Absorption and Fluorescence Spectra of 4, 7-Di (alkoxy-substituted) pheny1-1, 2, 5-thiadiazolo [3, 4-c] pyridine

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Absorption and Fluorescence Spectra of 4, 7-Di (alkoxy-substituted) phenyl-1, 2, 5-thiadiazolo [3, 4-c] pyridine

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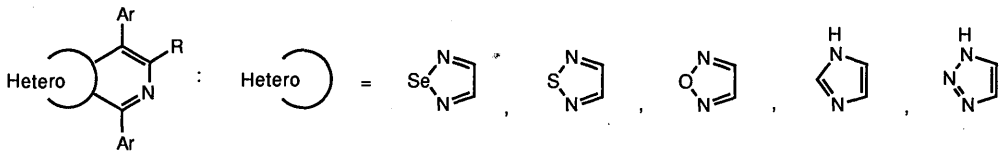
A series of 4, 7-Di (alkoxy-substituted) phenyl-1,2,5-thiadiazolo[3, 4-c]pyridines were prepared and their absorption and fluorescence spectre were obatined. These compounds showed a large stokes shift of 115—135 nm and 6-aryl derivatives and 6-alkoxycarbonyl ones are strongly fluorescent in a solid state.

Introducrtion

Recently, electroluminescence (EL)[1] and a liquid crystalline property[2] of organic substance have been attracting attentions as a possible candidate for a large area flat panel display device of next generation. Much efforts have been devoted in searching for strongly fluorescent organic dyes which work as a light emitting source of an EL display device.

Previously, it was reported the preparation of di- and triphenylpyridine derivatives annelated by 5- and 6-membered heterocyles such as 1, 2, 5-thiadiazole, 1, 2, 5-oxadiazole, 1, 2, 3-triazole, imidazole, and pyrazine (Scheme 1).[3] Of these, 1, 2, 5-thiadiazolo- and 1, 2, 5-oxadiazolo[3, 4-c]pyridine are strongly fluorescent in a solid state and, as a dyestuff, the former is superior to the latter in the durablity.[4]

As a part of our studies on fluorescent heterocycles, we now report on the fluorescence of alkoxy-substituted 4, 6, 7-tri- and 4, 7-diaryl-1, 2, 5-thiadiazolo[3, 4-c]pyridines.



[Scheme 1]

Results and discussion

Triaryl derivaties (**1**) were prepared by the condensation reaction of 3, 4-diaroyl-1, 2, 5-thiadiazole (**2**) with corresponding arylmethylamine in the presence of a base catalyst as

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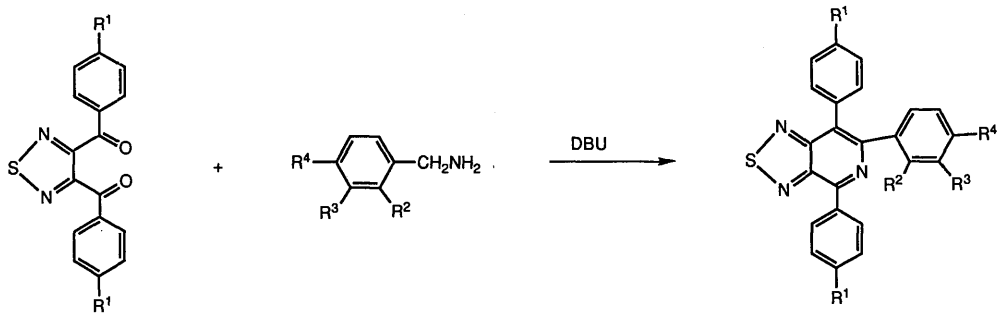

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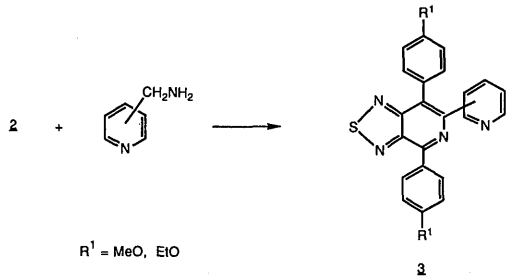
R^1 = MeO, EtO, BuO, H ; R^2 ~ R^4 = MeO, H, Cl, CH_3

