Quinolinium derived acentric single crystals

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Abstract

Derivatives of quinolinium-iodide exhibit a second-order nonlinear optical (NLO) response in their crystalline form. Here we present single crystal growth of three quinolinium-derivatives by the hanging drop method and their characterization by X-ray diffraction (XRD). These latter provided a rationale for the NLO response of these materials, allowing an application of general theoretical approaches, connecting second harmonic generation (SHG) response with structural parameters. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A number of fundamental and applied issues are linked to the field of crystalline engineering of organic materials with enhanced nonlinear quadratic properties.[1] Single crystals containing hyperpolarizable chromophores which are packed in a noncentrosymmetric space group are among the most promising bulk materials for nonlinear optical applications.[2] They are widely studied because of their large nonlinear optical (NLO) coefficients and their maximized chromophore number densities and orientation temporal stability, as compared with poled polymers.[3] The NLO response arises from the hyperpolarizable constituent chromophores, which are macroscopically aligned in a polar manner and thus the response of the individual molecules adds constructively.

Organic materials exhibit larger nonlinear optical coefficients and also have the advantage of higher synthetic flexibility. Organic synthesis allows employment of a new level of molecular design in which molecular assemblies are controlled by characteristics of individual substituent groups, to optimize the nonlinear optical properties. Realization of bulk materials having a large macroscopic second-order nonlinear optical response, $\chi^{(2)}$, requires not only molecular constituents with a large microscopic second-order molecular susceptibility, β_{ijk}, but also macroscopic noncentrosymmetric packing of the assemblies, aligned in a manner that the individual

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tensor components of β_{ijk} add constructively.[4] In this contribution, we report on single crystal growth of three quinolinium-derivatives by the hanging drop method and on their crystallographic packing.

2. Experimental

The synthesis of all investigated materials were carried out as described previously,[5] except in the case of 6-dimethylamino quinoline, which we did not obtain in a considerable amount due to some practical limitations of the Skraup synthesis.[6] Single crystal growth of the 6-methylquinolium iodide **3** and bulk nonlinear SHG response for **1-3** were previously reported.[7] The SHG response obtained from the organic salts was compared to urea powder of similar particle size. Although SHG efficiency cannot provide the average nonlinearity coefficient unless the particle size and coherence length are known,[8] it can however serve for ranking these NLO materials. The especial feature of optical spectra of quinolinium derivatives is their transparency in the blue the absorption being cut off below 400 nm.[7] This property is of practical importance for NLO usage including diode laser applications with $\lambda \approx 800$ nm.

R=OMe (**1**), H (**2**), Me (**3**)
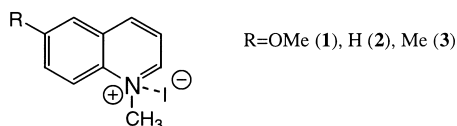
Crystals of 6-methyl derivative **3** were obtained by the traditional 'batch' method by slow evaporation of a water saturated solution. Since we did not succeed in the single crystal growth of the rest of the derivatives by this method, the alternative crystallization approach has been applied. Crystals of **1** and **2** were grown by the hanging drop vapor diffusion method, which is widely used for crystallization of biological macromolecules. This method uses the vapor phase to bring about equilibration and is very well suited for screening a large number of conditions when only a small quantity of material is available. The procedure, known as the 'factoral method' allows a rational approach to screening potential crystallization conditions.[9]

We obtained a few crystal forms for both derivatives, but only one form for each of them was useful for crystallographic analysis. Crystals of derivative **1**[10] grew in 10 microliter drops, which contained 5 microliter of 15 mg/microliter sample, dissolved in water and 5 microliter of reservoir solution. The reservoir contained: 0.2 M zinc acetate, 0.1 sodium cacodilate pH = 6.5, 18% w/v PEG 8000. Crystals of derivative **2**[11] grew in 10 microliter drops, which contained 5 microliter of 40 mg/ml, dissolved in water and 5 microliter of reservoir solution. The reservoir contained 2.0 M ammonium sulfate.

3. Results and discussion

The crystallographic data and bulk nonlinear SHG response are summarized in Table 1. Crystal structures of **1** and **2** are shown in Figs. 1 and 2. Derivative **2** crystallized only in the presence of ZnI_4 salt. However, the measurement of $\Theta/2\Theta$ X-ray powder diffraction spectra with

Table 1

Single crystal X-ray data and SHG efficiency for quinolinium derivatives

Material, (R)	space group	a, b, c, Å	V, Å	z	SHG
1 (CH_3O)	$Pna2_1$	10.706; 9.910; 10.591	1123.7	4	0.84
2 (H)	C2/c	13.681; 10.535; 17.628	2529.3	4	1.67
3 (CH_3)	$P2_1/c$	17.083; 7.250; 19.581	2346	8*	3×10^{-4}

