyridine (Lancaster, 99%) in chloroform (Mallinckrodt, reagent grade), water (EM Science, HPLC grade), or 1 M HCl or KOH. Samples were contained in quartz cells with 1 cm path lengths. A Hewlett-Packard 8452A diode array spectrophotometer with 2 nm resolution was used to collect background spectra of the solvents and spectra of the solutions.

(b) Infrared spectroscopy: FTIR spectra were collected with 2 cm^{-1} resolution on a Nicolet Magna 550 instrument equipped with a HgCdTe detector. Samples of PyNP from the melt were examined as both Nujol and Fluorolube mulls between NaCl disks.

Results and Discussion

Of the five para-substituted pyridine derivatives examined, the three that were effective for second harmonic generation when cocrystallized with 4-nitrophenol were 4-pyrrolidinopyridine, 4-(dimethylamino)pyridine, and 4-hydroxypyridine. Of these, the last two derivatives were successfully grown as single cocrystals with 4-nitrophenol.

4-(Dimethylamino)pyridinium 4-Nitrophenolate 4-Nitrophenol (DMAPNP2). *(a) Proton transfer*: From a consideration of the dissociation constants of 4-(dimethylamino)pyridine[25] and 4-nitrophenol,[26] an aqueous equimolar solution of the two materials is expected to have an equilibrium that favors the respective conjugate acid and base. In contrast, the asymmetric unit of the crystals grown under these conditions includes a neutral nitrophenol molecule in addition to the ionic species. Thus, DMAPNP2 has a ternary composition (Figure 1). The presence of both the anionic and neutral forms of the acid is confirmed by a comparison of the C−O bond lengths and C−C(O)−C bond angles with the reported

---

(21) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. *MULTAN 77*, University of York, England, and Louvain La Neuve, Belgium, 1977.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, Tables 2.2a, 2.2c, 2.3.1.

(23) *Structure Determination Package*, Version RSX 11M, 1977, Enraf-Nonius, Delft.

(24) Cense, J. M. (MOLVIEW) *Molecular Graphics for the Macintosh in Modelling of Molecular Structures and Properties*; Elsevier: Dordrecht, 1990; p 763.

(25) Cruége, F.; Girault, G.; Coustal, S.; Lascombe, J.; Rumpf, P. *Bull. Soc. Chim. Fr.* **1970**, *11*, 3889.

(26) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986; p D-162.

