

Synthesis and crystal structure of a new stilbazolium salt with large second-order optical nonlinearity

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The novel stilbazolium salt 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium 2-naphthalenesulfonate (DSNS), has been synthesized and small single crystals were grown. The crystal structure of the resulting crystals was determined *via* X-ray crystallography and it was found to be non-centrosymmetric with the chromophores aligned perfectly parallel. The Kurtz powder test of the crystals at $\lambda = 1.9 \mu\text{m}$ reveals that they have around 50 percent higher second-order nonlinearity than the presently best organic nonlinear optical crystal 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium tosylate (DAST).

Introduction

Organic materials with high second order optical nonlinearities have attracted a lot of attention because of their potential for optical frequency conversion, THz generation, electro-optical and integrated optics applications.¹ High nonlinearities and the almost purely electronic origin of the nonlinear effects in organics with short response times make them highly superior to their inorganic counterparts.¹ Ionic organic crystals are of special interest due to their chemical, mechanical and physical properties such as the orientation of ionic chromophores that can be arranged simply by changing the counter-ions, and typically larger macroscopic second-order nonlinear susceptibilities compared to non-ionic materials.^{2–4} From these materials, DAST (4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium tosylate) is the one most investigated^{2,3} and also the one presenting the highest electro-optical and nonlinear optical figures of merit among the presently available bulk organic crystals.¹ However, the theoretical limits for the macroscopic second-order nonlinearities in organic crystals are still far from being achieved.¹ In addition, the growth of high quality nonlinear optical bulk or thin film organic crystals such as DAST remains a big challenge.^{5,6} Much effort has been spent in the design of new molecules with high molecular nonlinearities that would promote a better non-centrosymmetric crystal packing and enable an easier bulk growth of crystals with various degrees of success.^{4,7–9} Here we report the synthesis and crystal structure of a new stilbazolium salt with powder second harmonic generation (SHG) efficiency around 1.5 times that of DAST. This is, to the best of our knowledge, the first time that a stilbazolium derivative with an even higher macroscopic second-order nonlinearity than DAST has been synthesized.

Results and discussion

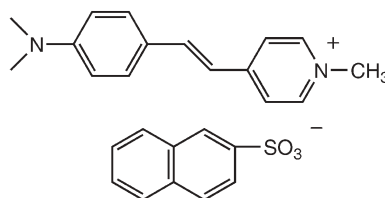
Synthesis

The chemical structure of DSNS (4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium 2-naphthalenesulfonate) is shown in Scheme 1.

This material was prepared by the metathesization of 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium iodide¹⁰ with the sodium salt of the 2-naphthalenesulfonic acid. DSNS was then recrystallized from methanol to get high purity material for crystal growth.

Crystal growth

The crystal growth method based on melt is not suitable for DSNS because its melting point is higher than 300 °C. Therefore the slow cooling and slow evaporation techniques were adapted for the growth. It was carried out with four different solvents: methanol, water, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The solubility in the first three solvents is low and thus the growth of the crystal was difficult and slow, yielding brown–purple polycrystals and small needles. DMSO is a very good solvent for DSNS but its elevated boiling point makes this material very difficult to remove. Nevertheless we obtained single crystals of good optical quality using this solvent. The crystals were grown by slow evaporation. A solution of DSNS in DMSO with a concentration of 10 g 100 ml⁻¹ was heated up and stirred until all the powder had dissolved. Afterwards, droplets of the solution were placed between glass plates and left to slowly evaporate at 50 °C. Fig. 1a shows thin needles of DSNS crystal



Scheme 1 Molecular diagram of DSNS.

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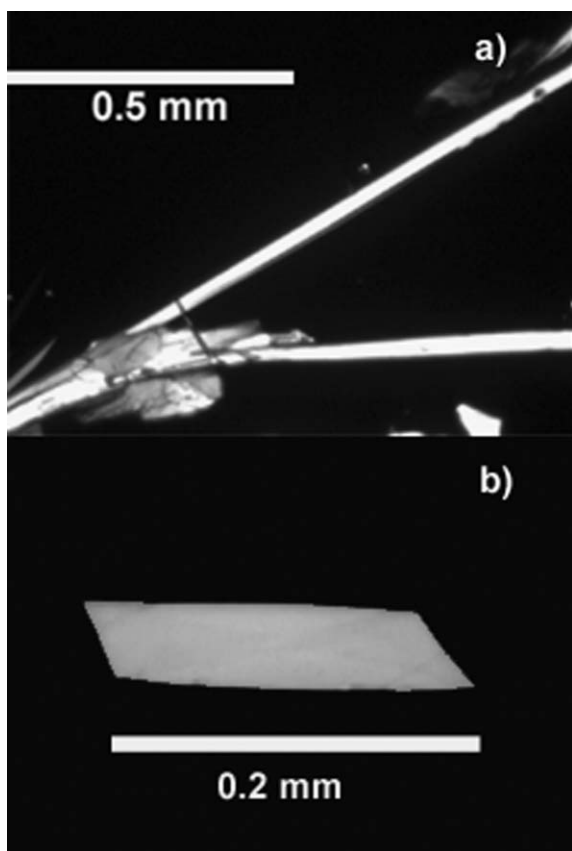


Fig. 1 Crystal of DSNS grown by a) evaporation and b) slow cooling from solution in DMSO as observed between crossed polarizers in a microscope.

grown by this method. The thin single crystalline needles are approximately 2 mm in length with a square cross section of a few tens of square microns.

