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Second-Harmonic Generation from Single and Mixed Crystals of *p*-Nitroaniline and Its Derivatives

Ryoka MATSUSHIMA,* Kiyonari HIRAMATSU, and Katsuhisa SHIMAMOTO
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432

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Synopsis. Noncentrosymmetric and thermostable single crystals (space group of $Pna2_1$) of *N*-(2-butenyl)-*p*-nitroaniline were obtained by slow crystallization from solution, with SH activities of 150—200×urea measured by the SHG powder method with a 1064 nm Nd : YAG laser source. Single crystals of *N*-(3-methyl-2-butenyl)-, *N*-(2-propenyl)-, or *N*-butyl-*p*-nitroaniline showed nil SH activities. On the other hand, mixed crystals of these derivatives with *p*-nitroaniline showed much higher SH activities (up to 2000), though thermally not stable.

Though donor–acceptor conjugated organic π-electron systems feature large and rapid nonlinear optical responses and high fatigue resistances, they tend to align in a nonpolar packing in condensed phases, and hence some means for noncentrosymmetric packing are necessary to obtain a high second-order nonlinear activity in the bulk.[1)] Among many approaches, enforced molecular alignment, such as poling under electric field or the use of Langmuir–Blodgett film, is highly effective for polar alignment, but is subject to substantial thermal relaxation. Intermolecular hydrogen bonding[2,3)] or crosslinking[4)] is often effective for retaining or freezing the polar molecular alignment.

On the other hand, SH-active and thermostable crystals or complexes can be obtained by spontaneous molecular alignment,[5)] providing a simple and yet highly effective method. Thus, highly SH-active and thermostable crystals have been obtained with *p*-nitroaniline (pNA)[6—8)] or with new chiral compounds,[2,9,10)] often by the aid of intermolecular hydrogen bonding and/or host–guest interactions.

The highly SH-activie mixed crystals of pNA tend to suffer from thermal relaxation in several weeks.[11)] In order to depress any thermal relaxation of the SH-active crystals we prepared *N*-alkenyl derivatives of pNA, expecting that upon subsequent crosslinking the polar alignment could be freezed. Unexpectedly, however, a few of these derivatives showed significant thermostability and high SH activity in the single crystals as such, without the aid of crosslinking. This paper is concerned with the SH-active single and mixed crystals of *N*-alkenyl derivatives of pNA.

Experimental

The SH intensities were measured with a 1 kHz Q-switched Nd : YAG laser source (1064 nm, 1 mJ per pulse, 11 kW peak power) by the powder method[12)] using powdered crystals of urea (ca. 0.1 mm), as previously described.[13)] As a powder sample, a rectangular hole (8 mm×8 mm) hollowed out in a sheet of silicone rubber was filled with powdered crystals, then sandwiched between two glass plates. The laser beam was irradiated at five different areas of the sample, over which the SH signals were averaged. Usually, the mean error in the SH intensity was less than 10%.

^{1}H NMR (60 MHz) spectra were recorded on a Hitachi R-24 spectrometer, while UV spectra were on a Hitachi 200-10 spectrophotometer. X-Ray diffraction patterns of powdered crystals were obtained with a Rigaku RAD-2B diffractometer using Cu $K\alpha$ radiation, while those of single crystals were obtained on a Rigaku AFC7R diffractometer through the courtesy of Rigaku-Denki Co. Commercial *p*-nitroaniline (pNA) of purest grade (Wako Chemicals) was purified by crystallization from ethanol. Mixed crystals were obtained from a homogeneous solution (usually in 10 cm^3) containing pNA and its derivatives, by rapid removal of the solvent (usually 10—20 min at 15 °C) under reduced pressure (unless otherwise noted). Derivatives of pNA were prepared as follows according to the literature.[14)]