Table 5. Main Interatomic Distances (Å) and Bond Angles (deg) and Their Esd's

Dimethylaminopyridinium 4-Nitrophenolate 4-Nitrophenol			
4-(Dimethylamino)pyridinium Cation			
N3−C13	1.343(5)	C18−N3−C19	117.3(3)
N3−C18	1.466(7)	C18−N3−C13	121.3(4)
N3−C19	1.447(7)	C19−N3−C13	121.3(4)
N4−C15	1.354(5)	C15−N4−C16	119.6(3)
N4−C16	1.334(5)	C15−N4−HN4	114(3)
N4−HN4	0.93(4)	C16−N4−HN4	126(3)
C13−C14	1.401(5)	N3−C13−C14	121.5(4)
C13−C17	1.408(5)	N3−C13−C17	121.4(3)
C14−C15	1.350(5)	C17−C13−C14	117.1(3)
C16−C17	1.356(5)	C13−C14−C15	120.3(4)
		C14−C15−N4	121.3(4)
		N4−C16−C17	122.1(4)
		C16−C17−C13	119.5(4)
4-Nitrophenolate Anion			
N2−O4	1.226(6)	O4−N2−O5	123.7(4)
N2−O5	1.224(6)	O4−N2−C7	118.3(4)
N2−C7	1.455(5)	O5−N2−C7	118.0(4)
C7−C8	1.376(6)	N2−C7−C8	118.9(4)
C7−C12	1.374(6)	N2−C7−C12	119.2(4)
C8−C9	1.397(5)	C7−C8−C9	118.9(4)
C9−C10	1.394(5)	C8−C9−C10	120.4(4)
C10−O6	1.316(5)	O6−C10−C9	121.0(3)
C10−C11	1.397(5)	O6−C10−C11	120.8(3)
C11−C12	1.370(6)	C9−C10−C11	118.2(4)
		C10−C11−C12	121.8(4)
		C11−C12−C7	118.9(4)
		C8−C7−C12	121.8(4)
4-Nitrophenol Molecule			
N1−O1	1.226(6)	O1−N1−O2	122.6(3)
N1−O2	1.220(4)	O1−N1−C1	118.8(3)
N1−C1	1.451(5)	O2−N1−C1	118.6(3)
C1−C2	1.370(5)	N1−C1−C2	119.8(3)
C2−C3	1.387(6)	N1−C1−C6	118.4(3)
C3−C4	1.387(5)	C1−C2−C3	119.6(3)
C4−O3	1.333(5)	C2−C3−C4	119.6(3)
C4−C5	1.389(5)	O3−C4−C3	123.7(3)
C5−C6	1.380(6)	O3−C4−C5	116.6(3)
C6−C1	1.375(5)	C3−C4−C5	119.7(4)
HO3−O3	0.94(4)	C4−C5−C6	120.6(3)
		C5−C6−C1	118.7(3)
		C2−C1−C6	121.8(3)
		HO3−O3−C4	109(3)
4-Pyridone 4-Nitrophenol			
4-Nitrophenol Molecule			
N1−O1	1.225(5)	O1−N1−O2	122.0(4)
N1−O2	1.223(5)	O1−N1−C1	118.8(3)
N1−C1	1.442(6)	O2−N1−C1	119.2(3)
C1−C2	1.381(6)	N1−C1−C2	119.3(4)
C2−C3	1.370(7)	N1−C1−C6	119.5(4)
C3−C4	1.391(6)	C1−C2−C3	118.9(4)
C4−O3	1.347(6)	C2−C3−C4	120.2(4)
C4−C5	1.387(5)	O3−C4−C3	117.5(4)
C5−C6	1.367(6)	O3−C4−C5	122.4(4)
C6−C1	1.374(6)	C3−C4−C5	120.1(4)
HO3−O3	0.99(4)	C4−C5−C6	119.4(4)
		C5−C6−C1	120.1(4)
		C2−C1−C6	121.2(4)
		HO3−O3−C4	111(3)
4-Pyridone Molecule			
N2−C10	1.343(7)	C10−N2−C9	120.0(4)
N2−C9	1.342(6)	N2−C9−C8	121.4(4)
C9−C8	1.346(6)	C9−C8−C7	120.8(4)
C8−C7	1.409(7)	O4−C7−C8	122.2(4)
C7−O4	1.275(5)	O4−C7−C11	121.9(4)
C7−C11	1.419(6)	C8−C7−C11	115.9(4)
C11−C10	1.346(6)	C7−C11−C10	120.3(4)
HN2−N2	0.99(5)	C11−C10−N2	121.6(4)
		HN2−N2−C9	117(3)
		HN2−N2−C10	122(3)

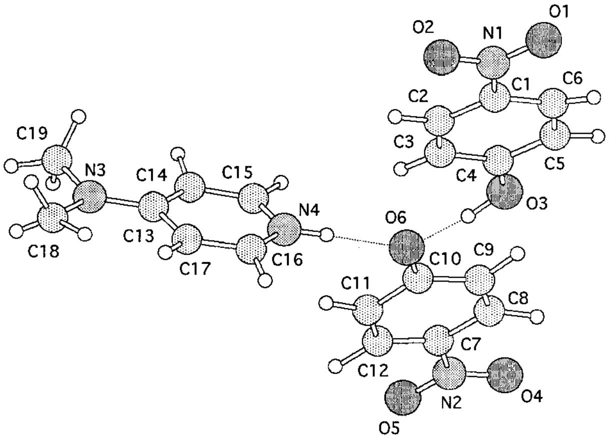


Figure 1. Asymmetric unit of 4-(dimethylamino)pyridinium 4-nitrophenolate 4-nitrophenol.

