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Linear and nonlinear optical properties of substituted pyrrolo[1,2-a]quinolines

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Abstract

Synthesis and characterization of a class of chiral nonlinear optical organic materials, viz. pyrrolo[1,2-a]quinolines with chiral molecular structure, are presented. Both single crystals and crystalline thin films of **1a** have been grown. Structural parameters have been determined by X-ray diffraction. Linear and nonlinear optical properties of the crystals have been analyzed. The transparency range extends into the near-UV-region. The nonlinear coefficients d_{ijk} have been measured by second harmonic generation (SHG) using the Makerfringe and phase match techniques.

1. Introduction

Interest in organic materials is still growing because of their potential use in optical communication, optical switching, frequency conversion etc. The main advantage of organic materials is the possibility to manipulate their optical properties by molecular engineering. Specifically optimization of the nonlinear optical properties of the molecule and elaboration of efficient solid state phases. Organic materials with very large second order nonlinear coefficients d_{ijk} up to more than one order higher than those of LiNbO_3 are known. These high d values are a result of the large molecular hyperpolarizability β caused by the highly delocalised π -electron systems with suitable donor and acceptor groups and of the crystallization in a noncentrosymmetric point group.

In principal the materials may be incorporated in thin crystalline films, however, the crystal orientation with respect to the propagation direction has to be adjusted for optimization of the nonlinear optical process. Another promising approach is the polymerization of the organic material which allows poling in the case of thin film applications.

In spite of the promising aspects of the nonlinear organic materials still extensive research is required on the characterization of their optical properties.

In this paper the first results of the characterization of a new group viz. the pyrrolo[1,2-a]quinolines is described. Of this group the basic molecule and some substituents were synthesized. The crystal structure was analyzed by X-ray diffraction. Both linear and nonlinear optical properties were determined.

2. Synthesis

Molecules possessing an electron donor and acceptor moiety at opposite sides of a long π -conjugated system (D- π -A) in principle have an enhanced molecular hyperpolarizability β [1]. The major disadvantage of these polar molecules is the centrosymmetric crystallization that nullifies the macroscopic nonlinear susceptibility $\chi^{(2)}$. By introducing a chiral group in the molecule the centrosymmetric crystallization is ruled out. Other possibilities are the attachment of a sterically hindering group or introducing another nonconjugated unit with charge separation. The three possibilities are incorporated in the chiral pyrrolo[1,2-a]quinolines **1** and **2** [2] (figure 1).

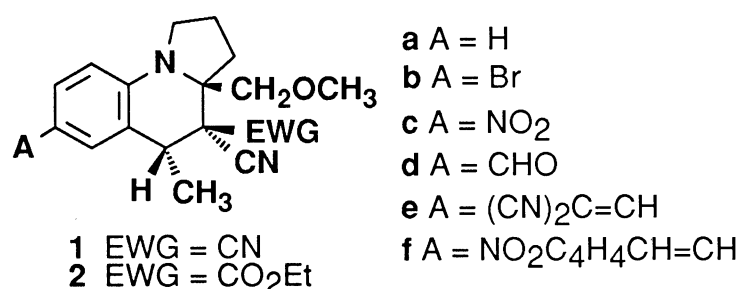


Figure 1: Chiral pyrrolo[1,2-a]quinolines.

The basic chiral pyrrolo[1,2-a]quinoline **1a** was easily obtained in a three step synthesis using the 'tert-amino effect', with self-reproduction of chirality of the newly formed bridgehead carbon atom, for the final, stereo- and regioselective ring closure (figure 2). The *para* electron-withdrawing groups were easily introduced using common reagents and reaction conditions.

