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2-cyclooctylamino-5-nitropyridine, a new nonlinear optical crystal with orthorhombic symmetry

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A new nonlinear optical crystal 2-cyclooctylamino-5-nitropyridine (COANP) with point group symmetry mm2 has been grown by a temperature difference solution growth technique. Its linear and nonlinear optical properties have been investigated. The refractive indices $n_a = 1.702$, $n_b = 1.847$, and $n_c = 1.681$ ($\lambda = 550$ nm) and the nonlinear optical susceptibilities d_{31} and d_{33} ($\lambda_\omega = 1.06\,\mu$m) have been determined. Type I phase matching for Nd:YAG lasers ($\lambda = 1.06\,\mu$m) has been demonstrated for the configuration using a combination of d_{31} and d_{32} by angle tuning. A peak efficiency $\eta = P_{2\omega}/P_\omega = 3.6\%$ has been observed with a 0.90-mm-thick crystal and a fundamental power $P_\omega = 560$ W.

Nonlinear optical crystals appear very attractive for applications in image processing and optical communication. In recent years the interest in using organic crystals with charge correlated and highly delocalized π-electron states (e.g., nitroanilines with donor and acceptor substitution at parapositions) has increased considerably, since very large nonlinear optical susceptibilities have been measured in some of the materials[1–3] which make them attractive for future cw laser applications. In addition, some of the nonlinear optical molecular crystals can be prepared in the form of thin-film layers,[4] grooves, capillaries, or crystal-cored optical fibers[5] which make them particularly interesting for guided wave nonlinear optics.[6]

In this letter we report on the growth and properties of 2-cyclooctylamino-5-nitropyridine (COANP), a new nonlinear optical crystal which has orthorhombic point group symmetry (mm2), large birefringence, and nonlinear optical susceptibilities. It will be shown that these properties make COANP a very interesting material for type I phase-matched frequency doubling or sum-frequency generation.

COANP is an amphiphilic molecule. The neutral part is formed by the octyl ring and the polar part by the nitropyridine; see Fig. 1. Second-harmonic tests on powders indicated that the material has a noncentrosymmetric structure and has large nonlinear susceptibility (efficiency 50 times larger than urea).

The material was synthesized by reacting 2-chloro-5 nitropyridine, N-methylpyrrolidinone, triethylamine, and cyclooctylamine in a round-bottom flask with a reflux condensor and a nitrogen bubbler. After cooling, ethylacetate and water were added, the pH was adjusted to 5.0, and the separated organic phase was washed and concentrated to dryness after adsorption on silica gel. An unidentified red by-product was separated by means of elution in a slow gradient of ethylacetate in hexane (0–10%) on a silica gel column. COANP from the middle chromatography fractions was recrystallized twice from a 4:1 isooctane/toluene mixture. The purified end product was checked by means of thermal analysis, elementary microanalysis, infrared (IR), nuclear magnetic resonance (NMR), and mass spectroscopy.

COANP exhibits an unusual solidification behavior upon cooling from its melt and first crystals had to be prepared by solution growth. Solubility versus temperature plots determined in ethyl acetate and acetonitrile revealed suitable solubility values with positive temperature coefficients for the application of a temperature difference procedure of solution growth based on spontaneous nucleation. Saturated solutions were prepared at room temperature and were placed in closed glass tubes with a quadratic cross section with a sufficient amount of starting powder at the bottom acting as feed. The tubes were placed in an inclined position into a temperature field enforcing thermal convection with spontaneous nucleation in the cold parts of the system. Details of the procedure are described in Ref. 7. Crystals for a first assessment of nonlinear optical properties, shown in Fig. 2, were grown in about a week's time after the growth system had reached a quasisteady state, in which the feed material is transported under constant supersaturation to the crystal nuclei formed in the cold part.

The structure of COANP was solved by single-crystal x-ray diffraction. Computations were performed by means of the X-RAY system (Stewart *et al.*[8]) and figures drawn with the help of the ORTEP program.[9] The complete resolution of the structure was obtained from the use of direct methods (MULTAN).[10] Parameters relevant to the measurements and calculations are summarized in Table I.

