2-(1-Pyrrolyl, Diazolyl, and Triazolyl)-Substituted 5-Nitropyridines for Nonlinear Optical Materials

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2-Azolyl-5-nitropyridines (the generic name "azoles" is hereafter used for pyrrole, diazoles, and triazoles, and "azolyls" for any substituents derived from them) were examined from the viewpoints of the UV-vis absorption properties, the molecular hyperpolarizabilities (β), the second-harmonic generation (SHG) activities and the crystal structure compared with *N*-(4-nitrophenyl)azoles. In the azolyl-5-nitropyridines, although an expected remarkable hypsochromic shift of the absorption maxima (λ_{max}) was not observed, a hypsochromic shift of the absorption edge (λ_{cutoff}) was observed. All of derivatives discussed in the present paper, except for 2-(3,5-dimethyltriazolyl)-5-nitropyridine (**14**), did not show any SHG activity. The inactive results in SHG suggest that the displacement of benzene to pyridine causes a significant change in the molecular arrangement in the crystalline state. The phase-matchable property in the SHG of **14** is suggested by its crystal structure as well as an SHG experiment.

The blue-light second-harmonic generation (SHG) device is one of the desirable light sources used for optical-disk writing, because the memory density increases as the wavelength of the coherent light source becomes short. The SHG device needs, as an indispensable component, nonlinear optical (NLO) materials with some properties which are difficult to achieve. It has been believed that organic materials having π-conjugate systems with an electron donor and an acceptor are highly efficient NLO materials. For example, 2-methyl-4-nitroaniline [MNA] has an extremely large diagonal secondary nonlinear optical coefficient for SHG, d_{11} of 250 pm V^{-1}.[1] However, MNA is not a suitable material for blue-light SHG devices, because it absorbs blue light. Much effort has therefore been made in investigations of blue-light transparent NLO compounds.[2]

3,5-Dimethyl-1-(4-nitrophenyl)pyrazole [DMNP] has already been recognized as being an excellent compound showing phase-matching properties at 1064 nm (one of the off-diagonal secondary nonlinear optical coefficients for SHG, d_{32}=90 pm V^{-1}),[2—4] and realizes blue-light generation by using a cored fiber.[5] However, a further improvement in the blue-light transparency of the material is desired from viewpoints of the SHG efficiency and the light durability. It is well-known that the transformation of 4-nitroaniline (**1**) into 2-amino-5-nitropyridine (**2**) causes a hypsochromic shift of more than 30 nm in the absorption maximum for the lowest excitation.[6] This hypsochromic shift can be explained by using perturbation theory[7] for the frontier orbital, namely HOMO and LUMO. *N*-(4-Nitrophenyl)azoles (the generic name "azoles" is hereafter used for pyrrole, diazoles, and triazoles, and "azolyls" for the substituents derived from them), including DMNP as a representative derivative, have similar frontier molecular orbitals as those of 4-nitroaniline (Fig. 1).[2,3] By analogy with relationship between **1** and **2** from the viewpoint of perturbation theory, 2-azolyl-5-nitropyridines

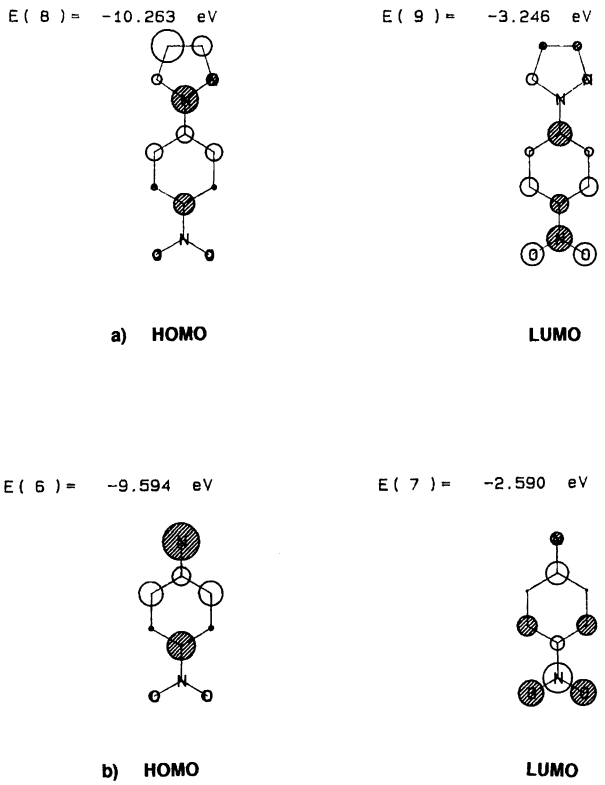

Fig. 1. a) HOMO and LUMO of 1-(nitrophenyl)pyrazole and b) HOMO and LUMO of 4-nitroaniline.

were expected to improve the blue-light transparency of the corresponding benzene derivatives, compared with *N*-(4-nitrophenyl)azoles based on the UV-vis absorption properties, secondary nonlinear optical properties, and crystal structure.