***N*-(2-Butenyl)-*p*-nitroaniline (1).** pNA and 1-bromo-2-butene were stirred at 30 °C for 3 h in the presence of sodium hydrogencarbonate in hexamethylphosphoric triamide under nitrogen atmosphere. On work up, yellow prisms of **1** were obtained in 41% yield by repeated (5 times) crystallization from ethanol; mp 66.5—67.5 °C and single spot on TLC (silica gel benzene); ^{1}H NMR (acetone-d_6) δ/ppm=1.10 (s, 3H), 2.21 (s, 2H), 5.03 (s, 2H), 5.3—5.9 (br, 1H), 6.09 (d, 2H, J=9 Hz), 7.48 (d, 2H, J=9 Hz). By similar method, *N*-(2-propenyl)-pNA (**2**; mp 66.6—67.0 °C), *N*-(3-methyl-2-butenyl)-pNA (**3**; mp 68.5—69.5 °C), and *N*-butyl-pNA (**4**) were prepared in pure crystals. Their ^{1}H NMR spectra were satisfactory.

Results and Discussion

Single Crystals. Table 1 lists the SH activities of the single crystals of **1** obtained by slow crystallization from various solvents. The SH activities in the range of 150—200×urea are almost constant against a change in the solvent for crystallization. They are substantially stable, and some of them tend to increase to a value close to 200 upon standing at room temperature for over several months. Upon annealing at 50 °C, close to its melting point (67.5 °C), the SH activity of **1** (crystallized from ethyl acetate/hexane) is relatively constant at around a value of 200, after some changes at the beginning, as described in the footnote d) in Table 1. These results suggest that the single crystals formed under different conditions have (more or less) packing strains and are subject to subsequent thermal relaxation to the same (stable) packing structure.

Figure 1 shows the X-ray structure of a single crys-

Table 1. SH Activities of Single Crystals of **1**[a)]

Solvent for crystallization	SH activity (× urea) on standing for		
	0 day	22 days	110 days
Ethanol	172 (171)[b)]	197	
Toluene	160	153	162
Ethyl acetate	195	205	214
1-Propanol	166	168	172
1,2-Dimethoxyethane	177	201	206
Pyridine	205	207	196
Chloroform	157	175	144
Methyl ethyl ketone	175	199	209
Acetonitrile	171	232	216
Ethyl acetate / Hexane[c)]	255[d)]		

a) Slowly crystallized from solvents of commercially available purest grade without further purification. b) Slowly crystallized from freshly distilled ethanol. c) 1:1 in volume. d) On annealing at 50 °C, the SH activities were changed with annealing time (in parenthesis) as follows: 280 (10 h), 275 (24 h), 205 (2 d), 220 (5 d), 225 (6 d), and 205 (7 d).