structures of 4-nitrophenol[27] and sodium 4-nitrophenolate hydrate.[15c] Such a behavior has been observed recently with the complexes formed by phenols of various pK_a with a strong N-base of guanidine-like character.[28]

As for the base, theoretical calculations on the electronic structures of aminopyridines have shown that protonation is more energetically favorable at the ring nitrogen than at the amino nitrogen.[29] In DMAPNP2 the protonated character of the heteroatom is supported by a comparison of the molecular geometry reported here (Figure 1, Table 5) with previously published work. The C15−N4−C16 bond angle in the pyridine ring is 119.6(3)°. This value compares favorably with figures reported for two crystallographically unique 4-(dimethylamino)pyridinium ions in the chloride salt[14] and for the proton-transfer adduct with 2,5-dihydroxy-*p*-quinone.[13a] On the other hand, a smaller bond angle of 114.5(2)° is reported for pure 4-(dimethylamino)pyridine.[30] A second comparison can be made of the length of the bond between the amino nitrogen and the ring carbon. In DMAPNP2 this distance (N3−C13) is 1.343(5) Å and agrees favorably with values given for other examples of the protonated species.[13b, 14] The bond length is 0.02 Å longer in the crystal of the neutral molecule.[31]

(b) NLO chromophores: When protonation of 4-(dimethylamino)pyridine occurs in solution, the charge-transfer band is red-shifted by 18 nm relative to the neutral form (Table 2). Furthermore, with respect to the free base, the protonated species has a larger linear absorption coefficient and a greater integrated area under the absorption spectrum. This area is proportional to the oscillator strength, *f*. Similarly, for 4-nitrophenol, λ_{max}, the corresponding linear absorption coefficient, and the integrated area are greater for the phenolate anion than for the conjugate acid. Therefore, in expression 2 for the two-level model, $E_{g,e}$ is smaller and $\mu_{g,e}$ is larger for both ions than for the corresponding neutral molecules. The transfer of a proton from 4-nitrophenol to 4-(dimethylamino)pyridine thus tends

---

[27] (a) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 62. (b) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 654.

[28] Brzezinski, B.; Zundel, G. *J. Mol. Struct.* **1996**, *380*, 195.

[29] Konishi, H.; Kato, H.; Yonezewa, T. *Theor. Chim. Acta* **1970**, *19*, 71.

[30] Ohms, U.; Guth, H. *Z. Kristallogr.* **1984**, *166*, 213.

[31] Kurtz, H. A.; Stewart, J. J. P.; Dieter, K. M. *J. Comput. Chem.* **1990**, *11*, 82.

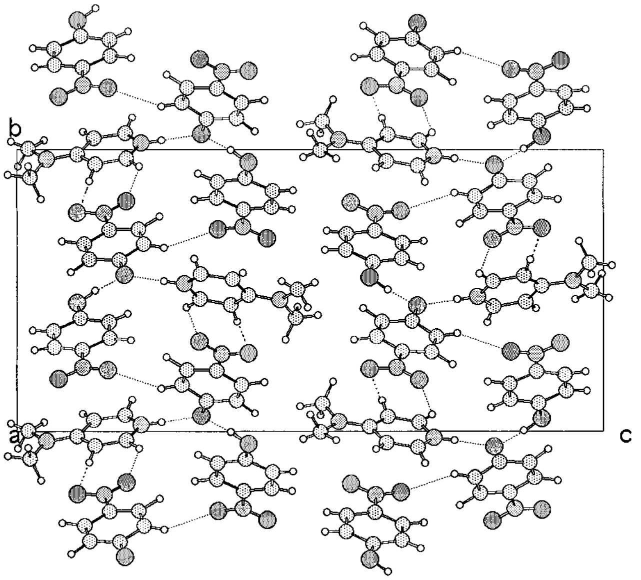


Figure 2. View of the packing in the (100) plane of 4-(dimethylamino)pyridinium 4-nitrophenolate 4-nitrophenol.

to increase the molecular hyperpolarizabilities of these components in the DMAPNP2 crystal relative to the β values of the corresponding neutral molecules.