The growth by cooling of the solution yielded plate like crystals. Starting with a saturated solution at 100 °C placed between two glass plates, we cooled it down to room temperature in a period of one hour. Different cooling rates yielded similar results except for the case of very low cooling rates (3 °C h⁻¹) in which no crystallization was visible. Fig. 1b shows a thin plate crystal grown by slow cooling that was placed between crossed polarizers in a microscope. Rotation of the crystal around the direction of light propagation turned it completely dark when the indicatrix axis (or its projection to the plane of the crystal plate) was aligned parallel to the polarization of the transmitted light, which indicates that the crystals are single crystalline.

X-Ray crystallographic study

The crystallographic structure† of DSNS was determined via X-ray analysis of single crystals. The data obtained is listed in Table 1. DAST data² was added for comparison.

DSNS crystals are triclinic and have a *P1* space group. The packing diagram obtained from X-ray analysis is presented in

† CCDC reference number 292764. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603049a

Table 1 Crystallographic data of DSNS and DAST crystals

	DSNS	DAST
Formula	C ₂₆ H ₂₆ N ₂ O ₃ S	C ₂₃ H ₂₆ N ₂ O ₃ S
Formula weight	446.55	410.5
Crystal system	Triclinic	Monoclinic
Space group	<i>P1</i>	<i>Cc</i>
Point group	<i>1</i>	<i>m</i>
<i>a</i> /Å	7.864(4)	10.365
<i>b</i> /Å	8.054(4)	11.322
<i>c</i> /Å	9.893(5)	17.893
α /°	70.04(5)	90
β /°	73.31(5)	92.24
γ /°	83.69(5)	90
<i>V</i> /Å ³	564.1(5)	2098.21
<i>T</i> /K	294(2)	—
<i>Z</i>	1	4
μ /mm ⁻¹	1.52	1.72
Reflections (measured/indep)	4377/3313	3891/1850
<i>R</i> _{int}	0.187	—
<i>R</i> ₁ for 1392 obs. Data (<i>I</i> > 2σ(<i>I</i>))	0.13	—

Fig. 2. The chromophore's non-centrosymmetric alignment is a prerequisite for second order optical effects such as second harmonic generation (SHG) and electro-optical modulation. In DSNS the planar stilbazolium chromophores are aligned perfectly parallel, which represents the ideal case for adding up the microscopic polarizabilities into a macroscopic effect, maximizing the diagonal electro-optic and nonlinear coefficients. Such a configuration may be not optimized for phase-matched nonlinear optical applications in bulk crystals,¹¹ but is optimal for electro-optics.

Kurtz powder test

We measured the relative second harmonic generation (SHG) activity of DSNS by using the Kurtz powder technique.¹² An idler wave with a wavelength $\lambda = 1907$ nm from an optical parametrical amplifier pumped by an amplified Ti:sapphire laser was used to determine the SHG efficiency. The back-scattered light at the second-harmonic wavelength (953.5 nm) was detected with a Si photodiode, which was not sensitive to the fundamental wavelength. Contributions from third-harmonic generation ($\lambda = 635.6$ nm) were eliminated with appropriate filters. After grinding, the microcrystalline material was sieved to a particle size distribution of 63–90 μm and put into a 1.00 mm Hellma UV quartz sample cell to give a constant sample thickness. The SHG signals were calibrated with respect to similarly prepared powdered DAST samples. By this method we obtained SHG efficiency of DSNS around 1.5 times that of DAST, which is the highest powder SHG efficiency among the studied complexes.

Discussion

It has already been identified that counter-anions play an important role in tailoring crystal packing and produce non-centrosymmetric bulk structures in stilbazolium salts.² In our previous study, it was found that minor modification of *p*-substituents on the counter-anion would basically change the crystal structure and SHG activity of stilbazolium salts.⁷ Several other reports show that in general medium size counter anions like tosylate are advantageous in achieving large second