[Scheme 2]



R^1 = MeO, EtO

3

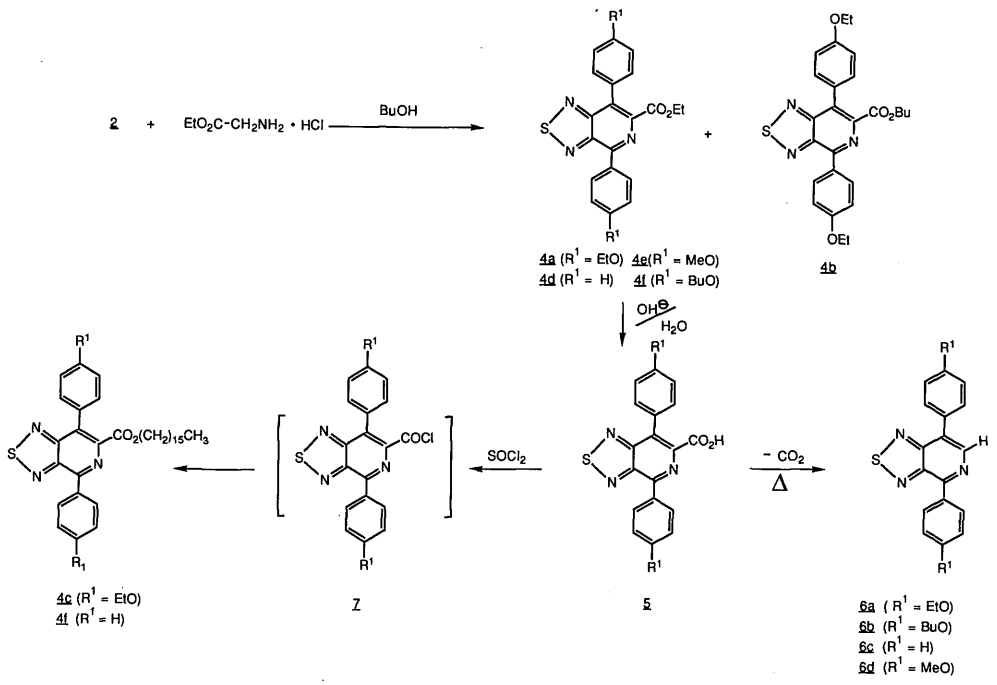
[Scheme 3]

previously reported (Scheme 2).[5] Pyridyl derivative (**3**) was similarly prepared (Scheme 3).

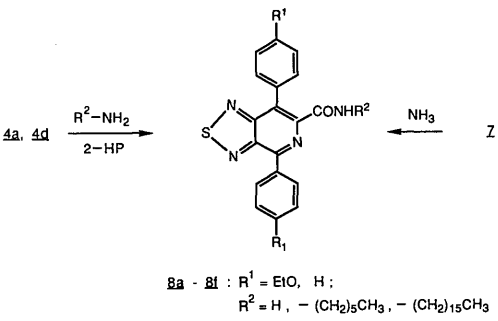
Compounds (**4, 5,** and **6**) were prepared according to Scheme 4. Ethyl ester (**4a**) was prepared by the reaction of the corresponding **2** with ethyl glycinate hydrochloride in refluxing butanol.[6] Ester-exchanged (**4b**) was obtained in a small amount in this reaction. Hydrolysis of **4a** and **4d** under basic conditions afforded carboxylic acid (**5a**) and (**5b**), which were converted to ester (**4c**) and (**4f**), respectively, via acid chloride (**7a**) and (**7b**). Diaryl derivative (**6**) was prepared by thermal decarboxylation of **5**. Primary amide (**8a**) and (**8d**) were prepared by the reaction of **7a** and **7b** with ammonia, respectively, and secondary amide (**8b**), (**8c**), (**8e**), and (**8f**) by the one of ester (**4**) with the corresponding primary amine in the presence of 2-hydroxypyridine (2-HP)[7] (Scheme 5).

The absorption and fluorescence spectral data of alkoxysubstituted (**1a-n, 3, 4a-c, 5a, 6a-b,** and **8a-c**) were summarized in **Tables 1-4.** For comparison, those of 4, 7-diphenyl (**1o-p, 4d-f, 6c,** and **8d-f**) are also given.