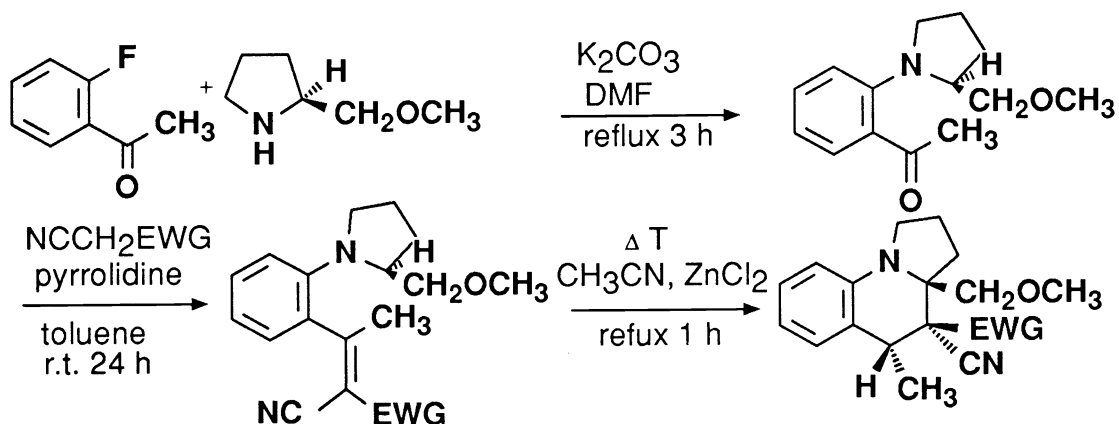


Figure 2: Synthesis of the chiral pyrrolo[1,2-a]quinolines **1a** and **2a**.

The bromo derivative, for example, was obtained as a colorless solid in a 78% yield by refluxing **1a** in tetrachloromethane in the presence of 1 equiv *N*-bromosuccinimide and a catalytic amount of dibenzoylperoxide for 1.5 h. By a Vilsmeier/Haack reaction **1a** or **2a** was converted to the aldehydes **1d** or **2d**, respectively. Subsequent Knoevenagel or Wittig/Horner reaction yielded **1e** or **2e** and **1f** or **2f**, respectively, with a longer π -conjugated system.

3. Sample preparation

Although single crystals of **1a** with dimensions up to 5 mm were obtained from the solution, these could not be processed by optical techniques. Crystals of optical quality were obtained by melting some material between two amorphous quartz plates separated by spacers. Subsequently the melt was cooled down by ~ 0.5 °C/h. To prevent degradation of the material at high temperatures these processes have to take place in an oxygen depleted atmosphere e.g. under argon atmosphere. Single crystalline platelets of ~ 0.5 cm² and thickness of 100–500 μ m were obtained as could be observed between crossed polarizers.

4. Characterization

4.1 X-ray measurements

The crystal point group and the molecular orientation within the crystal lattice were determined by X-ray diffraction.

Crystals grown from the solution and recrystallized thin layers displayed the same crystal structure. The orientation of the crystal *a*, *b* and *c* axes relative to the orientation of the quartz substrate was determined. Basic molecule **1a** crystallizes in the orthorhombic space group $P2_12_12_1$ (point group 222, like e.g. POM). with lattice parameters $a = 0.95$, $b = 0.96$ and $c = 1.68$ nm. If the molecule crystallizes in the optimum orientation nonvanishing *d* coefficients can efficiently be approached by 19% [1]. The bromo derivative **1b** crystallizes in the more favorable monoclinic space group $P2_1$ (point group 2, like e.g. NPP and MAP). The angle between the charge transfer axis and the twofold crystal axis is 60° which is very close to the optimum angle of 54.74° [1] and involves near optimum contribution (38%) of the nonzero *d* coefficients.

4.2 Linear optical properties

Since **1a** is orthorhombic, point group 222, the crystal axes *a*, *b* and *c* correspond directly to the principal dielectric axes. The optical transmission spectrum of **1a** was measured. The transparency range extends into the UV-region to 330 nm (figure 3).

Refractive indices were determined using a Michelson interferometer. The procedure involved counting of the number *N* of interference fringes produced by rotation of the crystal sample and by a similar rotation of an empty sample holder. The difference in the number of fringes counted can be attributed to the crystal platelet. For the refractive index it was derived,

