CHEMISTRY LETTERS, pp. 1743-1746, 1992.

Crystal Engineering and Substituent Effect of Hindered Phenols for SHG Materials

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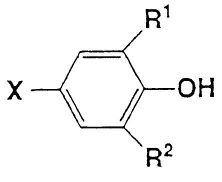
2,6-Di-tert-butylphenol moiety was found to be effective to control molecular packing in crystals for SHG materials. Many derivatives having compact acceptor group at 4-position of hindered phenols showed SHG responses depending on the electron withdrawing effect of an acceptor. The X-ray structural analyses revealed that molecular packing was controlled both by the steric requirements and the intermolecular hydrogen bonding.

Molecular design of SHG materials can be conducted by MO method in molecular level but the macroscopic arrangements of molecules in crystals are difficult to be controlled. Various chemical modifications of molecules to get valuable single crystals with high SHG response have been reported.1) The relationship between SHG response and structures of the twisted biphenyls having hindered phenol moiety was studied in the previous paper,2) in which 2,6-di-tert-butylphenol moiety was effective for SHG response. In this paper, relationship between molecular arrangements and substituent effects of hindered phenols for SHG materials was systematically examined.

Table 1 showed alteration of SHG efficiency of phenols depending on the alkyl substituents at 2- and 6-positions and substituents at 4-position. Among the 4-formyl derivatives, 2,6-di-tert-butyl-4-formylphenol(1a) only showed SHG response of 3.8U but all others(1b-1d) were inactive. Furthermore, the nitro derivative(1e) showed quite large SHG efficiency of 20.3U but the diisopropyl analogue(1f) was inactive. The powder efficiency of 1e was about 4.6 times that of biphenyls containing the hindered phenol moiety.2) The other derivatives (1g-1i) were active except for 4-cyano one (1j). Thus, the 2,6-di-tert-butylphenol moiety may play an important role

Table 1. The SHG efficiency and λ_{max} value of 1[3)]



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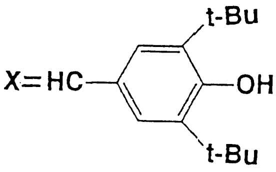
No.	R^1	R^2	X	λ_{max} a)	SHG	PE b)
1a	t-Bu	t-Bu	CHO	281	A	3.8U
1b	i-Pr	i-Pr	CHO	280	N	
1c	Me	t-Bu	CHO	282	N	
1d	Me	Me	CHO	279	N	
1e	t-Bu	t-Bu	NO_2	320 c)	A	20.3U
1f	i-Pr	i-Pr	NO_2	320 c)	N	
1g	t-Bu	t-Bu	COOH	275	A	1.8U
1h	t-Bu	t-Bu	$CONH_2$	220	A	1.3U
1i	t-Bu	t-Bu	NO	420	A	1.2U
1j	t-Bu	t-Bu	CN	249	N	

a) In acetonitrile. b) Powder efficiency against urea.
c) In benzene. A: active. N: not detectable.

in the effective molecular packing of these compounds. Styryl derivatives of hindered phenol were also synthesized and the results were summarized in Table 2. The methylester(2a) obtained by condensation of 1a with methylcyanoacetate showed SHG response of 7.5U, but the ethylester(2b) showed very weak response of 0.2U and the benzoyl derivative(2c) did not show any SHG response. It was proposed that larger substituents in 2b and 2c disturbed the effective molecular packing for SHG response. The amide derivative(2d) was also inactive, in which unfavorable intermolecular hydrogen bonding of the amino group was proposed. The N-butylamino derivative(2e) showed weak response of 0.8U. Then, the 2,6-di-tert-butylphenol moiety played an effective role in the molecular packing to a certain size of acceptor group. Methoxy derivatives[5)] of 1a(3a) and 1e(3b) were inactive, so that the intermolecular hydrogen bondings between the hydroxy group and 4-acceptor group consequently were presumed to play a significant role for effective SHG response.

Table 2. The SHG efficiency and λ_{max} value of 2[4)]



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No.	X	λ_{max} a)	SHG	PE
2a	C(CN)COOMe	320	A	7.5U
2b	C(CN)COOEt	345	A	0.2U
2c	C(CN)COPh	355	N	
2d	$C(CN)CONH_2$	381	N	
2e	N-Bu	389	A	0.8U

a) In benzene.

Molecular packings of some compounds were examined by X-ray crystal analyses.[6)] The crystal data of 1a, 1h, and 2a were summarized in Table 3.

Table 3. Crystal data of 1a, 1h, and 2a

Compound	1a	1h	2a
Formula	$C_{15}H_{22}O_2$	$C_{15}H_{23}NO_2$	$C_{19}H_{25}NO_3$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pmn2_1$	$Pna2_1$	$Pna2_1$
Cell dimension			
a/Å	18.58	9.68	12.20
b/Å	6.15	12.78	25.03
c/Å	6.10	12.24	6.03
$U/Å^3$	697	1514	1841
Z	2	4	4
D/gcm^{-3}	1.16	1.09	1.14
R	0.058	0.063	0.065
$(Mo\text{-}K\alpha)/cm^{-1}$	0.672	0.670	0.711
Measured reflections	973	2004	2466
Used reflections	136	168	192

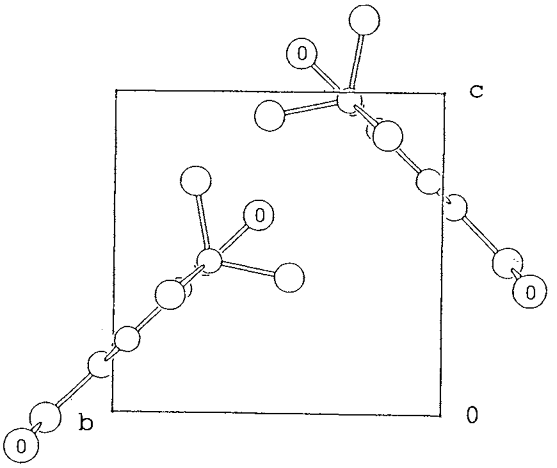

Fig. 1. Crystal structure of 1a viewed along the a-axis.