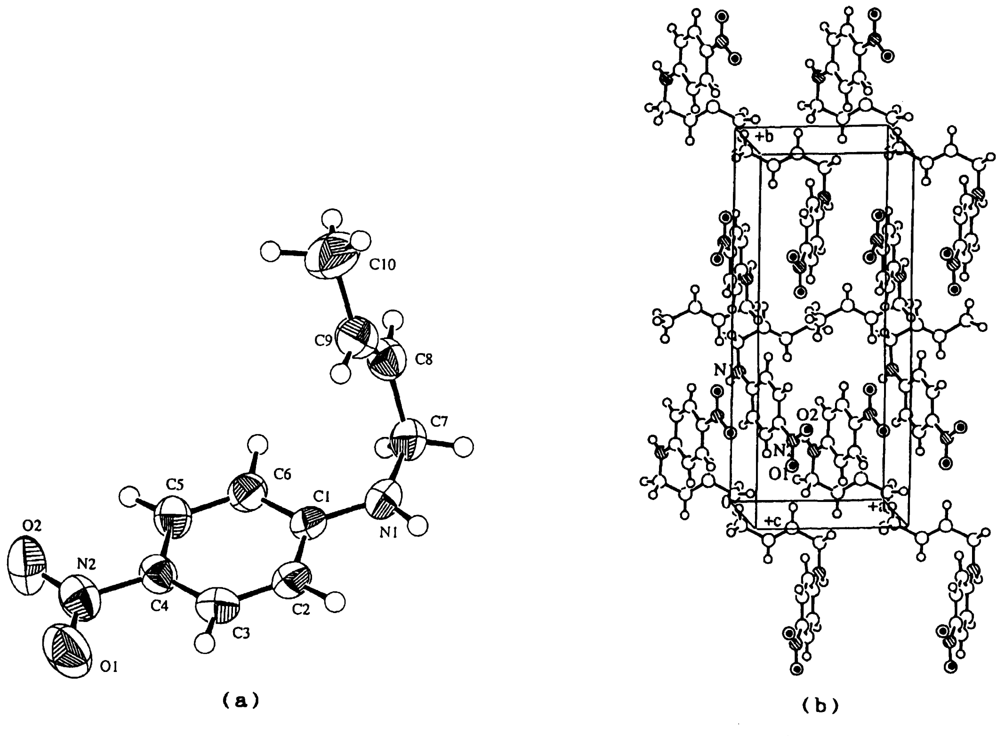

Fig. 1. Molecular (a) and packing (b) structures of the SH-active single crystals of **1** (SH activity=172×urea). ● and ◉ refer to the nitrogen and oxygen atoms, respectively.

tal of **1** obtained from ethanol (SH activity 172×urea). In molecule (a) the torsion angle of C1–N1–C7–C8 is 72 degrees, and the *N*-(2-butenyl) plane is almost perpendicular to the nitroaniline plane. In crystal (b), the alkenyl moiety lines along the *a*-axis while the nitroaniline planes are stacked face-to-face with ca. 3.7 Å distance, eventually in noncentrosymmetric packing with a space group of $Pna2_1$ (orthorhombic, $a=7.457$, $b=18.282$, $c=7.347$ Å, and $V=1001$ Å^3). The single crystals of **1** obtained from different solvents are assumed to have the same crystal structure, since their powder XRD patterns (Fig. 2a) were essentially the same.

On the contrary, single crystals of *N*-(2-propenyl)-*p*-nitroaniline (**2**), *N*-(3-methyl-2-butenyl)-*p*-nitroaniline (**3**), or *N*-butyl-*p*-nitroaniline (**4**), showed nil or very low SH activity. This implies very specific and subtle structural effects in determining the molecular packing in the crystal: Either the addition or subtraction of a methyl group can disturb the favorable packing structure. Also, a planar 2-butenyl group may be necessary for the packing, while a more flexible butyl group is unfavorable. Though the melting point of **1** is rather low, as such, an intermolecular cycloaddition or crosslinking

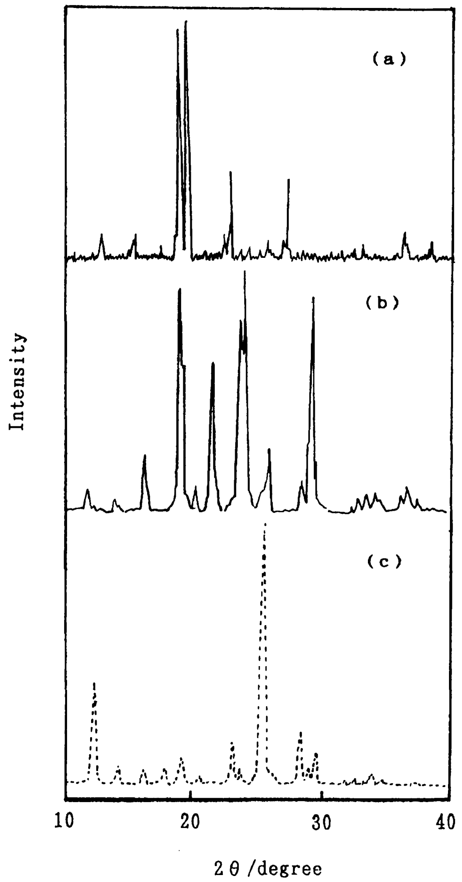

Fig. 2. XRD patterns of SH-active single crystals of **1** with SH activity of 172×urea (a), and of the mixed crystals of pNA and **1** with SH activity of 1600×urea (b), as compared with the SH-inactive pure pNA crystals (c). The mixed crystals of pNA with **2** (f_G =0.9, SH activity=1120×urea), and those with *N*-isopropyl-*p*-nitroaniline (f_G = 0.8, SH activity= 1880×urea showed quite similar pattern to that of (b).

reaction of the butenyl double bond, or more ideally a polymeric analog, would improve the thermal stability.