To confirm our analysis, we calculated the hyperpolarizabilities of the neutral and ionic NLO chromophores. The geometries of the four chromophores were optimized by the ab initio DFT method with DMOL 3.00 software from Molecular Simulations Insight II (MSI). The β tensor components were then computed from these optimized structures by using the semiempirical AM1 parameters and the finite field method available in MOPAC 6.[31] All the chromophores were planar, and only the one-dimensional charge-transfer *z* axis was considered. The results for β_{zzz} are shown in Table 3. Our calculations clearly indicate that the hyperpolarizabilities are increased by the proton transfer. The hyperpolarizability is doubled when DMAP is protonated as the pyridinium and more than tripled when 4-nitrophenol loses its proton to become a 4-nitrophenolate anion.

(c) Structural description: The strongest hydrogen bonds in the structure of DMAPNP2 form on the nitrophenolate O6 oxygen atom (Figure 1, Table 4). The values of the angles around this atom[32] and their sum of 360° indicate the directions of the O6 atom lone pairs and the coplanarity of atoms O6, C10, N4, and O3. The asymmetric unit (Figure 1) is acted upon by 2_1 screw axes parallel to the *b* axis and located at (*a*, *a*/2, 3*c*/4) and (*a*, 3*c*/4) (Figure 2). In this way, a three-dimensional network of chromophores is established through van der Waals contacts and hydrogen bonds of varying energies (O−H- - -O, N−H- - -O, and C−H- - -O, Table 4). The dense, noncentrosymmetric packing of chromophores, all of which have nonzero values of β, gives rise to a strong second harmonic signal when a powder sample is illuminated by Nd^{3+}:YAG laser radiation.

4-Pyridone 4-Nitrophenol (PyNP). *(a) Pyridone tautomer:* The material obtained from an aqueous equimolar solution of 4-hydroxypyridine and 4-nitrophenol is centrosymmetric and therefore useless for second harmonic generation. ^{1}H NMR and elemental analysis reveal that the composition is 4-pyridone(4-nitrophenol)$_2$ (PyNP2). The structure of this cocrystal will be described elsewhere. However, the yellow material grown from the melt of 4-nitrophenol and 4-hydroxypyridine is highly efficient in second harmonic generation and has an equimolar composition (PyNP). In contrast to the work with DMAPNP2, in the solid state there is no proton transfer from 4-nitrophenol to 4-hydroxypyridine, regardless of the conditions of crystal growth. The observed C−O bond length and the C−C(O)−C bond angle of 4-nitrophenol agree well with values reported for the polymorph of the pure material[27a] but are considerably larger than those observed for sodium 4-nitrophenolate.[15]

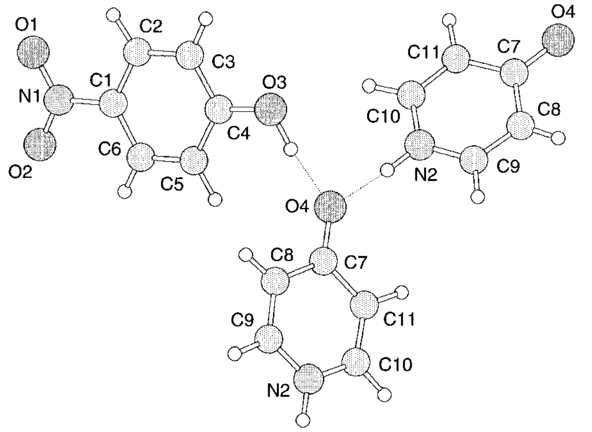


Figure 3. Molecular components of 4-pyridone 4-nitrophenol (not the asymmetric unit).

