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Nonlinear Optical Properties and Structure of Biphenyls Containing Donor-Acceptor Chromophores and Bulky Substituents

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Effects of various substituents including chromophores on the second harmonic generation(SHG) of biphenyls were examined. Among them, 4-hydroxy-3,5-di(t-butyl)-2',4'-dinitrobiphenyl(**1d**) exhibited effective SHG response. The X-ray structure of **1d** shows that the molecule is skewed around the 1-1' bond and the molecular arrangement along the c-axis in the space group of $Pca2_1$ is favorable for SHG.

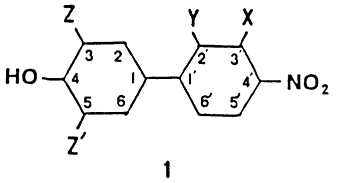
There is currently extensive interest in the nonlinear optical properties of organic compounds.$^{1)}$ Especially, the large second or third order nonlinear optical responses are important in the fields of optical device technology.$^{2)}$

The experimental searches of new organic materials possessing properties desirable for nonlinear optical devices have led almost exclusively to molecules with strong intramolecular charge-transfer functionality.$^{3)}$ The best-known examples contain an amino group as donor connected through a π-electron linkage to a nitro group as acceptor.$^{4)}$ However, macroscopic properties of an organic crystal must be also considered for the successful engineering with high second order nonlinear response.$^{5)}$

Some biphenyls have been studied for the SHG response. However, they hardly showed the SHG response, except a part of fluorene derivatives with an effective π-conjugate system.$^{6)}$ In this paper, the relationships between substituents and SHG efficiency are discussed for the biphenyls containing bulky substituents and donor-acceptor chromophores. The crystal structure of the compound showing SHG is also described.

The biphenyls were prepared by the method described in the literature.$^{7)}$ The compounds, **2** and **3**, were also prepared by similar methods.$^{8)}$ Some properties of the biphenyls are summarized in Table 1.

These compounds have a hydroxy group as donor and nitro or cyano groups as acceptor. The bulky alkyl groups at 3 and 5 positions were introduced to



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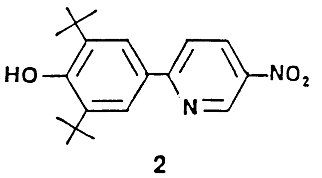

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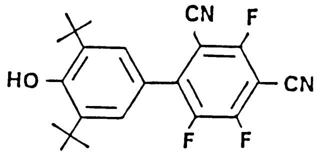

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Table 1. Absorption maximum and SHG efficiency of biphenyls

No.	Substituents X	Y	Z	Z'	λmax/nm a)	SHG efficiency b)
1a	H	H	t-Bu	t-Bu	343	—— c)
1b	H	CN	t-Bu	t-Bu	350	—— c)
1c	CN	H	t-Bu	t-Bu	360	—— c)
1d	H	NO_2	t-Bu	t-Bu	350	4.4
1e	H	NO_2	Me	Me	345	2.1
1f	H	NO_2	i-Pr	i-Pr	347	—— c)
1g	H	NO_2	Me	t-Bu	345	—— c)
2					360	—— c)
3					340	—— c)

a) Measured in benzene.

b) Measured by the powder method using YAG laser light(1064 nm). Values are against it of urea under arbitrary size of crystal.

c) SHG was not detected.

expect an asymmetric molecular arrangement in the crystal. As shown in Table 1, 1d exhibited SHG among the compounds(1a-1d, 2, and 3) containing the same donor moiety. Neither the compound 1b, in which 2'-nitro group is substituted with the 2'-cyano group, nor the compounds 1a, 1c, and 2 containing no 2'-nitro group exhibited SHG. Then, 2'-nitro group seems to play an important role for the molecular arrangement in the crystal. On the other hand, 1e, 3,5-dimethyl analogue of 1d, gave two crystalline forms when 1e was recrystallized from benzene; one showed an aggregated O-H stretching vibration at 3340 cm^{-1} and exhibited SHG but the other gave a free O-H stretching vibration at 3530 cm^{-1} and didn't exhibit it. Furthermore, both 1f and 1g, which have different alkyl substituents at 3 and 5 positions of 1e, didn't show SHG. They also showed free O-H streching vibrations at 3520 and 3540 cm^{-1}, respectively when they were recrystallized from benzene. These findings suggest that the alkyl substituents at the 3- and/or 5-positions also played an important role during molecular packing by the interaction between alkyl groups and solvent.

To elucidate the molecular structure and the packing mode of 1d in the crystal, an X-ray structure analysis has been carried out.

Slow evaporation of an acetone solution of 1d gave columnar yellow crystals.

Crystal data of $C_{20}H_{24}N_2O_5$(1d): M_r = 372.42; Orthorhombic, space group $Pca2_1$; unit cell dimensions, a = 11.490(1), b = 9.704(1), c = 17.482(1) Å, V = 1949.2(3) $Å^3$; D_x = 1.2691(2) g/cm^3; Z = 4. X-Ray intensities were collected on a four-circle diffractometer using Mo Kα radiation up to 55°. Altogether 2319 reflections were measured, of which 1780 reflections with $|F_0| > 3\sigma(|F_0|)$ were used for the structure determination. The structure was solved by the direct method using the program MULTAN 78,$^{9)}$ and was refined by the least-squares method. About half of the hydrogen atoms were found from a difference Fourier map, and the rest hydrogen atoms were located on the geometrical basis. In the final least-squares cycle all the hydrogen-atom parameters were fixed. The final residual index, R, was 0.076.

