Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis, Crystal Growth and Structure of N-(4-cyano-2-nitro-phenyl)-L-serine and Investigation of SHG Activity

X. M. Zhao [a] , X. Chen [a] , L. B. Cheng [a] , N. H. Hu [b] , H. Q. Jia [b] & Y. Xing [b]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, 116012, P.R. China

[b] Changchun Institute of Applied Chemistry, Chinese Acad. of Science, 130022, P.R. China

Version of record first published: 24 Sep 2006

To cite this article: X. M. Zhao, X. Chen, L. B. Cheng, N. H. Hu, H. Q. Jia & Y. Xing (1998): Synthesis, Crystal Growth and Structure of N-(4-cyano-2-nitro-phenyl)-L-serine and Investigation of SHG Activity, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 325:1, 7-11

To link to this article: http://dx.doi.org/10.1080/10587259808025379

Mol. Cryst. Liq. Cryst., Vol. 325, pp. 7–11
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis, Crystal Growth and Structure of *N*-(4-cyano-2-nitro-phenyl)-L-serine and Investigation of SHG Activity

X. M. ZHAO[a], X. CHEN[a], L. B. CHENG[a], N. H. HU[b], H. Q. JIA[b] and Y. XING[b]

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, Postcode 116012, (P.R. China);*
[b] *Changchun Institute of Applied Chemistry, Chinese Acad. of Science, Postcode 130022, (P.R. China)*

(Received 22 October 1996; In final form 22 December 1997)

N-(4-cyano-2-nitro-phenyl)[NCP]-L-serine has been synthesized from L-serine. Crystals of NCP-L-serine • DMSO complex having good optical quality were grown from solution. The crystal structure and the nonlinear optical properties were determined. Second harmonic generation (SHG) measurements according to powder method reveals that NCP-L-serine • DMSO complex possesses SHG activity.

Keywords: Nonlinear optical crystal; crystal growth; crystal structure; second harmonic generation

1. INTRODUCTION

In recent years, interest in using organic crystals with charge correlated and highly delocalized π-electron states has increased considerably, since very large nonlinear optical susceptibilities have been measured in several materials. Nonlinear optical crystals may be used as SHG and ultrafast light modulators for applications in optical memory and optical communication [1–3].

In this paper, the synthetic scheme of NCP-L-serine and crystal growth, crystal structure, and SHG activity for NCP-L-serine • DMSO complex are reported.

2. SYNTHESIS, X-RAY ANALYSIS OF MOLECULAR AND CRYSTAL STRUCTURES

2.1. General Synthetic Procedures

NCP-L-serine (4) was prepared according to Scheme 1. Initially, (1) was treated with *p*-Toluenesulfonamide and phosphorus pentachloride under 200 – 202°C to yield (2) [4]. The main intermediate, (3), was obtained from a mild fluorination between (2) and powdered anhydrous potassium fluoride (dried by spraying) in dimethyl sulphoxide (DMSO) [5]. The product, (4), was prepared by (3) using triethylamine as a catalyst in a mixture of DMSO and water with l-serine [6].

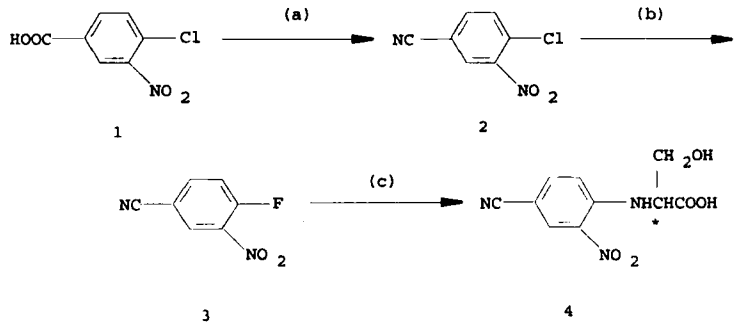
2.2. X-ray Analysis of Molecular and Crystal Structures

An X-ray structural analysis of NCP-L-serine was carried out on single crystals obtained from a DMSO and water solution. X-ray intensities were collected on a four-circle diffractometer using Mo-K_α radiation. A total of 2745 reflections was used for the structure determination.

The structure was solved by the direct method using the program (SHELXTL) and was refined by the least-squares method.

The residual index, R, was 0.045. The space group is the triclinic, non-centrosymmetric; the crystallographic parameters are listed in Table II.

The molecular structure is shown in Figure 1. Figure 2 illustrates a part of the crystal structure showing a hydrogen-bonded molecular layer parallel to the (1 0 0) plane. The measurement shows that there are three molecules in a unit cell, which are one of DMSO and two of NCP-L-serine respectively.



SCHEME 1 Preparation of NCP-L-serine. Treatments: (a) $CH_3C_6H_4SO_2NH_2$, PCl_5, 200 – 202°C; (b) DMSO, KF, 100°C, 8 h; (c) DMSO-H_2O, $N(C_2H_5)_3$, room temperature.