Color-deepening effect of alkoxy group on organic compounds are well known. In the absorption spectra of the compounds prepared above, one alkoxy group on para-position of phenyl group on 4-, 6-, and 7-position caused a bathochromic shift of an average of 13—17 nm in the absorption band. On the other hand, the shift by meta- and ortho-alkoxy group of phenyl ring on 6-position are small. Bathochromic solvent effect, which is characteristic



[Scheme 4]



[Scheme 5]

for $\pi \rightarrow \pi^*$ excitation, was observed (**Table 1-3**).

The λ_{max} values of **5a**, **6a**, and **8b** in a solid state were very similar to those in cyclohexane solution. Triaryl (**1i**) formed a glassy amorphous solid on spontaneous evaporation of its methylene chloride solution. The absorption of this solid was observed at 10 nm longer wave length than the one in cyclohexane. The amorphous solid of 4-methoxy (**1i**) are stable at room temperature in air and it took three months for crystallization. Each amorpous solid of 3-methoxy (**1g**) and 2-methoxy (**1c**) was less stable than that of **1i** and crystallized within a month. Ester (**4c**) also formed a glassy solid, which gradually crystallized and, after two weeks, its absorption spectrum was very similar to that of crys-

Table 1. Absorption and emission spectra of 4, 6, 7-triaryl-1, 2, 5-thiadiazolo[3, 4-c]pyridine (**1**)[a].

	Substance				Absorption		Emission[b]		
1	R^1	R^2	R^3	R^4	λ max,	nm (log ε)	λ max,	nm (rel. int.)[c]	Stokes shift, nm
a	MeO	H	H	H	436	(4.04)	564	(8)	128
b	EtO	H	H	H	439	(4.06)	565	(10)	126
c	MeO	MeO	H	H	435	(4.04)	559	(9)	124
d	EtO	MeO	H	H	435	(4.05)	562	(12)	127
e	EtO	Cl	H	H	432	(4.18)	557	(13)	125
f	BuO	MeO	H	H	436	(4.06)	562	(12)	126
g	MeO	H	MeO	H	436	(4.02)	563	(8)	127
h	EtO	H	MeO	H	435	(4.03)	564	(10)	129
i	MeO	H	H	MeO	444	(3.87)	568	(6)	124
j	EtO	H	H	MeO	446	(4.02)	574	(5)	128
k	EtO	H	H	Me	442	(4.04)	567	(7)	125
l	MeO	H	MeO	MeO	445	(3.99)	568	(5)	123
m	EtO	H	MeO	MeO	446	(4.01)	570	(5)	124
n	BuO	H	MeO	MeO	447	(3.99)	572	(4)	125
o	H	H	H	H	405	(3.94)	530	(16)	125
p	H	H	MeO	H	424	(3.87)	547	(12)	123

a) Solvent: $CHCl_3$. b) Concentration of the substrate: $1.25\sim2.33\times10^{-5}$ mol/l.
c) Normalized by such a way that intensity of **8e** is 1.0 with correction of the concentration.

Table 2. Absorption and emission spectra of 4, 7-diaryl-6-pyridyl-1, 2, 5-thiadiazolo[3, 4-c]pyridine (**3**)[a].

	Substance		Absorption		Emission[b]		
	R	Py	λ max,	nm (log ε)	λ max,	nm (rel. int.)[c]	Stokes shift, nm
a	MeO	4-Pyridyl	431	(4.10)	558	(14)	127
b	MeO	3-Pyridyl	433	(4.06)	558	(15)	125
c	EtO	4-Pyridyl	432	(4.08)	560	(16)	128
d	EtO	3-Pyridyl	434	(4.08)	561	(13)	127

a) Solvent: $CHCl_3$. b) Concentration of the substrate: $1.62\sim2.08\times10^{-5}$ mol/l.
c) Normalized by such a way that intensity of **8e** is 1.0 with correction of the concentration.

talline (**4c**). The absorption band of primary amide (**8a**) in the solid state were observed at 10 nm longer wave length region than those in cyclohexane, suggesting the presence of an intermolecular attactive interaction in a crystalline state (**Table 4**).