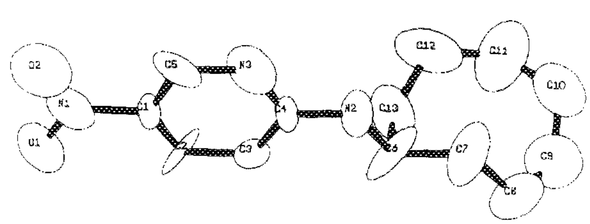

FIG. 1. ORTEP of a single molecule of COANP with 50% thermal ellipsoids.

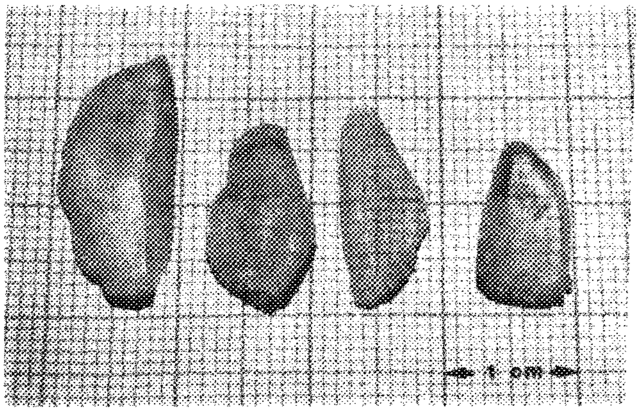

FIG. 2. COANP crystals grown from ethylacetate and acetonitrile.

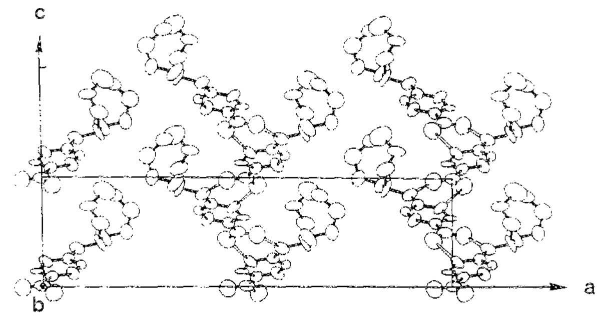

FIG. 3. Projection of the COANP structure along the b axis. The hydrogen bond N(2)–O(2) and the noncovalent N(3)–O(1) bonding are schematically represented by open bonds between the N and O atoms.

The amphiphilic property gives rise to the packing of the molecules as shown in Fig. 3. In the layers perpendicular to the a axis the polar and neutral parts alternate. Each layer is formed by a series of infinite chains linked by hydrogen bonds. The chains are parallel to the $(\mathbf{b}+\mathbf{c})$ direction or alternatively to the symmetry equivalent $(-\mathbf{b}+\mathbf{c})$ direction. The oxygen atoms of the nitro group are directed towards the nitrogen atoms N(2) to form a hydrogen bond with a N...O distance of 2.9 Å. The N(3)–O(1) interaction is weakly bonding, but it is not a hydrogen bond. Its N...O distance is 3.9 Å.

The optical and nonlinear optical properties of COANP were observed on plates of dimensions up to $9\times4.5\times1.3$ mm^3 oriented along the crystallographic c, b, and a direction respectively, cut with a 0.22-mm-diam diamond wire saw, and polished with diamond paste (0–3 μm) in Vaseline. The samples were of optical quality showing homogeneous extinction over the whole crystal surface. Figure 4 shows the absorption spectrum of a 0.90-mm-thick crystal for light propagating along the a axis polarized parallel to the bc plane. The optical transmission range extends from 470 to 1500 nm (50% points), with some absorption bands near 1200 and 1400 nm with a minimum absorption constant $\alpha < 1$ cm^{-1} for $\lambda \approx 1350$ nm. The refractive index was measured by means of the immersion technique,[11] n_b using a micro-interferometric technique.[12] n_a was determined from the measured value of the optical angle $V = (22.7 \pm 1.0)$ degrees ($\lambda = 547$ nm) with respect to the b axis. The refractive index $n_a = 1.702$ was determined from the optic angle V and $n_b = 1.847$, $n_c = 1.681$ by using the relation[13]