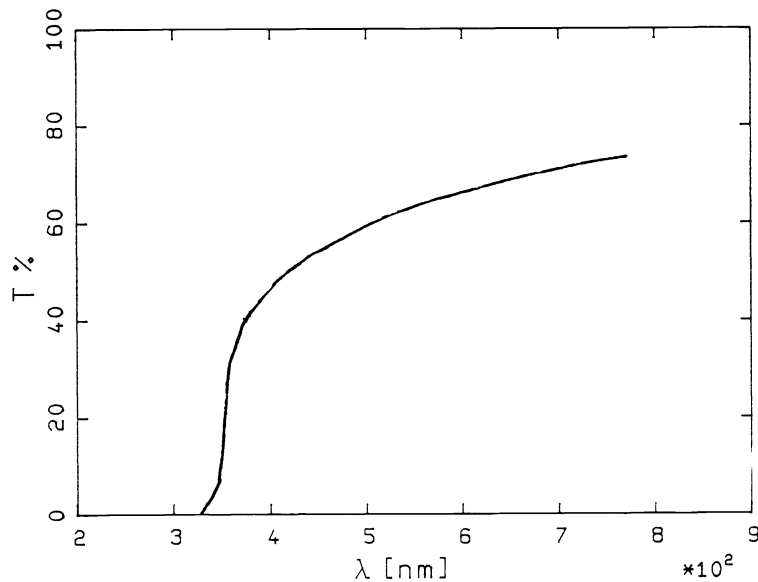


Figure 3: Transmission threshold of 1a.

$$n - 1 = \frac{\left(\frac{N\lambda}{2d}\right)^2 + 2\left(\frac{N\lambda}{2d}\right)\cos\theta}{2\left(1 - \cos\theta - \frac{N\lambda}{2d}\right)} \quad (1)$$

with, θ : arc of rotation
 d : sample thickness

Measurements were done in a crystalline area in which the crystal b and c axes were within 2% parallel to the quartz surfaces. Thus it was found at $\lambda = 632.8$ nm,

$$\begin{aligned} n_b &= 1.65 \pm 0.02 \\ n_c &= 1.56 \pm 0.02 \\ \Delta n &= 0.09 \pm 0.01 \end{aligned}$$

Due to a possible slight difference between the two sample holders a small systematic error in the measured value of the refractive indices might have been occurred. Improvement of the results is still possible by using thinner sample plates relative to the thickness of the crystal platelet. Similar measurements at 854 nm showed the dispersion as expected from absorption at $\lambda < 330$ nm to be very small, especially compared to the birefringence.

Observation of crystal axes between crossed polarizers indicated the value of n_a to be very close to n_b .

4.3 Nonlinear optical properties

4.3.1 Theory

The nonlinear optical properties of the basic molecule **1a** were investigated. As **1a** crystallizes in the symmetry class 222 the only remaining nonlinear coefficients are d_{14} , d_{25} and d_{36} . Taking into account Kleinmann's symmetry which is valid because the absorption threshold is at 330 nm, $d = d_{14} = d_{25} = d_{36}$. Thus,

$$\begin{aligned} \mathcal{P}_x &= 2 \cdot d \cdot E_y \cdot E_z \\ \mathcal{P}_y &= 2 \cdot d \cdot E_x \cdot E_z \\ \mathcal{P}_z &= 2 \cdot d \cdot E_x \cdot E_y \end{aligned} \quad (2)$$

Due to the symmetry only combination terms of the fundamental radiation contribute to the generated polarization. Thus SHG can only be accomplished with the fundamental polarization in a direction such that the projection along two optical axes is nonzero. Consequently if the fundamental polarization is confined to one optical plane the effective nonlinear coefficient d_{eff} takes the form,

$$d_{\text{eff}} = \sin(\alpha) \cdot \cos(\alpha) \cdot d \quad (3)$$

with α : angle of the polarization direction with respect to one of the axes.

Thus the maximum obtainable value of d_{eff} is $d_{\text{eff}} = d/2$ at 45° .

The generated second harmonic power in case of a parallel beam is given by [3].

$$P_x^{(2\omega)} = 2 \left(\frac{\mu_0}{\epsilon_0} \right)^{\frac{3}{2}} \frac{\omega^2}{n^3} d^2 P_y^{(\omega)} P_z^{(\omega)} \frac{L^2}{A} \text{sinc}^2(\Delta k \cdot L/2) \quad (4)$$

with, L: crystal length;
A: area of interaction;
 $\Delta k = k^{(2\omega)} - 2 k^{(\omega)}$

The second harmonic power is effectively generated over the coherence length $l_c = 2\pi/\Delta k$. In case $l_c \ll L$ Makerfringes [4] are observed when varying the argument of the sinc-function which in our case is achieved by rotating the sample in the laser beam. The coherence length can be determined from the period of the Makerfringes while the amplitude of the Makerfringes is a direct measure for the d coefficient. In case $l_c \gg L$ so called phase matching occurs and second harmonic radiation is now generated over the full length of the crystal.