Results and Discussion

Light Absorption Properties in UV-vis Region. Four compounds of 2-azolyl-5-nitropyridine derivatives were synthesized and their light-absorption

properties in the UV-vis region were compared with those of the corresponding *N*-(4-nitrophenyl) azoles (Fig. 2). The observed values of the wavelength of each absorpsion maximum (λ_{max}) and the absorption edge (λ_{cutoff}) for the compounds are listed in Table 1. Surprisingly, these results do not indicate the expected hypsochromic shift, which was observed in the case of **2**. This behavior should be caused by a complex effect, such as a combination of annelation of the amino group with the conjugation ability of the azole moieties, since the conversion of 1-(4-nitrophenyl)-2-pyrrolidinemethanol [NPP] to 2-(2-hydroxymethyl-1-pyrrolidinyl)-5-nitropyridine [PNP] (Fig. 3), which is annelated by saturated carbon atoms, results in a hypsochromic shift.[8]

This behavior was considered based on molecular orbital theory. The calculated λ_{max} values by the PPP-CI MO method[9] are listed in Table 1. The calculated results did not indicate any hypsochromic shift, like that in the experimental results. Changes in energy levels of frontier molecular orbitals concerning the first excitation, however, showed a consistency with an expectation based on the parturbation theory (Table 2). We therefore supposed that a conformation interaction (CI) might participate in an electronic transition which

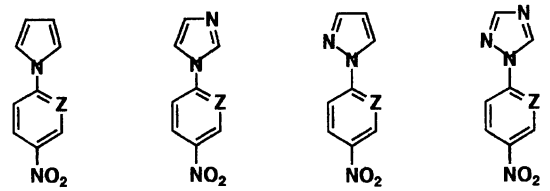

Fig. 2. Compounds used for the light absorption study.

Table 1. Comparison of Experimental and Calculated Light Absorption Properties between Pyridine and Benzene Derivatives

	λ_{max}/nm		λ_{cutoff}/nm[a]		Calcd λ_{max}/nm	
Azole/Z[b]	N	CH	N	CH	N	CH
Pyrrole	326	327	409	410	300	297
Imidazole	300	294	390	393	300	294
Pyrazole	312	312	396	399	305	303
1,2,4-Triazole	292	285	387	389	293	288
Amino	342	375			295	303

a) The 95% transmitted wavelength in 4×10^{-4} M ethanol solution (M=mol dm^{-3}). b) N indicates pyridine derivatives and CH indicates benzene derivatives.

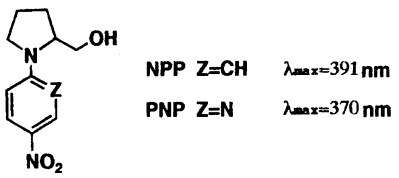

Fig. 3. Structures of NPP and PNP.

is different from the case of the corresponding *N*-(4-nitrophenyl)azole derivatives, like that mentioned in Adachi's study.[11] The CI characteristics of the pyridine and benzene derivatives of triazole are listed in Table 3. Decreases in the CI coefficient in transition 8 to 9, and the inversion of the phase in transitions 5 to 9, 6 to 9, and 7 to 9 were observed. These changes would cause the 2-azolyl-5-nitropyridines not to show any hypsochromic shift.

On the other hand, the values of λ_{cutoff} showed a slightly decreasing tendency (Table 1).

Nonlinear Optical Properties. 2-Azolyl-5-nitropyridine derivatives did not show the expected hypsochromic shift in λ_{max}, but did show a slight hypsochromic shift in λ_{cutoff}, which should increase the blue-light transparency. The transparency at the second-harmonic wavelength of NLO materials significantly affects the SHG efficiency, as suggested in Azéma's work.[12] Therefore, the 2-azolyl-5-nitropyridine derivatives were expected to be good nonlinear optical materials for blue-light SHG devices.

