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Molecular and Crystal Structures of 5-Nitrofuran-2-aldoxime and Thiophene Analogues as SHG Materials

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5-Nitrofuran-2-aldoxime (**1b**) exhibits crystallographic polymorphism. The isolated two crystals show SHG efficiency of 12 and 3 times that of urea. 5-Nitrothiophene-2-aldoxime (**2b**) shows weak SHG response because of the hypervalent interactions of O-S-O atoms. Two crystals of **1b** and **2b** belong to $P2_12_12_1$ space group.

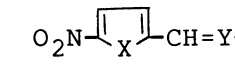
There is currently extensive interest in the nonlinear optical (NLO) properties of organic compounds.[1] Especially, the large second or third order NLO responses are important in the fields of optical device technology.[2]

The experimental searches of new organic materials possessing properties desirable for NLO devices have led almost exclusively to molecules with strong intramolecular charge-transfer (CT) functionality. Furthermore, crystal engineering to get noncentrosymmetric crystals must be also considered for high SHG response.

In this paper, molecular design of furan and thiophene derivatives, having large molecular hyperpolarizability (β) with intramolecular CT chromophore, was carried out by means of the PPP MO method using Oudar's equation.[3] The crystal structure was decided by the results of X-ray analysis to know the molecular packing. We intend to obtain the effective SHG crystals which can be used for the frequency doubling of the diode laser (780 - 830 nm), and the material should not absorb the light over 400 nm. The SHG efficiency and other properties of nitrofuran and nitrothiophene derivatives are summarized in Table 1.

2-Formyl-5-nitrofuran **1a** has very small β value because introduction of the two strong accepting groups, 5-nitro and 2-formyl groups, into the

Table 1. SHG efficiency and properties of nitrofuran and nitrothiophene derivatives



1: X=O
2: X=S

Dye No.	Substituent X	Y	Z	Mp θm/°C[a]	λ_{max}[b] nm		λ_{calcd}[d] nm	β[e] (×10^{-30}esu)	SHG[f] (PE)
1a	O	O		33-35	303		290	1.3	N
1b	O	N	OH	119.5-120.5	339	(410)[c]	322	24	12(3)
1c	O	N	OMe	120.5-121.5	334				N
2a	S	O		75-77	311				N
2b	S	N	OH	162-163	354	(420)[c]	347	31	0.5
2c	S	N	OMe	78-79	353				N

a) All compounds were identified by NMR and satisfactory elemental analyses were obtained.
b) Measured in ethanol.
c) Cutoff wavelength at the concentration of 1×10^{-4} mol l^{-1}.
d) Calculated by PPP MO method.
e) Calculated β values by PPP MO method at 1064 nm.
f) SHG efficiency was determined by a powder test method using YAG laser. Values of powder efficiency (PE) are against that of urea in arbitrary size of crystals. N denote that SHG was not detectable.

furan nucleus has no more intramolecular CT chromophoric system, and consequently no SHG response was observed. Similar results are also observed in thiophene analogue **2a**. The oxime **1b** has quite large β value by strong intramolecular CT chromophoric system calculated by the PPP MO method (Fig. 1).

The oxime **1b** showed crystallographic polymorphism and gave two types of SHG effective crystals; plate crystals from benzene (PE=12 U) and needle crystals from ethanol (PE=3 U). They can be isolated and have different physical properties[4] but come to equilibrium in solution under prolonged time. Plate crystals belong to the $P2_12_12_1$ space group from X-ray analysis. Needle crystals can not be analyzed because of its too small crystals in size. The packing is controlled by the intermolecular hydrogen bonding between the hydroxy group and the imino nitrogen. The methoxy derivative **1c**, having no ability to form the intermolecular hydrogen bonding, gives no SHG response. Similar result is also observed in **2c**. The thiophene analogue **2b** showed no polymorphism and gave only one type of crystals which belong to the $P2_12_12_1$ space group. Compound **2b** has SHG response of 0.5 U but its efficiency is very weak comparing with those of **1b**. The crystallographic data are summarized in Table 2. Accurate unit cell parameters were obtained with graphite-monochromatized Mo-Kα radiation (λ=0.71069 Å) from the least-squares treatment of high-angle 2θ reflections carefully measured

on a four-circle diffractometer.

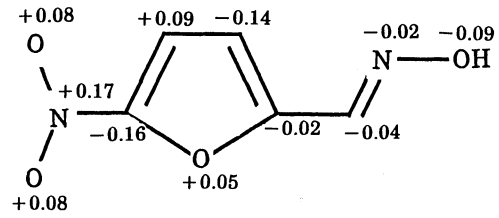


Fig. 1. π-Electron density changes accompanying the transition to the first excited singlet state in **1b**.