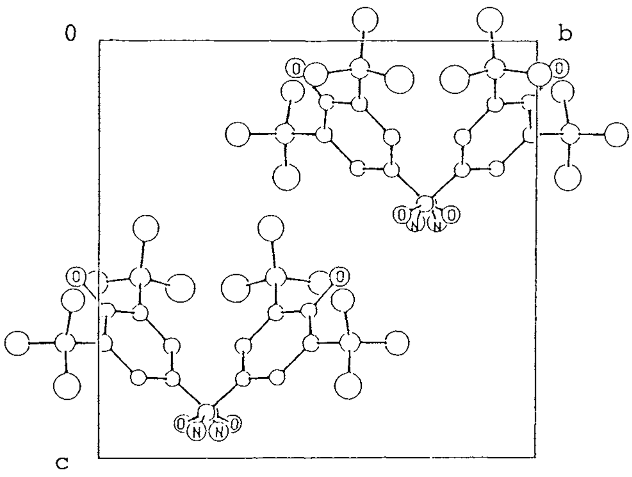

Fig. 2. Crystal structure of 1h viewed along the a-axis.

Fig. 1 and 2 showed crystal structures of the compounds(1a and 1h) projected along the a-axis. The methylester derivative(2a) projected along the b-axis is shown in Fig. 3. In every cases, intermolecular interactions of the hindered phenol moiety firstly contributed to effective molecular packing, and consequently the component of molecular dipole moment along to c-axis was remained, which caused the observed SHG efficiency. Intermolecular hydrogen bonding between the hydroxy group and the oxygen atom of the carbonyl group was suggested in 1a and 1h. Their distances were 2.56Å and 2.00Å, respectively. But there was no hydrogen bonding in 2a containing larger acceptor group. Thus, the X-ray analyses indicated that the strong van der Waals interaction of hindered phenol moiety and the intermolecular hydrogen bonding played a role in effective molecular packing to induce SHG response. However, larger substituent at 4-position disturbed the effective molecular packing by their steric requirements in crystals.

In this series, molecular arrangement was controlled by 2,6-di-tert-butylphenol moiety, depending on the size of acceptor group. As the PE values of **1h** and **2a** were quite different in spite of same space group of the crystals, the SHG efficiency was roughly influenced by the electron withdrawing effect of acceptor. Consequently, nitro group was the best substituent for large SHG response.

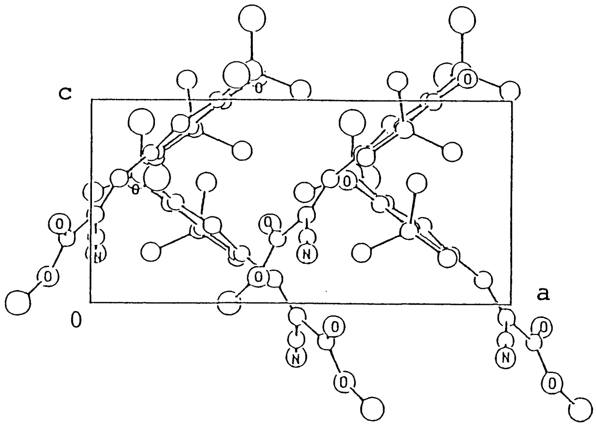

Fig. 3. Crystal structure of **2a** viewed along the b-axis.

References

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2) K.Takagi, A.Mizuno, K.Nakatsu, S.Abe, and M.Matsuoka, Nonlinear Optics, **1**, 31(1991).
3) Compound **1a** and **1g** were commercially available. Formyl derivatives were prepared by following method. W.E.Smith, J.Org.Chem., **37**, 3972(1972). Mp; **1b**, 114-116 °C; **1c**, 155-157 °C; **1d**, 116-117 °C: Nitro derivative(**1e**) was obtained by nitration of 2,6-di-tert-butylphenol with the mixture of acetic acid and nitric acid in hexane. Mp; 153-154 °C: Nitroso derivative (**1i**) was prepared by following method. G.M.Coppinger, Tetrahedron, **18**, 61(1962). Mp; 205-207 °C; Compound **1h** was prepared by reaction of acid chloride of **1g** with ammonia gas. Mp;250 °C(decompose); Compound **1j** was prepared by dehydration of **1h** with phosphorous pentaoxide. Mp;144-146 °C.
4) Mp;**2a**,100-101 °C; **2b**,98-101 °C; **2c**,144-145 °C; **2d**,201-203 °C; **2e**,119-121 °C.
5) 2,6-Di-tert-butyl-4-formylanisole(**3a**), mp;64-65 °C: 2,6-di-tert-butylphenol-4-nitroanisole(**3b**), mp; 54-56 °C.
6) X-Ray analyses were conducted by RIGAKU RASA-5R equipments and intensities were measured by a four-circle automatic diffractometer with Mo-Kα radiation. The structures were solved by the direct method using the program TEXSAN run on VAX station 3200.

(Received May 28, 1992)