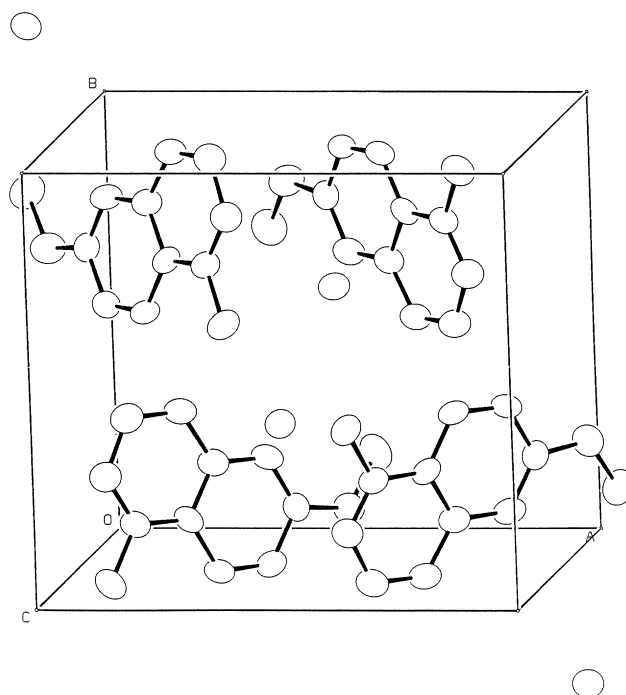*There are 2 independent molecules in cell

Figure 1. Crystal structure of 6-methoxy (*N*-methyl-quinolinium iodide) **1**

following crystallographic parameters calculation[12,13] reveals the same group *P*2/c symmetry of **2** (**H**) derivative with ZnI_4^- and I^- counter-ions.

Calculation of the elemental unit cell shows that all the salts studied (**1–3**) have a different symmetry group: from the orthorhombic *P*na2_1 for **1** and *P*2$_1$/c for **3** to the monoclinic symmetry group C2/c for **2**. There is remarkable correlation of crystallographic parameters with molecular
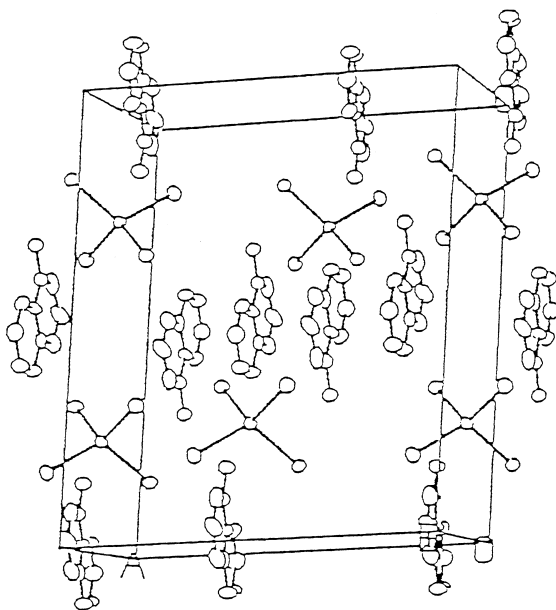
Figure 2. Crystal structure of 6-H (*N*-methyl-quinolinium iodide) **2**

hyperpolarizability of **1**–**3**: the large material molecular hyperpolarizability, the dipole–dipole interaction, leads to more centrosymmetric structure. The bulk SHG response for materials **1**–**3** change in a range $1–10^{-4}$.[7] Our study supports the well-established fact that solid-state packing is responsible for SHG: a more non-centrosymmetric structure leads to a higher SHG response. The low SHG response exhibited by **3** could be explained by its special structure: there are two independent molecules in a unit cell, which are almost parallel to each other.

For SHG application, materials have to exhibit high hyperpolarizability combined with a noncentrosymmetric structure. However, higher molecular polarizability leads to intensive dipole–dipole interactions. The chromophores tend to compensate the total dipole moment by packing in more centrosymmetric structures, that in turn, are unfavorable for NLO application.[14] Less molecule polarizability increases the possibility of noncentrosymmetric packing. For every organic compound the chromophore packing and resulting SHG response seems to be the result of close interplay of energy and entropy factors. In this context it is obvious that the counter-ions play an extremely important structural role in possible screening of intermolecular interactions or in balancing and defeating the weaker dipole–dipole interactions by stronger ionic interactions which would not favor centro-symmetry.[15,16c] Starting with the engineering of the first quasi-optimal crystalline structure for quadratic NLO,[17] namely *N*-(4-nitrophenyl)-(L)-prolinol, the importance of the negative ion type in a strongly polarized organic molecule was emphasized within the combination of organic and inorganic materials in an asymmetric crystalline structure.[16] It was demonstrated that the dihydrogen phosphate anion can be employed to enhance the NLO efficiency of the common organic molecule 2-amino-5-nitropyridine.[16] This allows the aforementioned tendency to format the centric structure due to the ionic interaction to be overcome. In the quinolinium derived materials the role of the counter-ion can be illustrated on substitution of I^- for Br^- in the nitro-derivative ($R = NO_2$). This modification changes the monoclinic symmetry group $P2_1/c$[7] of the I^- derivative to orthorhombic $Pna2_1$[18] lattice for the quinolinium derivative with Br^- anion.

