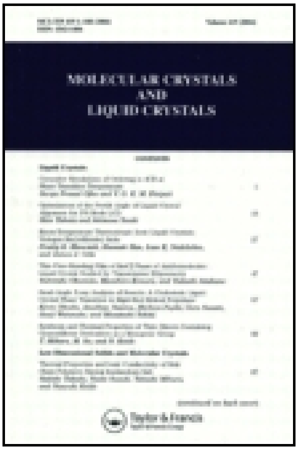

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Novel Organic SHG Materials

Tokiko Uchida [a] , Kozo Kozawa [a] , Tetsuya Sakai [a] , Masamichi Aoki [a] , Hiroyuki Yoguchi [a] , Abduaini Abdureyim [a] & Yuichi Watanabe [b]

[a] Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba, 278, Japan

[b] Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba, 278, Japan

Version of record first published: 04 Oct 2006

To cite this article: Tokiko Uchida, Kozo Kozawa, Tetsuya Sakai, Masamichi Aoki, Hiroyuki Yoguchi, Abduaini Abdureyim & Yuichi Watanabe (1998): Novel Organic SHG Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 135-140

To link to this article: http://dx.doi.org/10.1080/10587259808044322

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 135–140
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in India.

Novel Organic SHG Materials

TOKIKO UCHIDA[a], KOZO KOZAWA[a], TETSUYA SAKAI[a], MASAMICHI AOKI[a], HIROYUKI YOGUCHI[a], ABDUAINI ABDUREYIM[a] and YUICHI WATANABE[b]
[a]Faculty of Science and Technology; [b]Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278 Japan

Of 140 newly synthesized chalcone-analogous materials, 56 specimens were observed to be efficient for nonlinear optical second harmonic generation (SHG). The SHG efficiency of 3-(4-chlorophenyl)-1-(3-pyridyl)-2-propen-1-one is discussed on the basis of crystal structure and MO calculation. In this crystal, molecules arrange themselves almost ideal manner for SHG.

Keywords: second harmonic generation; chalcone derivatives

INTRODUCTION

Second order nonlinear optically active materials are required to be composed with the molecules which possess large second-order hyperpolarizability, and are also required to crystallize in non-centrosymmetrical structure. The former requirement is fulfilled by designing molecules to possess conjugated π electron system together with both donor- and acceptor-type substituents in it. However, the latter requirement is difficult to be fulfilled, since it includes crystal structure control.

Among the many organic compounds reported for their second order non-linear optical activity, chalcone derivatives are noticeable materials for their excellent blue light transmittance and good crystallizability[1]. In this report, we propose several new chalcon-type derivatives, which are composed of three planar moieties; namely, two aromatic rings (Ar1 and Ar2) and an aliphatic conjugated ketone bridge (a pentadienone or a propenone) , which connects the terminal Ar1 and Ar2.

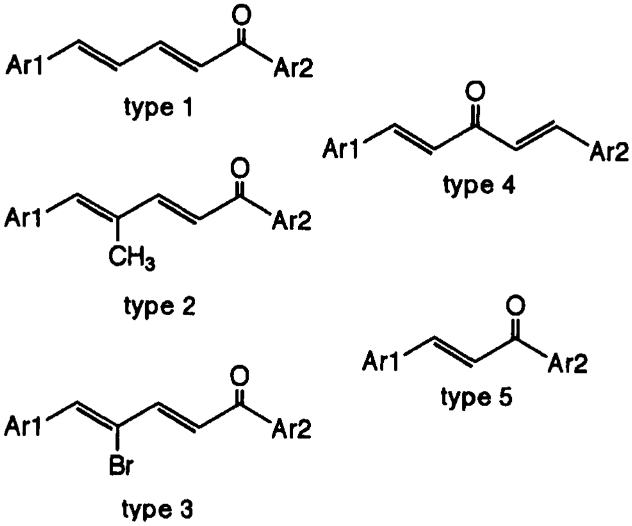

FIGURE I Basic molecular structure.