The molecular hyperpolarizabilities (β) of the four 2-azolyl-5-nitropyridines given in Table 1 were calculated. The calculated results are listed in Table 4 and compared with the values of *N*-(4-nitrophenyl)azoles. Although each of the values of the pyridine derivatives is fairly large, they are smaller than those of the corresponding benzene derivatives. The origin of β can be interpreted using the 2-level model equation (Eq. 1).[13]

$$\beta_{ct} = \frac{3e^2\hbar^2 W f \Delta\mu}{2m[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]}, \quad (1)$$

where, $\hbar\omega$: photon energy of LASER fundamental wave,
e: electronic charge,
m: mass of an electron,
W: transition energy for intramolecular CT,
f: oscilator strength for the intramolecular CT, and
$\Delta\mu$: change in dipolemoment by CT transition.

This equation indicates that the transition energy, oscillator strength (f) and change in the dipole moment due to excitation ($\Delta\mu$) are important factors, and that the increase in two factors, except for the transition energy, results in an enlargement of β. Only in the transition energy, the decrement results in an enlargement of β. The factors of f and $\Delta\mu$ of the derivatives are listed in Table 4. Both the f and $\Delta\mu$ values for the pyridine derivatives are smaller than those for the corresponding benzene derivatives. This tendency makes the β values of the pyridine derivatives smaller than those of the benzene derivatives, despite an advantage in the factor of the transition-energy effect.

By analogy of the relationship in the similarity between the crystal structure of NPP and PNP, whose skeletons are a benzene and a pyridine, respectively,[8] some of the 2-azolyl-5-nitropyridines were expected to

Table 2. Comparison of Calculated HOMO, LUMO, and Differences of Them (ΔE) between Pyridine and Benzene Derivatives

	HOMO/eV		LUMO/eV		ΔE/eV	
Azole/Z[b)]	N	CH	N	CH	N	CH
Pyrrole	−10.436[a)]	−10.317[a)]	−3.311	−3.255	7.125	7.062
Imidazole	−10.958[a)]	−10.856[a)]	−3.406	−3.345	7.552	7.511
Pyrazole	−10.383	−10.263	−3.304	−3.246	7.079	7.017
1,2,4-Triazole	−10.818	−10.692	−3.403	−3.338	7.415	7.354

a) Next HOMO. b) N indicates pyridine derivatives and CH indicates benzene derivatives.

Table 3. CI Characters of Compounds **6** and **10**

Transitions	**6**	**10**
8→9	0.911	0.952
1→9	0.001	—
2→9	0.038	0.035
3→9	−0.019	—
4→9	0.061	0.098
5→9	0.178	−0.016
6→9	−0.008	0.112
7→9	0.128	−0.084

be good NLO materials, since some of the *N*-(4-nitrophenyl)azoles, especially DMNP, have been found to be good NLO materials for blue-light SHG devices.[2,3,14)]

The SHG activity of five 2-azolyl-5-nitropyridine derivatives (Fig. 4) were examined using Kurtz's powder method.[15)] The results are given in Table 5. Surprisingly, almost all of the derivatives were found to be SHG inactive, except for one, despite the SHG activities of the corresponding *N*-(4-nitrophenyl)azoles. A noncentrosymmetric molecular arrangement is required for SHG activity. Therefore, the results given in Table 5 indicate that the molecular arrangement of each SHG inactive pyridine derivatives is centrosymmetric, and is different from that of the corresponding benzene derivatives.

Crystal Structure of 2-(3,5-Dimethyl-1*H*-1,2,4-triazolyl)-5-nitropyridine (14). The crystal structure of SHG-active 2-(3,5-dimethyl-1*H*-1,2,4-triazolyl)-5-nitropyridine (**14**) was analyzed in order to estimate the NLO ability of the crystal. The crystallographic data are listed in Table 6, and the crystal structure is shown in Fig. 5. Although the crystal space group of the pyridine derivative is identical with 3,5-dimethyl-1-(4-nitrophenyl)-1*H*-1,2,4-triazole [DMNT],[14)] the molecular arrangement is considarably different. This result also indicates that a displacement of the benzene ring to the pyridine ring produces a considerable difference in the molecular size, and therefore causes changes in the molecular arrangement.

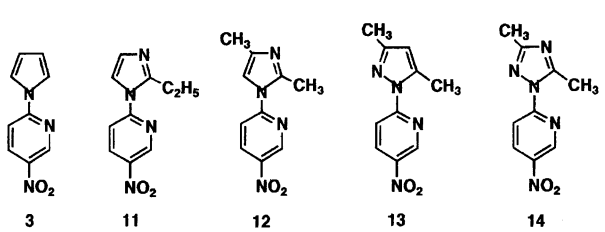

Fig. 4. Compounds used for the SHG study.