The geometry of the second component, the pyridine derivative, shows that the molecule is present as the 4-pyridone tautomer (Figure 3, Table 5). The observed C−O bond length (1.275(5) Å) falls between that reported for quinone (1.22 Å)[33] and phenol (1.36−1.38 Å)[34] but is close to the range of C−O double bonds (1.23−1.26 Å).[22] Furthermore, examination of the four C−C bond lengths reveals that the ring does not have a high degree of conjugation. Bonds C7−C11 and C7−C8 are 1.4 Å, while C10−C11 and C8−C9 are 1.35 Å. These values compare, respectively, with lengths typically observed for a single bond between two sp^2 C atoms (1.465−1.49 Å) and for C=C (1.335 Å).[34] While to our knowledge the crystal structure of 4-pyridone has not been published, the molecular geometry reported here agrees well with the geometry of 4-pyridone derivatives.[18,19]

The X-ray evidence for the presence of the 4-pyridone tautomer is supported by FTIR data. For 4-pyridone in the solid state, the C=O stretch is at 1532 cm^{-1}; higher frequency modes between 1600 and 1650 cm^{-1} have been assigned to ring vibrations.[35] The $\nu_{C=O}$ band is very sensitive to the environment and redshifts by as much as 100 cm^{-1} upon complex formation.[35b] However, in PyNP, the band is present at 1537 cm^{-1}.

---

(32) The angles considered are C10−O6−HO3 (119(2)°), C10−O6−HN4 (117(1)°), and HO3−O6−HN4 (124(2)°).

(33) Trotter, J. *Acta Crystallogr.* **1960**, *13*, 86.

(34) Sutton, L. E. *Chem. Soc. Suppl.* **1965**, S14s−S22s.

(35) (a) Bell, C. L.; Shoffner, J.; Bauer, L. *Chem. Ind.* **1963**, 1435. (b) Cook, D. *Can. J. Chem.* **1963**, *41*, 515. (c) Bellamy, L. J.; Rogasch, P. E. *Spectrochim. Acta* **1960**, *16*, 30. (d) Katritzky, A. R.; Jones, R. A. *J. Chem. Soc.* **1960**, 2947.

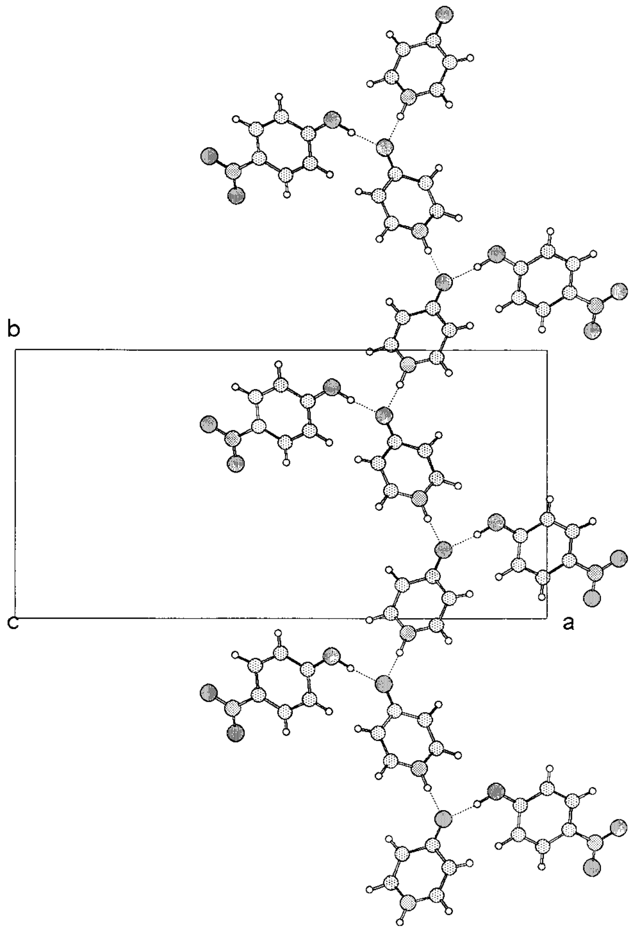


Figure 4. Chain of chromophores established by the glide plane **n** of 4-pyridone 4-nitrophenol.