Introduction of alkoxy groups in an aromatic nuclai, especially on para-position, tends to weaken the fluorescence (**Table 1**) and the relative intensity of the fluorescence of having three para-alkoxy substituted phenyl groups is almost one-third of that of triphenyl (**1o**). Pyridine ring seems to strengthen the fluorescence of **3,** since it exhibited the fluorescence of almost similar intensity with **1o** having no methoxy group. Compounds **1** and **3** having aryl or pyridyl group on 6-position showed a large stokes shift of 125 ± 4 nm.

As shown in **Table 3**, ester (**4**) is strongly fluorescent. The stokes shift of alkoxyphenyl derivative (**4a**), (**4b**), and (**4c**) were about 10 nm larger than those of the corres-

Table 3. Absorption and emission spectra[a] of 4, 7-diaryl-1, 2, 5-thiadiazolo [3,4-c]pyridine **4, 5, 6,** and **8**.

	Substance		Absorption		Emission[b]		
			λ max,	nm (log ε)	λ max,	nm (rel. int.)[c]	Stokes shift, nm
	R^1	Ester					
4a	EtO	EtO_2C	429	(4.12)	556	(21)	127
4b	EtO	BuO_2C	429	(4.13)	555	(21)	126
4c	EtO	$Me(CH_2)_{15}O_2C$	430	(4.14)	555	(23)	125
4d	H	MeO_2C	385	(4.00)	501	(36)	116
4e	H	EtO_2C	386	(4.00)	502	(35)	116
4f	H	$Me(CH_2)_{15}O_2C$	358	(4.03)	500	(40)	115
	R^1	Acid					
5a	EtO		438	(4.16)	557	(3)	119
	R^1	Diaryl					
6a	EtO		437	(4.14)	563	(16)	126
6b	BuO		437	(4.14)	564	(10)	127
6c	H		397	(4.02)	512	(36)	115
	R^1	Amide					
8a	EtO	H_2NCO	430	(4.05)	561	(3)	131
8b	EtO	$Me(CH_2)_{15}NHCO$	428	(4.04)	562	(2)	134
8c	EtO	$Me(CH_2)_5NHCO$	429	(4.01)	562	(2)	133
8d	H	H_2NCO	384	(4.02)	507	(2)	123
8e	H	$Me(CH_2)_{15}NHCO$	384	(3.90)	508	(1)	124
8f	H	$Me(CH_2)_5NHCO$	384	(4.03)	509	(1)	125

a) Solvent: $CHCl_3$. b) Concentration of the substrate: $0.61\sim1.76\times10^{-5}$ mol/l.
c) Normalized by such a way that intensity of **8e** is 1.0 with correction of the concentration.

Table 4. Absorption spectra of 4, 7-di (p-ethoxyphenyl)-1, 2, 5-thiadiazolo [3, 4-c] pyridine in solution and in a solid phase.

Compound	λ max (nm)				
	in CH_3CN	in MeOH	in $CHCl_3$	in c-C_6H_{12}	Solid phase[a]
1i	433	438	446	450	466 (glass)[b]
4c	415	420	429	433	444 (glass)[c]
5a	420	426	438	443	437
6a	426	430	438	441	442
8a	418	423	430	—[d]	456
8b	417	420	429	438	439

a) Prepared by casting the corresponding CH_2Cl_2 solution on glass plate and evaporating the solvent spontaneously.
b) Glassy state was stable in the air at ambident temperature for more than 2 months.
c) After standing for two weeks at room temperature, it crystallized (λ max=434 nm).
d) Insoluble in this solvent.

ponding phenyl one (**4d**), (**4e**), and (**4f**), but the fluorescent intensity was weakened (almost a half) by introduction of alkoxy group. Nevertheless, alkoxy-substituted (**4a**), (**4b**), and (**4c**) are more strongly fluorescent than triphenyl (**1o**). The Stokes shift

values of weakly fluorescent amide (**8a-8f**) are over 130 nm.

In 6-unsubstituted (**6**), alkoxy-substituted (**6a**) and (**6b**) showed a large stokes shift but are less fluorescent than diphenyl derivative (**6c**).