Bond distance(in Å)	
C(1)-C(1')	1.494(8)
C(2')-N(2)	1.457(7)
C(4')-N(1)	1.463(8)
C(3)-C(7)	1.554(9)
C(4)-O(1)	1.374(8)

Bond angle(in °)	
C(2)-C(3)-C(4)	116.9(5)
C(3)-C(4)-C(5)	123.2(5)
C(4)-C(5)-C(6)	117.2(5)
C(2')-C(1')-C(1)	125.1(5)
C(6')-C(1')-C(2')	116.2(5)
C(1')-C(2')-C(3')	122.8(5)
C(3')-C(2')-N(2)	115.5(5)

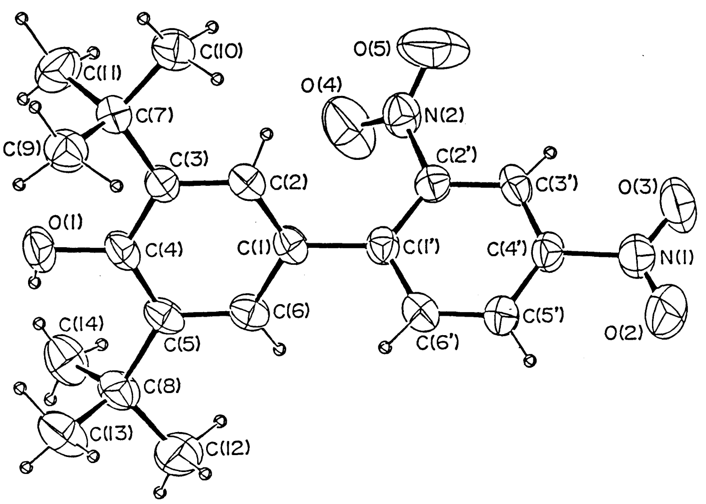

Fig. 1. A perspective view of 1d.

Figure 1 shows the molecular structure displayed by the thermal ellipsoids together with several selected bond lengths and angles. The two benzene rings are twisted by 57° to each other around the C(1)-C(1') bond, whose length of 1.494(8) Å is almost the same with that in biphenyl(1.49-1.51 Å)$^{10)}$ and corresponds to the single bond between the sp^2-carbon atoms. Thus no conjugation is recognized between the benzene rings. The NO_2 group bonded to the C(2') atom twists by 40° from the mother benzene ring. These twistings are mainly due to the steric hindrance between the C(2)-H group and the O(4) atom, the C(2)···O(4) distance being 3.17(1) Å. On the other hand, the NO_2 group at C(4') twists only slightly from the right benzene ring. The OH group seems to be not involved in any hydrogen bond owing to the adjacent two bulky tert-butyl groups.

Figure 2 shows the crystal structure projected down the b-axis. The molecular long axis, taken as the C(4)···C(4') direction, makes an angle of 48° with the c-axis or the polar 2_1-axis. Thus the component of the dipole moment of the molecule along the c-axis is not canceled out each other by neighboring molecules. This type of molecular arrangement along the 2_1-axis is a typical one in the SHG active crystals as is found in the crystals of space group $P2_1$ such as PAN,$^{11)}$ and should be understood as a favorable one for the observed SHG efficiency.

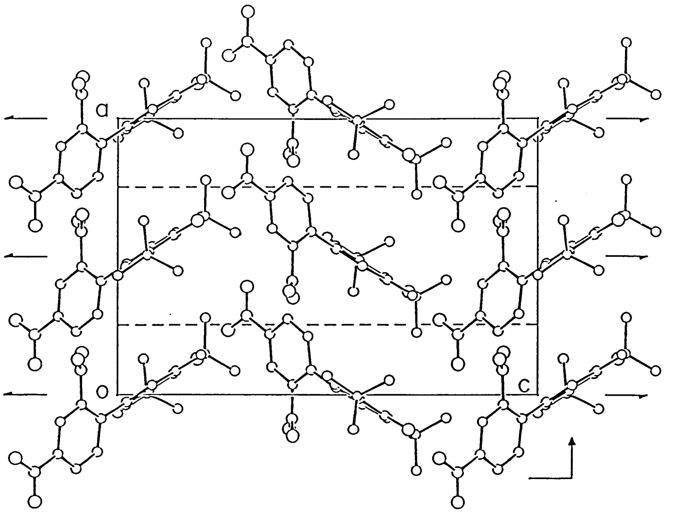

Fig. 2. Crystal structure of 1d viewed along the b-axis.

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8) Data of 2:mp 143-145°C(benzene);^{1}H-NMR(d^6-DMSO), δ(ppm) 1.46(8H,s), 7.44(2H,s), 7.47(1H,b); MS(relative intensity),m/e 328(M,27), 313(M-15,100).
Data of 3: mp 188-189°C(benzene);^{1}H-NMR(CDCl$_3$), δ(ppm) 1.52(18H,s), 5.59(1H,s), 7.79(1H,d,J=9.0 Hz), 7.94(2H,s), 8.45(1H,dd,J=9.0, 2.6 Hz), 9.44(1H,d,J=2.6 Hz); MS(relative intensity), m/e 386(M,27), 371(M-15,100).

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