4.3.2 Experimental set-up

As a source of fundamental radiation a 1.064 μm pulsed Nd:YAG laser (Spectra Physics DCR 11 3G, 10 Hz, $T_{\text{pulse}} \approx 10$ ns) was used. The peak energy level was attenuated to ~ 10 μJ by a CuSO_4 solution. Power and linear polarization of the incoming wave could be adjusted by use of a Soleil-Babinet compensator in combination with a Glan-Taylor polarizer. The sample was placed on a crystal manipulation stage which was placed on a computer controlled rotation stage ($\Delta\theta = 0.01^\circ$) thus allowing rotation about the three optical axes. The components of the generated second harmonic radiation were analyzed by use of a second Glan-Taylor polarizer. Separation of fundamental and harmonic radiation was achieved by use of a Pellin-Broca prism in combination with a suitable filter set (e.g. Schott KG5). As a detector for the harmonic radiation a photo multiplier tube (PMT, Hamamatsu R928) was used. Care was taken to keep the signal levels within the linear range of the PMT. The signal from the PMT was amplified by an Ortec fast pre-amplifier and was fed into a boxcar averager (EG&G 4121B).

In order to determine absolute d values we have used quartz as a reference material. To this end the organic sample was interchanged with a 1 mm thick crystalline α -quartz plate and the ratio of the second harmonic signal amplitudes for both samples were measured. The coherence length of quartz at $\lambda = 1.064$ μm was found to be $l_c = 40.9$ μm which corresponds to the literature value. Taking into account the coherence length effect the pyrrolo[1,2-*a*]quinoline 1a d value can be determined relative to the quartz $d_{11} = 0.50(8)$ pm/V nonlinear coefficient.

4.3.3 Results

A typical Makerfringe measurement is presented in figure 4a which was performed at the same sample ($d = 210 \pm 5$ μm) at which the refractive indices were determined. The crystal was rotated around the b -axis along which the fundamental radiation was polarized as well. The second harmonic radiation was analyzed in the ac -plane. It can be observed that the second harmonic signal is about zero for propagation along the a -axis ($\theta = 0^\circ$) as expected from theory because the field component of the $E(\omega)$ vector along the a -axis is zero. A signal increase is observed for rotation away from the a -axis because a field component along the a -axis becomes possible. This can only be obtained if the polarization of the fundamental wave is changed during propagation through the sample. The asymmetry can be attributed to the fact that the optical axes deviate a few degrees from the sample plane.

A fit (figure 4b) to the Makerfringes observed shows reasonable agreement except for the asymmetry. From this fit it is found: $\Delta n = 0.045$ and $l_c = 12$ μm . Similar measurements with other polarization directions and with other samples were performed. From all of these measurements it is consistently deduced,

$$d_{\text{eff}}/d_{11}(\text{SiO}_2) = 2.0 \pm 0.1$$

At a specific propagation direction through the crystal phase matching is observed (figure 5) as could be expected from the fact that the birefringence is larger than the dispersion. Maximum signal is obtained for an angle of 45° between fundamental and second harmonic polarization.