A study on electroluminescent properties of triaryl derivative (**1**), especially **1o** whose amorphous state are stable, is in progress[8] and the details will be published elesewhere.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko A-102 and IR-700 spectrophotometer as KBr pellets. ^{1}H-NMR (internal Me_4Si) spectre in $CDCl_3$ were taken on a JEOL FX-100 (at 100 MHz) and GSX-270 (at 270 MHz) NMR spectrometer unless otherwise stated. Mass spectra were recorded on a JMS-O1SG-2 mass spectrometer at 75 eV using a direct-inlet system. Absorption and emission spectra were measured on a Hitachi 220A spectrophotometer and a Hitachi F-4010 fluorescence spectrophotometer, respectively. Column chromatography was carried out on silica gel (Wako gel, C-300).

Materials. Preparation of **1a-1d**,[9] **1f-1j**,[9] **1l-1n**[9], **1o**,[5] **4d-e**,[6] and **6c**[3] were previously reported.

Preparation of 1 and 3. Compounds, **1e**, **1k**, and **1p**, were prepared by condensation reaction of diaroyl-1,2,5-thiadiazole (**2**) with corresponding arylamine derivative in the presence of DBU in xylene at reflux for 24 h according to the procedure reported previously.[5] Physical and spectral properties of newly prepared **1** and **3** are given below.

4, 7-Di(p-ethoxyphenyl)-6-(o-chlorophenyl)-1,2,5-thiadiazolo[3, 4-c]pyridine (1e): Yield 62%; yellow needles (ethanol): mp 178−180 ℃; ^{1}H NMR δ =1.36 (3H, t, J=7 Hz), 1.40 (3H, t, J=7 Hz), 3.97 (2H, q, J=7 Hz), 4.04 (2H, q, J=7 Hz), 6.74 (2H, dd, J=8 and 2 Hz), 6.97 (2H, dd, J=8 and 2 Hz), 7.00−7.48 (6H, m) and 8.58 (2H, dd, J=8 and 2 Hz); MS m/z 489, 487 (M^+).

Found: C, 66.32; H, 4.37; N, 8.67%. Anal. Calcd for $C_{27}H_{22}ClN_3O_2S$: C, 66.45; H, 4.54; N, 8.61%.

4, 7-Di(p-ethoxyphenyl)-6-(p-methylphenyl)-1,2,5-thiadiazolo[3, 4-c]pyridine (1k): Yield 78%; yellow needles (ethanol): mp 215−217 ℃; ^{1}H NMR δ =1.42 (3H, t, J=7 Hz), 1.48 (3H, t, J=7 Hz), 2.36 (3H, s), 4.08 (2H, q, J=7 Hz), 4.14 (2H, q, J=7 Hz), 6.92 (2H, dd, J=9 and 2 Hz), 7.08 (2H, dd, J=9 and 2 Hz), 7.10 (2H, dd, J=9 and 2 Hz), 7.36 (2H, dd, J=9 and 2 Hz), 7.52 (2H, dd, J=9 and 2 Hz), and 8.78 (2H, dd, J=9 and 2 Hz) MS m/z 467 (M^+).

Found: C, 72.09; H, 5.43; N, 8.82%. Anal. Calcd for $C_{28}H_{25}N_3O_2S$: C, 71.92; H, 5.39; N, 8.99%.

4, 7-Diphenyl-6-(p-methoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine (1p): Yield 86%; yellow needles (ethanol); mp 210−211 ℃; MS m/z 395 (M^+).

Found: C, 72.97; H, 4.52; N, 10.29%. Anal. Calcd for $C_{24}H_{17}N_3OS$: C, 72.90; H, 4.33; N, 10.63%.

4, 7-Di(p-methoxyphenyl)-6-(pyridin-4-yl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine (3a): Yield 38%; yellow needles (ethanol); mp 192 ℃; ^{1}H NMR δ =3.80 (3H, s), 3.88 (3H, s), 6.85 (2H, dd, J=9 and 2), 7.02 (2H, dd, J=9 and 2 Hz), 7.34 (2H, dd, J=9 and 2 Hz), 7.04

(2H, dd, J=4 and 2 Hz), 8.46 (2H, dd, J=4 and 2 Hz), and 8.65 (2H, dd, J=9 and 2 Hz); MS m/z 426 (M^+).