TABLE I Hydrogen bonds

Donor	*Acceptor*	*Symmetry operation for acceptor*	*D...A(Å)*
O(12)	O(1)	$x, y+1, z$	2.514
O(13)	O(11)	$x, y-1, z$	2.754
O(22)	O(23)	$x, y-1, z$	2.661
O(23)	N(13)	$x, y-1, z+1$	2.754

TABLE II Condition of structural analysis and crystallographic data. Z is the number of molecules in the unit cell

Formula	$C_{10}H_9O_5N_3$ 1.5DMSO (M = 290.26)
Melting point	T_m = 160°C
Crystal size/mm	0.46×0.58×0.50
Diffractometer	NICOLET *R* 3m/E four circle automatical diffractometer
Radiation	MoK_α (λ = 0.71073 Å)
Scan limit, 2θ	3 - 50°
Number of reflections	
measured	2745
used [$I > 3\sigma(I)$]	1702
Crystal system	triclinic
Space group	P1 (Z = 2)
Unit cell	a = 4.691(2) Å
	b = 6.154(2) Å
	c = 23.664(2) Å
	α = 95.75(3)°
	β = 93.96(3)°
	γ = 99.32(3)°
	v = 668.3(4) Å^3
Calculated density	D_c = 1.44 g/cm^3
Residual index	R = 4.5%

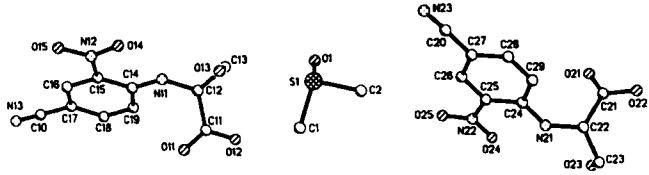


FIGURE 1 Structure of unit cell for NCP-L-serine • DMSO complex.

Intermolecular hydrogen bonds, O—H...O(C=O), O—H(COOH)... O(DMSO), and O—H...N(CN), hold the molecules in the layer tightly. The data of hydrogen bonds are listed in Table I. As shown in Figure 2, a crystal structure with orderly arranged molecules is formed by hydrogen bonds.

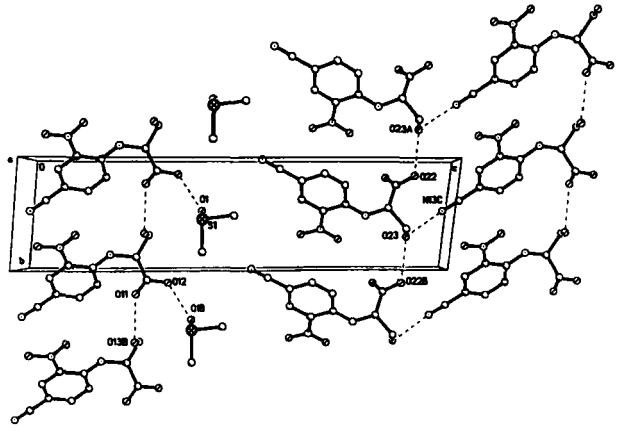


FIGURE 2 Part of the crystal structure of NCP-L-serine • DMSO complex packing on a plane parallel to the (1 0 0) plane is shown.

3. CRYSTAL GROWTH

The crude NCP-L-serine powder was purified by column-chromatography and recrystalization from several solvents. Quadrilateral plates were obtained from DMSO and water solution (3:7). Crystal growth was attempted by evaporation from DMSO and a water solution (3:7). The temperature was maintained at 20°C and the solvent was spontaneously evaporated at a rate of 1.5 ml/day. After 15 days, several single crystals of good optical quality were obtained.

4. RESULTS AND DISCUSSION

The absorption curve of UV-visible has been measured in methanol and it is found that its maximum absorption wavelength, λ_{max}, of NCP-L-serine is in the ultraviolet region (Tab. III). The SHG activity of NCP-L-serine • DMSO complex was measured by the powder method. The measurement demonstrates the compound, NCP-L-serine • DMSO complex, has good SHG activity (Tab. III).

SHG activity is related to both the crystal structure and the angle between the mean intramolecular charge transfer axis and the crystal twofold axis [7].

TABLE III Absorption maximum of NCP-L-serine and SHG powder efficiency of NCP-L-serine • DMSO complex

	λ_{max}		*SHG**
NCP-L-serine	406.8 nm	NCP-L-serine • DMSO complex	4.5

* Laser wavelength 1064 nm Urea = 1.

Crystals of NCP-L-serine • DMSO complex are triclinic, space group P1 has a non-centrosymmetric crystal structure. As is shown in Table III, the maximum absorption wavelength, λ_{max}, of NCP-L-serine is 406.8 nm and it has no effect on SHG.

From Figure 2 and Table II, it is known that molecules arrange parallel at a certain angle in the same direction by intermolecular hydrogen bonds. This kind of arrangement leads to counteracting the dipole moment in the *b* axis and partly reinforces it in the *c* axis, so NCP-L-serine demonstrates good SHG activity. In addition, further study need to be made about the effect of the existance of DMSO on the optical properties of the crystals.

Acknowledgments

Financial support from the National Natural Science Funds Program of China (29476227) is gratefully acknowledged.

References

[1] B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch and J. L. Bernstein, *J. Appl. Phys.*, **50**(4), 2523 (1979).
[2] J. L. Oudar and R. Hierle, *J. Appl. Phys.*, **48**(7), 2699 (1977).
[3] T. Uemiya, N. Uenishi, Y. Shimizu, T. Yoneyama and K. Nakatsu, *Mol. Cryst. Liq. Cryst.*, **182A**, 51 (1990).
[4] C. S. Miller, *Org. Synth.*, **CV3**, 646 (1955).
[5] J. Deutach and H. J. Niclas, *Syn. Communi.*, **21**(4), 505 (1991).
[6] J. F. K. Wilshire, *Aust. J. Chem.*, **20**, 2269 (1967).
[7] J. Zyss, J. F. Nicoud and M. Coquillay, *J. Chem. Phys.*, **81**(9), 4160 (1984).