$$\sin^2 V = \frac{1/n_b^2 - 1/n_a^2}{1/n_b^2 - 1/n_c^2}. \quad (1)$$

The results are shown in Table I. Since $n_c < n_a < n_b$, COANP is an optically biaxial crystal with the optical axes lying in the bc plane.

For crystals belonging to point group mm2, the second-harmonic polarization P is given by[14]

$$\begin{aligned} P_1 &= 2\epsilon_0 d_{15} E_1 E_3 , \\ P_2 &= 2\epsilon_0 d_{24} E_2 E_3 , \\ P_3 &= \epsilon_0 (d_{31} E_1^2 + d_{32} E_2^2 + d_{33} E_3^2) , \end{aligned} \quad (2)$$

where d_{ij} are the elements of the second-order polarizability tensor and E_1, E_2, and E_3 the electric field components of the fundamental wave (frequency ω) along the crystallographic a, b, and c axis, respectively.

For the ideal case of lightly focused monochromatic

TABLE I. Optical, nonlinear optical, and structural data of COANP crystals.

Formula	$C_{13}H_{19}N_3O_2$ ($M = 249.32$)
Density	$\rho = 1.24$ g/cm^3
Melting point	$T_m = 70.9$ °C
Space group symmetry	$Pca2_1$ ($Z = 4$)
(point group)	(mm2)
Unit cell	$a = 26.281(5)$ Å
	$b = 6.655(1)$ Å
	$c = 7.630(1)$ Å
	$v = 1334.5(6)$ Å^3
Refractive indices ($\lambda = 550$ nm)	$n_a = 1.702 \pm 0.010$
	$n_b = 1.847 \pm 0.006$
	$n_c = 1.681 \pm 0.004$
Nonlinear optical susceptibilities	$d_{33} = (10 \pm 2)$ pm/V
	$d_{31} = (15 \pm 2)$ pm/V
	$d_{\rm eff}^{\rm PM} = d_{32}\cos^2\theta_1 + d_{31}\sin^2\theta_1 = 24$ pm/V
	$[\theta_1 = (26.4 \pm 0.2)°]$

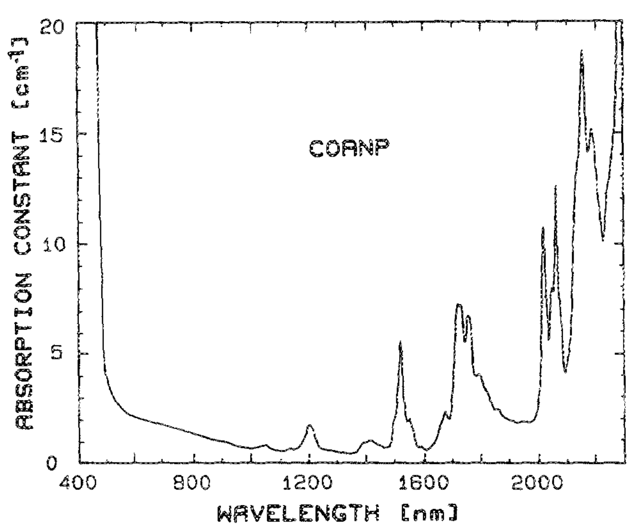

FIG. 4. Optical absorption spectrum of a COANP crystal (thickness $d = 0.90$ mm).