Found: C, 67.34; H, 4.10; N, 13.01%. Anal. Calcd for $C_{24}H_{18}N_4O_2S$: C, 67.58; H, 4.25; N, 13.14%.

4, 7-Di(p-methoxyphenyl)-6-(pyridin-3-yl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine (3b): Yield 58%; yellow prisms (ethanol); mp 214−216 ℃; ^{1}H NMR δ=3.84 (3H, s), 3.92 (3H, s), 6.85−7.40 (7H, m), 7.88 (1H, ddd, J=8, 2, and 2 Hz), 8.48 (1H, dd, J=5 and 2 Hz), 8.72 (2H, dd, J=9 and 2 Hz), and 8.80 (1H, m); MS m/z 426 (M^1).

Found: C, 67.60; H, 4.08; N, 13.16%. Anal. Calcd for $C_{24}H_{18}N_4O_2S$: C, 67.58; H, 4.25; N, 13.14%.

4, 7-Di(p-ethoxyphenyl)-6-(pyridin-4-yl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine (3c): Yield 18%; yellow needles (ethanol): mp 208−210 ℃; ^{1}H NMR δ=1.42 (3H, t, J=7 Hz), 1.45 (3H, t, J=7 Hz), 4.08 (2H, q, J=7 Hz), 4.15 (2H, q, J=7 Hz), 6.90 (2H, dd, J=9 and 2 Hz), 7.06 (2H, dd, J=9 and 2 Hz), 7.31 (2H, dd, J=9 and 2 Hz), 7.50 (2H, dd, J=4 and 2 Hz), 8.52 (2H, dd, J=4 and 2 Hz), and 8.72 (2H, dd, J=9 and 2 Hz); MS m/z 453 (M^+-1).

Found: C, 68.68; H, 4.91; N, 12.43%. Anal. Calcd for $C_{26}H_{22}N_4O_2S$: C, 68.71; H, 4.88; N, 12.33%.

4, 7-Di (p-ethoxyphenyl)-6-(pyridin-3-yl)-1,2,5-thiadiazolo[3, 4-c]pyridine (3d): Yield 32%; a mixture of yellow needles (mp 174-176 ℃) and orange prisms (mp 114 ℃) (ethanol): ^{1}H NMR δ=1.44 (3H, t, J=6 Hz), 1.48 (3H, t, J=6 Hz), 4.06 (2H, q, J=6 Hz), 4.16 (2H, q, J=6 Hz), 6.92 (2H, dd J=8 and 2 Hz), 7.09 (2H, dd J=8 and 2 Hz), 7.20−7.28 (1H, m), 7.36 (2H, dd J=8 and 2 Hz), 7.88 (1H, dt, J=8 and 2 Hz), 8.51 (1H, d, J=5 and 2 Hz), 8.78 (2H, dd, J=8 and 2 Hz), and 8.88 (1H, dd, J=2 and 1 Hz); MS m/z 454 (M^+).

Found: C, 68.94; H, 4.86; N, 12.37%. Anal. Calcd for $C_{26}H_{22}N_4O_2S$: C, 68.71; H, 4.88; N, 12.33%.

Preparation of 4a and 4b. After a mixture of 3, 4-di (p-ethoxybenzoyl) -1,2,5-thiadiazole (**2d**) (500 mg, 13 mmol) and ethyl glycinate hydrogen chloride (2.50 g, 20 mmol) in butanol (25 cm^3) was refluxed for 72 h, it was poured into water (300 cm^3) and extracted with benzene (50 cm^3). The extract was dried over $MgSO_4$ and evaporated in vacuo, leaving the residue which, on column chromatography, afforded **butyl 4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxylate (4b)** (60 mg, 10%) and **ethyl 4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxylate (4a)** (500 mg, 80%). Recrystallization of **4a** from hexane afforded yellow needles; mp 142−143 ℃; IR 1720 cm^{-1}; ^{1}H NMR δ=1.12 (3H, t, J=7 Hz), 1.44 (3H, t, J=7 Hz), 1.46 (3H, t, J=7 Hz), 4.08 (2H, q, J=7 Hz), 4.12 (2H, q, J=7 Hz), 4.24 (2H, q, J=7 Hz), 7.00 (2H, dd, J=9 and 2 Hz), 7.02 (2H, dd, J=9 and 2 Hz), 7.52 (2H, dd, J=9 and 2 Hz), and 8.68 (2H, dd, J=9 and 2 Hz); MS m/z 449 (M^+).