EXPERIMENTAL

Materials

The basic molecular structures, investigated, are summarized as type **1**-**5** in Fig.1. They were prepared by aldol condensation of appropriate aldehydes and substituted ketones. For example, type **2** compounds were obtained by condensation of 2-methylcinnamaldehyde derivatives and substituted acetophenones. They were purified by recrystallization. Purity of the compounds were checked by thin-layer chromatography. Absorption spectra were observed on a Hitachi 330 spectrophotometer.

SHG Measurements

The second harmonic generation (SHG) efficiencies of the materials were measured with the powder method[2]. An incident beam of Nd^+-YAG laser (fundamental wave length 1064 nm, beam diameter 6mm, pulse width 7 ns, power 10 mJ), was applied to the samples, and the generated SH wave of 532 nm was detected with photomultiplier with referring to that of urea.

X-Ray Structure Analysis and MO Calculation

X-ray diffraction data were collected with a Rigaku AFC-5 diffractometer (λ=0.71073 A). Structure was solved by the direct method, and refined by the block-diagonal least-squares calculation.

MO calculations and estimation of the hyperpolarizability values were done with MOPAC program package. The atomic coordinates of molecules, obtained by the X-ray analysis, were used for the calculation.

RESULTS AND DISCUSSION

Non-linear Optical Property

Of 140 prepared materials, 56 samples were observed to be SHG effective. Table 1 describes the optical properties and crystalline space group about several selected materials.

When alkoxyphenyl group was used as Ar1, obtainable possibility of non-centrosymmetrical crystals was high for all the type of our materials, as pointed out by Fichou *et al.* with methoxy-group substitution about chalcone (type **5**) derivatives[3]. Especially, in type **2** compounds, 10 materials were observed to be SHG efficient in total of 14 prepared samples. By introducing pyridyl group to Ar2, the obtained materials were observed to possess high SHG efficiency (**5-4**, **5-5**, and **5-6**), though powder test is not quantitative.

In general, the chalcone-type molecule has a dipole roughly along its long axis. If molecules crystallize in 2 or m point group, the angle between the dipole and the crystal symmetry element (rotation axis or mirror plane) plays an important role for the nonlinear optical constants. In the case of mm2 or 222 point group, steric structure of the molecule also affects the susceptibility value. For chalcone-type compounds, SHG efficient samples frequently give

TABLE I Optical properties and crystalline space group of several materials

No	Structure		λcutoff	SHG	β	Space
	Ar1	Ar2	(nm)	(vs. urea)	(10^{-30}esu)	group
Type 1						
1-1	4-MeO-Ph-	2-Furyl-	427	3.6	11.2	----a)
1-2	Ph-	4-Cl-Ph-	394	2.6	6.9	----a)
Type 2						
2-1	4-MeO-Ph-	4-Cl-Ph-	420	12.6	9.1	Pc
2-2	4-MeO-Ph-	4-Br-Ph-	422	15.2	10.5	Pc
2-3	4-MeO-Ph-	4-MeOPh-	412	12.2	7.7	Pc
2-4	4-MeO-Ph-	3-Me-Ph-	415	10.9	8.4	$P2_1$
Type 3						
3-1	Ph-	Ph-	385	12.1	4.5	$Pbn2_1$
3-2	Ph-	2-Thienyl	391	0.2	2.7	----a)
Type 4						
4-1	4-MeO-Ph-	4-MeO-Ph-	410	6.0	9.9	Pc
4-2	4-Cl-Ph-	4-Cl-Ph-	373	5.0	10.2	$P22_12_1$
Type 5						
5-1	4-(2-Me-BuO)Ph-b)	3-Cl-Ph-	349	weak	5.3	$P2_1$
5-2	4-(2-Me-BuO)Ph-b)	4-Cl-Ph-	345	2.8	5.4	$P2_12_12_1$
5-3	4-F-Ph-	2-Thiazolyl	365	7.8	1.5	$P2_1nb$
5-4	4-MeO-Ph-	2-Pyridyl	405	26.0	0.7	$Pbn2_1$
5-5	4-Cl-Ph-	3-Pyridyl	315	29.4	7.7	$P2_1$
5-6	4-PrO-Ph-	3-Pyridyl	407	75.0	9.8	----a)

a) Space group is not yet determined.

b) Chiral substituent: 4-[(S)-2-methylbutoxy]phenyl-.

a large dihedral angle between Ar1 and Ar2 (53.8^0 and 43.7^0 for **4-2** and **5-2**). However, the molecular twisting is not a main cause of the nonlinear activity.