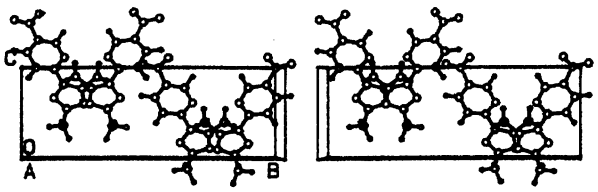

Fig. 5. The crystal structure of **14** viewed down the *a* axis.

The difference in the molecular arrangement influences the nonlinear optical coefficients for SHG (d_{ij}). The values of d_{ij} calculated based on the oriented gas model[16)] are listed in Table 7 and compared with the d_{ij} of DMNT.[14)] Both the increasing tendency in d_{33} and the decreasing tendency in d_{32} of **4** are suggested to be caused by the smaller incline angle of the molecular long axis from the *c*-axis of the crystal than that of DMNT.

A large single crystal (ca. 10×5×3 mm^3) was easily obtained from *N*,*N*-dimethylformamide by a method which involves cooling a saturated solution. The crystal showed phase-matchable SHG upon the irradiation of a Nd:YAG laser beam (1064 nm).

Conclusion

Although 2-azolyl-5-nitropyridines did not show the expected hypsochromic shift of absorption maxima, it improved the blue-light transparency, which is one of the valuable properties for those NLO materials which are suitable for blue-light SHG devices. The displacement of the benzene ring of *N*-(4-nitrophenyl)azoles to the pyridine rings also had an effect on the nonlinear optical properties. One was to reduce the molecular hyperpolarizability, the other was to change the SHG activity in the crystalline state, which would be caused by a change in the molecular arrangement. This effect was also clarified by a comparison of the crystal structure of 2-(3,5-dimethyl-1*H*-1,2,4-triazolyl)-5-nitropyridine (**14**) with that of DMNT. By using the crystallo-

Table 4. Comparison of Calculated Molecular Hyperpolarizabilities (β) and Components of Them between Pyridine and Benzene Derivatives

Azole/Z[c]	N			CH		
	$\beta/10^{-30}$esu	f[a]	$\Delta\mu$/D[b]	$\beta/10^{-30}$esu	f[a]	$\Delta\mu$/D[b]
Pyrrole	22.2	0.853	14.44	22.2	0.904	16.91
Imidazole	26.4	0.434	20.07	31.7	0.484	21.44
		0.264	12.99		0.421	15.29
		0.235	9.09			
Pyrazole	22.1	0.924	14.48	27.5	0.966	16.22
1,2,4-Triazole	12.3	0.804	9.32	18.5	0.929	11.34

a) Oscillator strength. b) The change of dipolemoment in excitation. c) N indicates pyridine derivatives and CH indicates benzene derivatives.

Table 5. Linear and Nonlinear Optical Properties of Pyridine Derivatives

Compounds	SHG[a]	λ_{max}/nm	λ_{cutoff}/nm
3	0	326	409
11	0	292	393
12	0	292	406
13	0	323	417
14	14	298	389

a) Relative efficiency vs. urea (=1) at 1064 nm (Nd:YAG).

Table 6. Crystallographic Data of **14** and DMNT

		14	DMNT
Crystal system		Orthorhombic	Orthorhombic
Space group		$Pna2_1$	$Pca2_1$
Point group		$mm2$	$mm2$
R-factor		0.047 for 882 unique reflections	0.081 for 1991 unique reflections
Cell constant	a/Å	8.054	62.046
	b/Å	18.790	3.891
	c/Å	6.557	12.678
	v/Å^3	992.3	3060.7
	z	4	12
D_x/g cm^3		1.47	1.42

Table 7. Calculated Values of d_{ij} of **14** and DMNT[a]

	14	DMNT
d_{31}/pm V^{-1}	8.4	9.2
d_{32}/pm V^{-1}	17.3	45.8
d_{33}/pm V^{-1}	46.1	17.8

a) Values of local field factors were employed that of DMNP.[14]

graphic data, the nonlinear optical coefficients for SHG (d_{ij}) were calculated based on the oriented gas model. In this calculation, the d_{32} value is smaller than that of DMNT. A large single crystal was easily obtained, and showed phase-matchable SHG.

An improved blue-light transparency, a phase-matchable property in SHG, and easy crystal growth of **14** will promise that **14** becomes an excellent NLO material for blue-light SHG devices.