This observation provides further evidence that the 4-pyridone tautomer rather than 4-hydroxypyridine or the protonated species is present in the cocrystal, since protonation of 4-pyridone would occur on the carbonyl oxygen rather than on the nitrogen.[35]

(b) Structural description: The carbonyl oxygen atom (O4) of the pyridone molecule acts as an acceptor of two short hydrogen bonds, which help to establish the supramolecular structure of the crystal (Figure 3). The coplanarity of this oxygen atom with the surrounding C7, O3, and N2 atoms is demonstrated by the 360° sum of the angles, although the distribution of oxygen atom lone pairs is considerably distorted from 120° angles.[36] One of the two hydrogen bonds on O4 links the pyridone and the nitrophenol of the asymmetric unit. The second hydrogen bond joins one asymmetric unit to the next to form a chain of chromophores through the effect of the glide plane **n** (Figure 4). The complete lattice is generated by the operation of the screw axes on this chain of chromophores and is maintained, in part, by a three-dimensional network of C−H- - -O interactions (Figure 5). The stuctural implications of C−H- - -O hydrogen bonds have been recently reviewed.[37]

Nonlinear Optical Properties. From the oriented gas description of Zyss and Oudar,[38] the 222 crystal class of DMAPNP2 is not the most favorable for phase-matching; the maximum macroscopic efficiency is only ${}^{1}/_{3}\sqrt{3}$. Three different NLO chromophores are present in DMAPNP2 crystal, and each can be modeled as having a one-dimensional charge-transfer (CT) axis. One can compare the observed orientation of each kind of chromophore with a regular tetrahedron, the optimal arrangement for point group 222. The donor−acceptor charge-transfer axis is along O6−N2 for the nitrophenolate anion, along O3−N1 for the neutral 4-nitrophenol, and along N3−N4 for the (dimethylamino)pyridinium cation. Each of these three chromophores makes a tetrahedron in the unit cell ($Z = 4$). Within each tetrahedron, 2θ describes the angle between two chromophores. θ is at the optimum value, 54.74°, for a regular tetrahedron. We have calculated the angle θ between each CT axis and the b axis and found $\theta = 61.9°$ for the nitrophenolate anion, 60.6° for the neutral 4-nitrophenol, and 80.38° for the (dimethylamino)pyridinium cation. Thus, the anionic and neutral nitrophenol chromophores have a favorable arrangement for second harmonic generation, but the four pyridinium cations of the unit cell constitute a nearly flat tetrahedron and probably contribute little to the overall nonlinearity of the crystal. In addition to θ, we should also consider the angle ψ, which describes the orientation of a tetrahedron in the lattice. The optimal value of ψ, 45°, is not observed here for any of the three chromophores. DMAPNP2 is only a first step; the strategy of β enhancement through solid-state acid/base chemistry could lead to a more efficient NLO crystal in which all chromophores have optimized orientations.

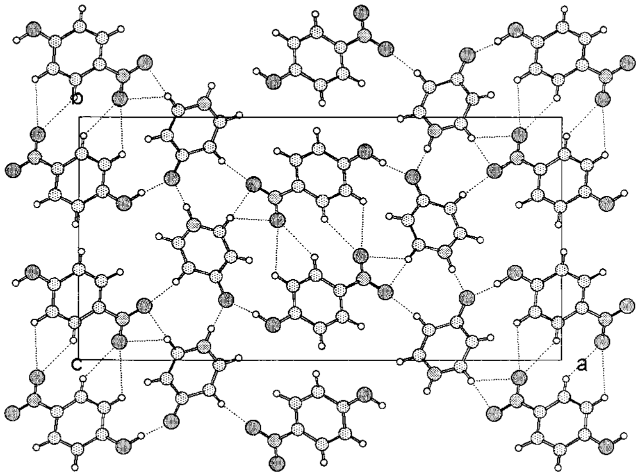


Figure 5. View of the packing in the (001) plane of 4-pyridone 4-nitrophenol.

The analysis of the chromophore orientation is more straightforward for PyNP, which belongs to the favorable crystal class $mm2$. The maximum efficiency of ${}^{2}/_{3}\sqrt{3}$ is achieved when two conditions are satisfied. The angle between the binary axis and the CT axis of each one-dimensional chromophore must be $\theta = 54.74°$, and the projection of the CT axis in the a,b plane must make an angle ψ of either 0° or 90° with the b axis.[38] The donor−acceptor charge-transfer axis is along O3−N1 for 4-nitrophenol and along O4−N2 for 4-pyridone. Both of these chromophores are oriented in the same direction along the c axis of PyNP, which means that their contribution to the overall macroscopic second-order nonlinearity is additive. The observed values of θ and

---

(36) The angles considered are C7−O4−HO3 (134(2)°), C7−O4−HN2 (132(2)°), and HO3−O4−HN2 (94(2)°).