3-(4-Chlorophenyl)-1-(3-pyridyl)-2-propen-1-one (5-4)

Crystal data: $C_{14}H_{10}ClNO$, $M_r = 243.7$, monoclinic, space group $P2_1$, $a = 20.285(4)$, $b = 4.8950(4)$, $c = 5.979(2)$ A, $\beta = 97.47(1)^0$, $V = 588.6(2)$ A^3, $Z = 2$, $D = 1.38$ Mg m^{-3}, $R = 0.046$, $R_w = 0.040$ (1148 reflections).

Atomic position of the nitrogen atom in the pyridine ring was computed by molecular dynamic calculation, and it agreed with that obtained by X-ray analysis. Fig. 2 illustrates the calculated differential electron densities of the atoms which are defined as the differences of the electron densities between HOMO and LUMO. In this figure, diameter of the circles is proportional to the electron density. Open circle means that electron density increases by electronic excitation, and closed circle means that it decreases by excitation.

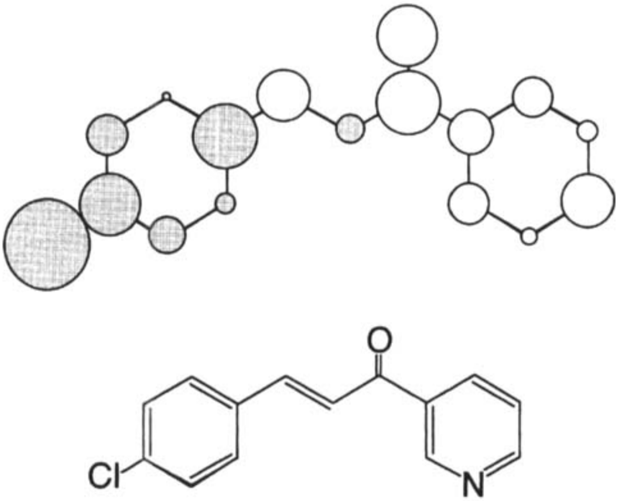

FIGURE 2 Differential electron densities of **5-4**. Captions are described in the text.

It is obvious from the figure that $\Delta\mu_{cg}$ (difference between the dipole moments in the ground state and excited state) directs from Ar1 to Ar2 (or from Cl atom to O atom or pyridine ring).

Fig. 3 shows the crystal structure projected along the c axis. Calculated angle between the b axis (parallel to the rotation axis and the optical axis because of the monoclinic system) and Cl-O direction is 51.9^0. This value is very close to the ideal value of 54.74^0, derived by the oriented gas model for point group 2 or m[4].

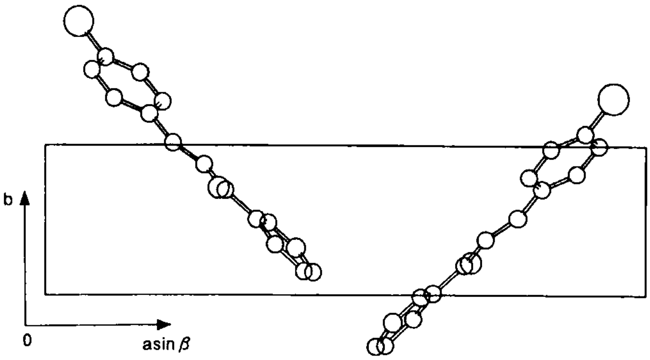

FIGURE 3 Crystal structure of **5-4** projected along the c axis..

References

[1.] Y. Goto, A. Hayashi, Y. Kimura and M. Nakayama, *J. Cryst. Growth*, **108**, 688(1991).

[2.] S. K. Kurtz and T. T. Perry, *J. Appl. Phys.* **39**, 3798(1968).

[3.] D. Fichou, T. Watanabe, T. Tanaka, S. Miyata, Y. Goto and M. Nakayama, *Japan J. Appl. Phys.*, **27**, L429(1988).

[4.] J. Zyss and D. S. Chemla, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss(Academic Press, Orland, 1987)Chap. II-1, p.118.