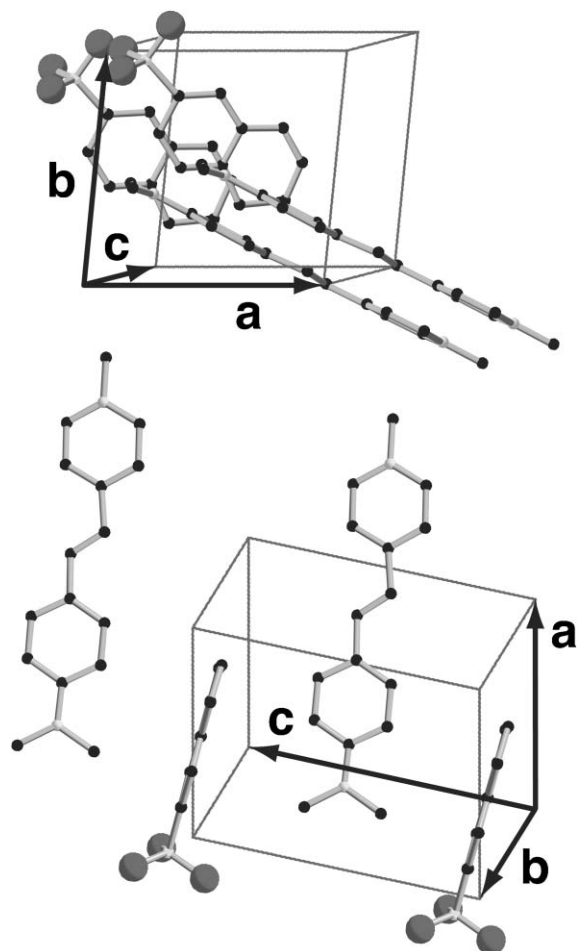


Fig. 2 Crystal packing diagram of DSNS including ions from two unit cells with the unit cell vectors **a**, **b** and **c** in two different projections, showing the planar configuration of the stilbazolium chromophores and the parallel arrangement of the molecules. The chromophores are aligned approximately along the $[0.85, -0.41, -0.035]$ crystallographic vector.

order nonlinearities.^{2,7,8} Recent studies of *N*-aryl pyridinium salts have shown that in some instances smaller anions like hexafluorophosphate are better than tosylate for generating non-centrosymmetric bulk structures.¹³ Here we show that the use of a relatively big naphthalenesulfonate anion can induce a non-centrosymmetric structure with an even higher SHG intensity. The increased susceptibility of DSNS compared to DAST can be explained for two reasons. First, the bulky counter-anion tends to decrease the intermolecular interaction – which mostly has a negative influence on the nonlinearity of the molecules.¹⁴ The second reason is that there is only a single chromophore in the unit cell and therefore all the stilbazolium chromophores are perfectly parallel, while in the case of DAST they are arranged in a cross pattern making an angle of 20° with the polar *a*-axis of the crystal. This allows for a maximal possible projection of the microscopic nonlinearities in DSNS.

Conclusions

In summary, a novel stilbazolium derivative with a 50 percent larger second-order nonlinear optical activity than DAST has

been synthesized, characterized and small crystals have been grown from solution. X-Ray diffraction shows that the structure is triclinic and that the chromophores are aligned perfectly parallel. This result implies that the macroscopic second-order nonlinear optical properties of the organic nonlinear optical salts can be further increased by selecting suitable counter-anions to optimize the intermolecular interactions and chromophore packing.

Experimental

Materials and methods

All reagents were purchased as high purity from Aldrich and used without further purification. ^1H NMR spectra were recorded on a Bruker 300 MHz spectrometer in DMSO-d_6 solutions. Elemental analyses were performed by the Microanalytical Laboratory, ETH. Thermal analysis was conducted on a Perkin-Elmer TGA-7 and DSC-7 spectrometer at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$, respectively.

Synthesis of DSNS (4-*N,N*-dimethylamino-4'-*N'*-methylstilbazolium 2-naphthalenesulfonate)

4-*N,N*-Dimethylamino-4'-*N'*-methylstilbazolium iodide was obtained by condensation reaction between 4-methyl-*N*-methyl pyridinium iodide, which was prepared from 4-picoline and iodomethane, and 4-*N,N*-dimethylamino-benzaldehyde in the presence of piperidine.¹⁰ Then the iodide salt was dissolved in a minimum volume of water and aqueous 2-naphthalenesulfonic acid sodium salt was added. A dark-gold precipitate was yielded and filtered off. After drying and heating at $140\text{ }^\circ\text{C}$ for 1 h to get rid of water, its color changed into deep red (yield 62%). Purification was effected by recrystallizing at least three times from methanol. ^1H NMR (300 MHz, DMSO-d_6): $\delta = 8.68$ (d, 2H, $J = 6.9\text{ Hz}$, $\text{C}_5\text{H}_4\text{N}$), 8.14 (s, 1H, $\text{C}_{10}\text{H}_7\text{SO}_3^-$), 8.04 (d, 2H, $J = 6.6\text{ Hz}$, $\text{C}_3\text{H}_4\text{N}$), 7.98–7.84 (m, 4H, $\text{C}_{10}\text{H}_7\text{SO}_3^- + \text{CH}$), 7.72 (d, 1H, $J = 8.7\text{ Hz}$, $\text{C}_{10}\text{H}_7\text{SO}_3^-$), 7.60 (d, 2H, $J = 9.0\text{ Hz}$, C_6H_4), 7.53 (m, 2H, $\text{C}_{10}\text{H}_7\text{SO}_3^-$), 7.18 (d, 1H, $J = 16.2\text{ Hz}$, CH), 6.79 (d, 2H, $J = 8.7\text{ Hz}$, C_6H_4), 4.16 (s, 3H, NMe), 3.02 (s, 6H, NMe_2). CHN analysis calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$: C 69.93, H 5.87, N 6.27%; found: C 70.03, H 5.69, N 6.20%.

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