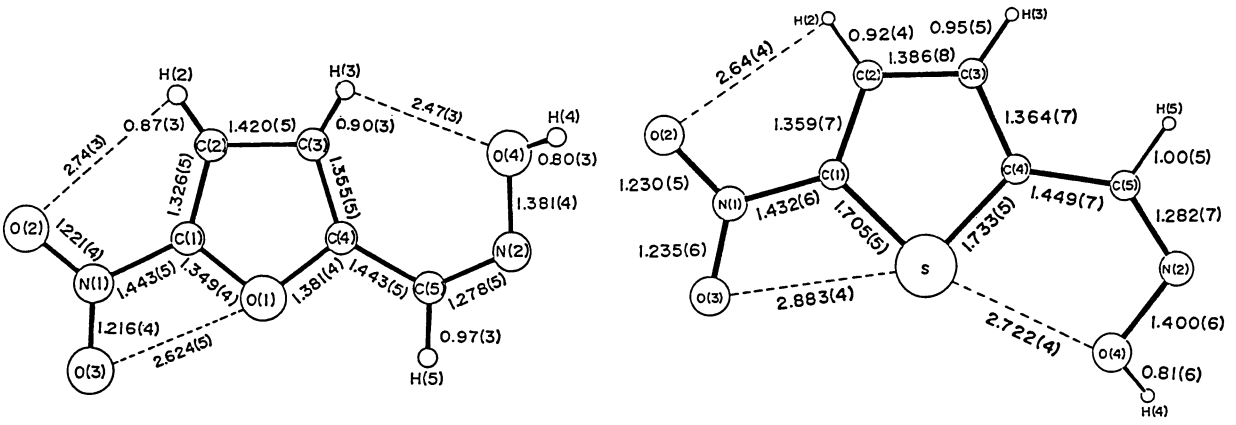
Table 2. Crystal data of **1b** and **2b**

Compound	**1b**	**2b**
Formula	$C_5H_4N_2O_4$	$C_5H_4N_2O_3S$
Formula weight	156.102(5)	172.164(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions		
a/Å	5.617(3)	5.791(3)
b/Å	21.17(1)	22.03(1)
c/Å	5.323(3)	5.366(1)
U/Å^3	633(2)	684.5(6)
Z	4	4
D_x/g cm^{-3}	1.623(5)	1.671(1)
D_m/g cm^{-3}	1.645	1.745
μ(Mo-Kα)/cm^{-1}	1.54	35.86

The structure of the crystals of **1b** was solved by the direct method using "MULTAN 78" program package. The final residual index R was 0.036. The structure of the crystals of **2b** was similarly done using "MONTEC-MULTAN" program package. The refinement converged to an R of 0.043.

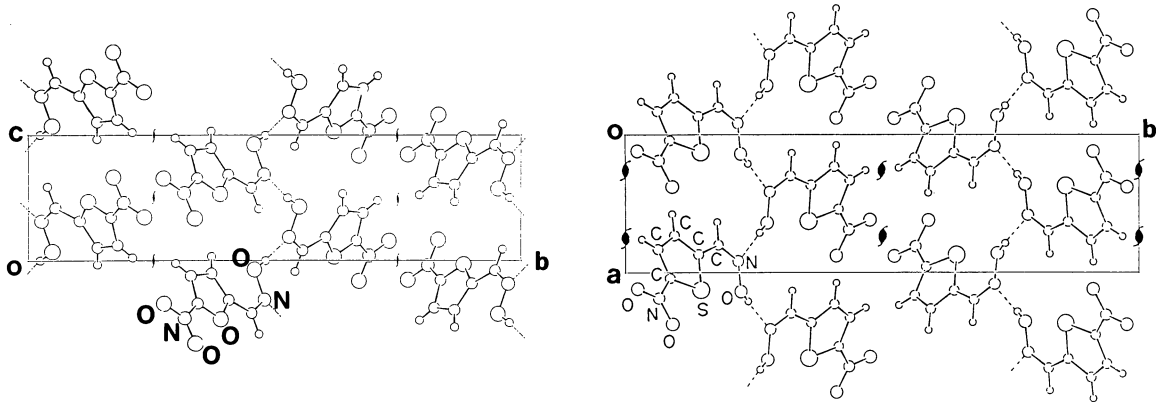
Figure 2 shows the molecular structures in **1b** (plate crystal) and **2b**. All atoms in the two molecules are roughly on a coplane. The furan-ring and the hydroxyl group of **1b** are located in positions cis to the double bond between C(5) and N(2), and O(1) and N(2) in positions trans to the single bond between C(4) and C(5). On the other hand, the thiophene-ring and the hydroxyl group of **2b** are also located in positions cis to the double bond between C(5) and N(2), but S and N(2) are in positions cis to the single bond between C(4) and C(5). There are conformational differences between **1b** and **2b**. The distance between S and O(3) is 2.883(4) Å, and that of S and O(4) is 2.722(4) Å. These are quite shorter than 3.35 Å which is the sum of the van der Waals radii of S and O. The angle of O(3)-S-O(4) is 146.6(1)°. Therefore, we proposed that the hypervalent interactions of O(3)-S-O(4)[5,6] may exist and they determine the cis-cis conformation of **2b**. This interaction decreased the intramolecular CT character and might cause to decrease SHG response in **2b**.

Figure 3 shows the $P2_12_12_1$ crystal structures of **1b** (plate crystal) and **2b**. Hydrogen bond exists between the hydrogen atom of the hydroxyl group and the nitrogen atom of the imino group, along the screw axis of the direction of the c axis (**1b**) and a axis (**2b**), respectively.



1b 2b

Fig. 2. Molecular structures and conformations of **1b**(plate crystal) and **2b**.



1b 2b

Fig. 3. Molecular packing of **1b** (plate crystal) and **2b**.

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4) Plate crystals : mp 156 - 158 °C ; ^{1}H NMR ($CDCl_3$) δ, 6.85 (1H, d), 7.37 (1H, d), 8.05 (1H, s). Needle crystals : mp 118 - 120 °C ; ^{1}H NMR ($CDCl_3$) δ, 7.39 (1H, d), 7.42 (1H, d), 7.57 (1H, s).
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