Experimental

Material. Synthesis of 2-(2-Ethyl-1-imidazolyl)-5-nitropyridine (11): A mixture of 2-chloro-5-nitropyridine (15.9 g (0.1 mol)), 2-ethylimidazole (9.60 g (0.1 mol)), triethylamine (20 ml), and acetonitrile (100 ml) in a 200 ml flask was heated and refluxed for 20 h under stirring. The reaction mixture was then cooled and poured into ice-water; the pricipitated crystals were filtered and dried. The crude materials were recrystallized three times from 2-propanol and the compound was obtained as slightly yellow colored crystals. Yield 6.4 g (29.3%), mp=142.5—143.5 °C. ^{1}H NMR (DMSO-d_6) δ=1.32 (t, 3H), 3.01 (q, 2H), 7.02 (d, 1H), 7.75 (d, 1H), 7.90 (d, 1H), 8.76 (dd, 1H), and 9.35 (d, 1H). Element Analysis. Found: C, 55.05; H, 4.70; N, 25.65%. Calcd for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68%.

Synthesis of 2-(3,5-Dimethyl-1*H*-1,2,4-triazolyl)-5-nitropyridine (14): A mixture of 2-chloro-5-nitropyridine (9.30 g (58 mmol)), 3,5-dimethyl-1*H*-1,2,4-triazole (5.69 g (58 mmol)), potassium carbonate (8.10 g (58 mmol)), and dimethyl sulfoxide (30 ml) in a 100 ml flask was heated at 40—50 °C for 6 h under stirring. The reaction mixture was then poured into ice-water, and the pricipitated crystals were filtered and dried. The crude materials were recrystallized twice from acetone and the compound was obtained as slightly yellow colored crystals. Yield 5.4 g (42%), mp=147—148°C. ^{1}H NMR ($CDCl_3$) δ=2.43 (s, 3H), 2.91 (s, 3H), 8.12 (d, 1H), 8.62 (dd, 1H), and 9.32 (d, 1H). Element Analysis. Found: C, 49.54; H, 4.02; N, 31.92%. Calcd for $C_9H_9N_5O_2$: C, 49.32; H, 4.14; N, 31.95%.

Other compounds were synthesized in the same manner as the above-mentioned methods. The data concerning the melting points and ^{1}H NMR are listed in Table 8.

Calculations of MO and β. PPP-CI MO calculations were carried out under the following conditions:

1) The bond lengths of the N–O of the nitro group are 1.2 Å. All of the others are 1.4 Å.

2) All of the bond angles are 120°, except for those related to the azole rings. The azole rings are regarded as being right pentagons.

3) All of the molecules have a planar structure.

4) The resonance integrals were evaluated iteratively using a linear relationship with the calculated bond orders (the

Table 8. Data of Melting Point and ^{1}H NMR of Compounds Used for the Study

Compounds	Mp/°C	^{1}H NMR (δ/ppm in $CDCl_3$)
3	167—168	6.43 (s, 2H), 7.58 (s, 2H), 7.40 (d,1H), 8.52 (d, 1H), 9.30 (s, 1H)
4	218—220	7.29 (s, 1H), 8.16 (s, 1H), 8.17 (d, 1H), 8.76 (s, 1H), 8.87 (d,1H), 9.39 (s, 1H)
5	189—190	6.69 (s, 1H), 7.98 (s, 1H), 8.13 (d, 1H), 8.73 (s, 1H), 8.80 (d,1H), 9.30 (s, 1H)
6	210—211	8.19 (d, 1H), 8.49 (s, 1H), 8.92 (d, 1H), 9.43 (s, 1H), 9.58 (s, 1H)
12	133—134	2.25 (s, 3H), 2.70 (s, 3H), 7.12 (s, 1H), 7.44 (d, 1H), 8.60 (d, 1H), 9.36 (s, 1H)
13	102—105	2.32 (s, 3H), 2.73 (s, 3H), 6.09 (s, 1H), 8.13 (d, 1H), 8.52 (d, 1H), 9.25 (s, 1H)

variable β method).[17]

5) The repulsion integrals were estimated using the Nishimoto–Mataga formula.[18]

The values of β were calculated based on Ward's equation[19] by using the MO calculation results.

Crystal Structure Analysis. The crystal of 2-(3,5-dimethyl-1*H*-1,2,4-triazolyl)-5-nitropyridine (**14**) used for the analysis was prepared by the evaporation method from a tetrahydrofuran (THF) solution. A $0.35\times0.25\times0.15$ mm^3 crystal was employed for an X-ray intensity measurement. The measurement was carried out on an Enraf–Nonius CAD4 four-circle diffractometer at room temperature with Cu $K\alpha$ radiation. The structures were solved using the program package TEXAN.

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