A possible modeling approach for this structural-dependent SHG may be developed considering the dependence of the crystallographic parameters with the intramolecular charge transfer axis. Supposing the existence of this dependence, the approach developed in Ref. 16 by Zyss et al. can therefore be applied, following optimization of nonlinear tensor coefficients. In conclusion, we introduce a crystal structure for a new family of quinolinium-derived acentric materials for second order NLO applications and discuss symmetry considerations in those NLO class of materials. The practical usage of **1**–**3** for NLO can be achieved by a scaling-up of hanging drop growth conditions to conventional crystallization methods. Along with a quality model connecting molecular properties, macroscopic packing and SHG response, we also provide data for the following modeling that can result in a predictable dependence of SHG response from packing parameters. The crystal growth of quinolinium derived acentric single crystals illustrate the unexplored potential of the hanging drop method for elucidating structure–property dependencies in organic materials for NLO.

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10. The crystallographic structure of **1** (Methoxy) $(C_{11}H_{12}NO)^{+}$*I^{-} space group: $Pna2_1$ where *a*, *b*, *c* are 10.706 Å; 9.910 Å; 10.591 Å, respectively; $V = 1123.7$ Å^3, $z = 4$, $\mu(MoK\alpha) = 27.87$ cm^{-1}; $\rho_{calcd} = 1.78$ g×cm^{-3}, no. of unique reflections: 1903, no of reflections with $I \geq 3\sigma_I$: 1355. The data were measured on a PW1100/20 Philips four-circle computer-controlled diffractometer. MoKα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $11 \leq \Theta \leq 3°$. Intensity data were collected using the ω-2Θ technique to a maximum 2Θ of 60°. The scan width, $\Delta\omega$, for each reflection was 1.00±0.35 tan Θ with a scan speed of 3.0°/min. Background measurements were made for a total 10 sec at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variation in intensities were found. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by the results of the SHELXS-86 direct method analysis. After several cycles of refinement the position of hydrogen atoms were calculated, and added to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma w(|f_0|-|f_c|)^2$. A final difference Fourier synthesis map showed several peak less than 0.87 e/Å^3 scattered about the unit cell without a significant feature. The discrepancy indices, $R = \Sigma(|f_0|-|f_c|)/\Sigma|F_0|$ and $R_w = [\Sigma w(|f_0|-|F_c|)^2/\Sigma w|f_0|^2]^{1/2}$ are 0.033 and 0.045, respectively. Complete details of the structure investigation were sent to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21 EZ, England.
11. The crystallographic structure of **2** (H) $(C_{10}H_{10}N)_2^{+}$*ZnI_4^{2-}: space group: $C2/c$ where *a*, *b*, *c* are 13.68 Å; 10.535 Å; 17.628 Å, respectively, and $\beta = 95.43°$; $V = 2529.3$ Å^3; $z = 4$; $\mu(MoK\alpha) = 58.36$ cm^{-1}; $\rho_{calcd} = 2.26$ g×cm^{-3}, no. of unique reflections: 2365, no of reflections with $I \geq 3\sigma_I$: 1388. The data were measured on a PW1100/20 Philips four-circle computer-controlled diffractometer. MoKα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 23 centered reflections in the range of $11 \leq \Theta \leq 15°$. Intensity data were collected using the ω-2Θ technique to a

maximum 2Θ of $50°$. The scan width, $\Delta\omega$, for each reflection was $1.00\pm0.35 \tan \Theta$ with a scan speed of $3.0°/$min. Background measurements were made for a total 10 seconds at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variation in intensities were found. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by the results of the SHELXS-86 direct method analysis. After several cycles of refinement the position of hydrogen atoms were calculated, and added to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma w(|f_0|-|f_c|)^2$. A final difference Fourier synthesis map showed several peak less than 1.3 $e/\text{Å}^3$ scattered about the unit cell without a significant feature. The discrepancy indices, $R = \Sigma(|f_0|-|f_c|)/\Sigma|F_0|$ and $R_w = [\Sigma w(|f_0|-|F_c|)^2/\Sigma w|f_0|^2]^{1/2}$ are 0.033 and 0.045, respectively. Complete details of the structure investigation were sent to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21 EZ, England.

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