(37) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

(38) Zyss, J.; Oudar, J.-L. *Phys. Rev. A* **1982**, *26*, 2028.

ψ are 60.8° and 62.5° for 4-nitrophenol, and 76.5° and 23° for pyridone, respectively. For neither chromophore does $\psi = 0°$ or $\psi = 90°$. 4-Nitrophenol, which has the higher molecular hyperpolarizability, also has a more favorable orientation than 4-pyridone for making a contribution to $\chi^{(2)}$. Thus from the highest values of the angular expressions $\sin^2 \psi \cos \theta \sin^2 \theta$ or $\cos^2 \psi \cos \theta \sin^2 \theta$ given by Zyss and Oudar,[38] we deduce that in PyNP 76% and 49% of the theoretical maximum efficiency are recovered from 4-nitrophenol and from pyridone, respectively.

Conclusion

Several combinations of 4-nitrophenol, an acid, and pyridine derivatives as bases have been prepared to check the role of proton transfer between acidic and basic chromophores in the crystal engineering of NLO materials. A first material, DMAPNP2, resulting from an acid/base reaction between 4-nitrophenol and 4-(dimethylamino)pyridine shows a high second harmonic signal at 1.06 μm. In this material, not only does proton transfer increase β, it also provides Coulombic interactions as cohesive forces. Its crystal structure has been presented that shows the role of a third component, the neutral 4-nitrophenol molecule, in the establishment of a hydrogen-bond network. No nitrophenolate salts of the 4-hydroxypyridinium cation have grown when equimolar quantities of 4-hydroxypyridine and 4-nitrophenol were dissolved under various conditions. The crystals that grow contain one unit of the pyridine derivative for two units of the acid. This material was centrosymmetric and therefore useless for second harmonic generation. However, a noncentrosymmetric crystal of 1:1 can be grown from the melt. In this PyNP cocrystal, which gives rise to a strong second harmonic signal, the pyridine derivative is present as the pyridone tautomer.

During the writting of this paper, a paper by the late Margaret Etter and co-workers appeared that reported the preparation by acid−base interactions of several phenol−pyridine cocrystals for second harmonic generation.[39] In this paper DMAPNP2 material was reported too but without its crystal structure determination. Two other ionic cocrystals were described, in which a neutral phenol molecule is present in addition to the phenolate anion and the pyridinium cation, confirming the general tendency of this kind of crystals.[28] However our study of DMAPNP2 demonstrates that efficient organic crystals for nonlinear optics can be designed using the hyperpolarizability enhancement occurring from acid/base proton transfer. The materials described here are composed of one-dimensional hyperpolarizable chromophores. Future work will involve ionic chromophores of higher dimensionality to further investigate this new engineering strategy for NLO-active crystals.

Acknowledgment. Work at Laboratoire de Cristallographie, CNRS, Grenoble was sponsored by the Groupement de Recherche, Matériaux pour l'Optique Nonlinéaire (no. 1181), CNRS. Cyril Bourgogne is thanked for help in the calculations using MSI software. C.C.E., on leave from the Department of Chemical Engineering and Materials Science, University of Minnesota, acknowledges support from a National Science Foundation Graduate Fellowship. C.C.E. would also thanks Laurence Oswald for performing many of the Kurtz and Perry powder tests and Christopher Yip for helpful discussions.

Supporting Information Available: Final atomic coordinates and temperature factors for DMAPNP2 and PyNP (9 pages); tables of structure factors (13 pages). Ordering information is given on any current masthead page.

CM970618G

---

(39) Huang, K.-S.; Britton, D.; Etter, M.; Byrn, S. R. *J. Mater. Chem.* **1997**, *7*, 713.