Gaussian beams, the second-harmonic intensity, neglecting pump depletion, is given by[14]

$$P(2\omega) = \frac{2\omega^2 d_{\rm eff}^2 l^2}{\pi\epsilon_0 c^3 n_\omega^2 n_{2\omega} w_0^2} P^2(\omega)\, {\rm sinc}^2\left(\frac{\Delta k l}{2}\right), \qquad (3)$$

where we denote $(\sin x)/x$ by ${\rm sinc}(x)$, l is the crystal length, w_0 is the beam waist, $d_{\rm eff}$ the effective nonlinear optical susceptibility, and $\Delta K = K_2 - 2K_1$ is the phase mismatch between the fundamental and second-harmonic waves with wave vectors K_1 and K_2, respectively.

For COANP with the refractive indices $n_c < n_a < n_b$ reported above we see that phase-matched second-harmonic generation ($\Delta K = 0$) is possible for the configurations using the nonlinear optical polarizabilities d_{31} and d_{32} (type I phase matching) but not for d_{23} and d_{15} (type II phase matching). The nonlinear optical susceptibilities d_{33} and d_{31} of COANP crystals were measured by using the Maker fringe method.[15] The light source was a Q-switched Nd:YAG laser operating at $\lambda = 1064$ nm (Spectra Physics 3000, peak power $P_\omega \leqslant 2.5$ kW, pulse duration $\tau = 250$ ns, repetition rate 400 Hz). The peak power incident on the crystal was 0.6 kW; the beam waist $w_0 = 0.12$ mm (power density $I = 1.3$ MW/cm^2). The second-harmonic power was detected by a photomultiplier, gated integrator system, and for the reference we used a quartz plate ($d_{11} = 0.4$ pm/V). Details of the computer-controlled experimental setup have been reported in Ref. 16. For the measurement we used polished plates oriented perpendicular to the b axis (thickness: 1.27 and 1.24 mm, respectively).

The nonlinear optical susceptibilities $d_{33} = 10 \pm 2$ pm/V and $d_{31} = 15 \pm 2$ pm/V were determined from the envelope of the fringe patterns. The coherence lengths calculated from our measured refractive index data by using

$$l_c = \frac{\lambda}{4(n^{2\omega} - n^{\omega})} \qquad (4)$$

were $l_c^{31} = 5.8\,\mu$m and $l_c^{33} = 3.5\,\mu$m. From the separation of fringe minima somewhat smaller values were determined, indicating some regions of optical inhomogeneities present in the samples.

Angle-tuned phase-matched second-harmonic generation for Nd:YAG lasers ($\lambda = 1.06\,\mu$m) has been observed by rotating an a plate (thickness $d = 0.904$ mm) by an angle $\theta = (48.9 \pm 0.5)^\circ$ around the c axis with respect to the a axis [propagation direction within the crystal $\theta_1 = (26.4 \pm 0.2)^\circ$].

The effective nonlinear susceptibility for this geometry is

$$d_{\rm eff} = d_{32}\cos^2\theta_1 + d_{31}\sin^2\theta_1\,. \qquad (5)$$

For a peak intensity $P_\omega = 560$ W ($P_\omega = 1.2$ MW/cm^2) the generated second-harmonic power was $P_{2\omega} = 20$ W (conversion efficiency 3.6%). Neglecting beam walk-off due to birefringence we estimate from (3) an effective nonlinear susceptibility $d_{\rm eff} = 24$ pm/V. Assuming that d_{32} and d_{31} have the same sign, we get from (5) the nonlinear optical susceptibility $|d_{32}| = 26$ pm/V and, for the case that the two signs are different, $|d_{32}| = 34$ pm/V. The accuracy of these values should, however, not be overestimated since they have been calculated by using a series of parameters of moderate accuracy.

Summarizing our results, COANP crystals of good optical quality having a large nonlinear optical susceptibility were grown. The crystal structure and the linear optical parameters (refractive indices, absorption constant) have been determined, indicating that COANP is a biaxial crystal with point group symmetry mm2. Angle-tuned second-harmonic generation of Nd:YAG laser radiation at $\lambda = 1.06\,\mu$m with a conversion efficiency $\eta = I_{2\omega}/I_\omega = 3.6\%$ (at a power level $P_\omega = 560$ W) has been demonstrated using a 0.9-mm-thick a-crystal plate.

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