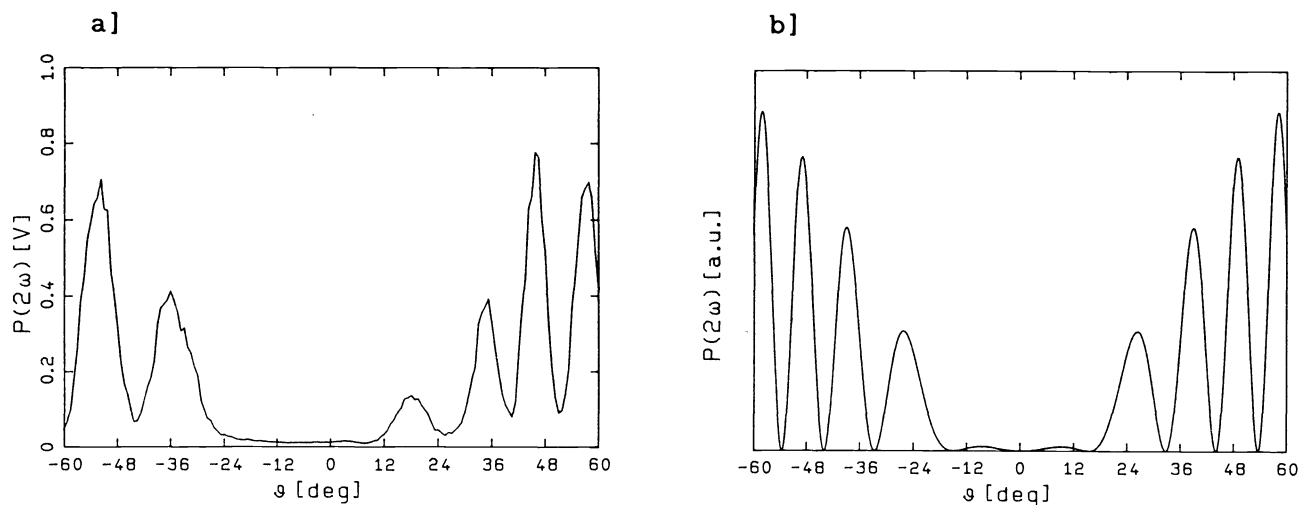


Figure 4a : Makerfringes as generated in a 0.210 mm thick crystal of 1a (at perpendicular incidence $\vartheta = 0^\circ$).
 b : Theoretical Makerfringes for $l_c = 12 \mu\text{m}$.

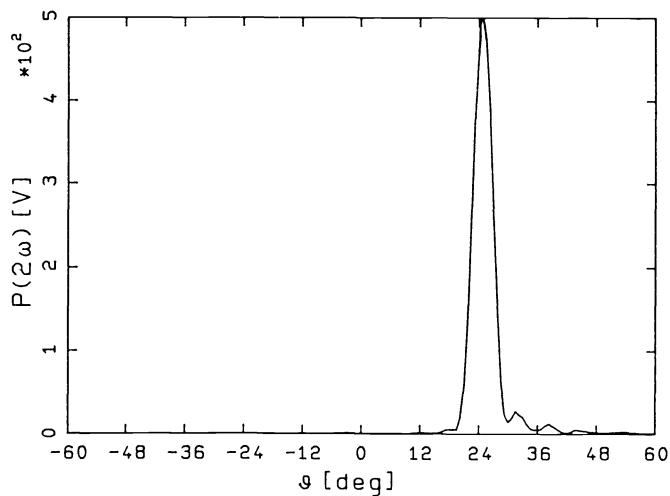


Figure 5: Phase match as observed in a 0.210 mm thick crystal of 1a.

From the phase match amplitude it can be deduced, $d_{\text{eff}}/d_{11}(\text{SiO}_2) \cong 2$ which is consistent with the result obtained from the Makerfringe technique. Therefore we may conclude, $d_{\text{eff}} = 1.0 \pm 0.1 \text{ pm/V}$ and so,

$$d = d_{14} = d_{25} = d_{36} = 2.0 \pm 0.2 \text{ pm/V}$$

5. Conclusions and discussion

Considering the transparency into the UV-region and the possibilities of phase matching the pyrrolo[1,2-a]quinolines might be useful for frequency doubling of diode lasers emitting in the red or the near infrared part of the spectrum. The possibility to fabricate thin crystalline layers allows incorporation in a waveguide structure [5].

We expect to be able to control the acentric crystallization for these large dipoles by carefully selecting the proper substituents.

Introductory measurements on 1b have shown that the nonlinear coefficients of this material are considerably larger than those of 1a. Even larger nonlinear coefficients are expected (if crystallization in an efficient condensed phase takes place) for component 1c because it has a larger hyperpolarizability β than 1a and 1b.

The ester group of the recently synthesized 2a could effectively be reduced to an alcohol and substituted with polymerizable and/or long aliphatic chains. This opens the possibility to control the macroscopic orientation even further.

Possibilities to fabricate thin polyester layers of component 2 will be investigated.

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