Mixed Crystals of pNA and Its Derivatives. Mixed crystals of pNA with **1** obtained by rapid solvent removal exhibit higher SH activities over 2000×urea at maximum, as shown in Table 2. However, when the mixture solution of pNA and **1** in ethanol were slowly crystallized by solvent removal over 3—4 d at room temperature, the SH activities/urea of the mixed crystals were low; e.g., 171 (with f_G=0.0), 310 (0.2), 8 (0.7), and 3 (0.8). The highly SH-active crystals are not thermostable and significantly lose their SH activities upon standing at room temperature for over one week (values in parenthesis), or upon annealing at a temperature above the melting point. Thus, the high SH activities of mixed crystals of pNA with **1** decreased down to 10 (f_G=0.0), 89 (0.2), 88 (0.4), 55 (0.6), 32 (0.8), and 12 (0.9), respectively, upon annealing at 150 °C for 6 h followed by slow cooling to room temperature. Since this process includes crystallization from the melt, the crystals are different in nature from those crystallized from solution.

Table 2. SH Activities of the Mixed Crystals of pNA with **1**—**4**[a)]

f_G	SH activity (× urea) of pNA mixed with			
	1[b)]	**2**	**3**	**4**
0.0	177(177)	0	0	0.7
0.2	222(208)	65	152	
0.4	209(177)		508	
0.5		377	877	39
0.6	1190(892)		1110	
0.7	1650(1180)	1440	1630	54
0.8	1770(1370)		1940	
0.9	2010(1460)	1420	2150	540
1.0	0	0	0	0

a) Obtained by rapid removal of the solvent (over 10—20 min) under reduced pressure at 15 °C, from freshly distilled tetrahydrofuran (THF) solutions. f_G refers to the mole fraction of pNA mixed in solution rather than in the mixed crystals. b) Freshly distilled acetone was used as a solvent instead of THF, but similar results were obtained from THF. Values in parenthesis refer to the SH activities measured after 8 d upon standing at room temperature.

While **2**—**4** showed nil or very low SH activity in their single crystals, their mixed crystals with pNA showed high SH activities over 1400—2100 (with f_G=0.7—0.9). These highly SH-active mixed crystals showed common and characteristic XRD patterns (Fig. 2(b)), which are entirely different from those of the SH-active single crystals of **1** (a) or SH-inactive pure pNA crystals (c). The XRD patterns of the SH-active mixed crystals of pNA were quite similar to each other, regardless of the structures of the mixed host molecules.

This implies similar crystal habit and growth induced by common effects, such as controlling of the growth rates in the crystal faces that adsorb the foreign substances, as recently documented.[15)] Thus, the crystal growth and morphology is markedly changed by selective adsorption-inhibition of the additives (**1**—**4**), which interact with a selected face of the growing pNA crystal. The nitro groups of additives are capable of forming hydrogen bonds with the amino group of pNA, while their secondary amino groups do not act as suitable proton donors for hydrogen-bonded chains, since the *N*-alkenyl substituents would sterically interfere with the interactions. Therefore, the additives may be selectively adsorbed at those faces of the growing pNA crystal that contain nitro groups, thus retarding the growth rate in these directions while other unaffected surfaces maintain regular growth. Such face-selective adsorption-inhibition by the additives would produce noncentrosymmetric crystals and/or provide pre-nucleation sites for epitaxial-like crystal growth.

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surement of the X-ray crystallography shown in Fig. 1.

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