Found: C, 64.05; H, 5.12; N, 9.38%. Anal. Calcd for $C_{24}H_{23}N_3O_4S$: C, 64.12; H, 5.16; N, 9.35%.

Compound **4b** was recrystallized from hexane, giving orange prisms; mp 85−87 ℃; IR 1720 cm^{-1}; ^{1}H NMR δ=0.80 (3H, t, J=7 Hz), 1.00−1.36 (4H, m), 1.44 (6H, t, J=7 Hz), 4.08 (2H, q, J=7 Hz), 4.12 (2H, q, J=7 Hz), 4.16 (2H, q, J=7 Hz), 7.00 (2H, dd, J=9 and 2 Hz), 7.06 (2H, dd, J=9 and 2 Hz), 7.52 (2H, dd, J=9 and 2 Hz), and 8.68 (2H, dd, J=9

and 2 Hz); MS m/z 477 (M^+).

Found: C, 65.79; H, 5.61; N, 8.78%. Anal. Calcd for $C_{26}H_{27}N_3O_4S$: C, 65.39; H, 5.70; N, 8.80%.

Hydrolysis of 4a. After a mixture of **4a** (300 mg, 0.7 mmol) and NaOH (300 mg, 75 mmol) in ethanol (60 cm^3) was refluxed for 3 h, it was poured into water (50 cm^3) and acidified with conc. hydrochloric acid. Yellow precipitates were collected by filtration and recrystallized from ethanol, giving **4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c] pryidine-6-carboxylic acid (5a)** (260 mg, 93%) as orange needles; mp 185 − 189℃ (decomp); ^{1}H NMR δ =1.44 (3H, t, J=7 Hz), 1.48 (3H, t, J=7 Hz), 4.00 (2H, q, J=7 Hz), 4.07 (2H, q, J=7 Hz), 6.90 (2H, dd, J=9 and 2 Hz), 6.98 (2H, dd, J=9 and 2 Hz), 7.34 (2H, dd, J=9 and 2 Hz), and 8.43 (2H, dd, J=9 and 2 Hz); MS m/z 421 (M^+).

Found: C, 62.50; H, 4.44; N, 9.86%. Anal. Calcd for $C_{22}H_{19}N_3O_4S$: C, 62.54; H, 4.53; N, 9.95%.

Preparation of 4c and 4f. Typical procedure. After a mixture of **5a** (100 mg, 0.3 mmol) and thionyl chloride (2 cm^3) was heated at 70 ℃ for 2h, thionyl chloride was evaporated in vacuo. To the resultant residue, a mixture of cetyl alcohol (100 mg, 0.4 mmol) and benzene (5 cm^3) was added and the whole mixture was heated at reflux for 20h. The reaction mixture was condensed, chromatographed using CH_2Cl_2 as an eluant, and recrystallized from ethanol to afford **cetyl 4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c] pyridine-6-carboxylate (4c)** (100 mg, 56%) as orange prisms: mp 80−82 ℃; IR 1730 cm^{-1}; ^{1}H NMR δ =0.88 (3H, t, J=6 Hz), 1.10−1.54 (28H, br s), 1.46 (3H, t, J=6 Hz), 1.48 (3H, t, J=6 Hz), 4.06−4.24 (6H, m), 7.03 (2H, dd, J=8 and 2 Hz), 7.07 (2H, dd, J=8 and 2 Hz), 7.56 (2H, dd, J=8 and 2H), and 8.72 (2H, dd, J=8 and 2 Hz); MS m/z 645 (M^+).

Found: C, 70.86; H, 7.96; N, 6.44%. Anal. Calcd for $C_{38}H_{51}N_3O_4S$: C, 70.66; H, 7.96; N, 6.51%.

Similary, **5b** (100 mg, 0.3 mmol) was derived to **cetyl 4, 7-diphenyl-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxylate (4f)** (80 mg, 33%): green needles (ethanol); mp 74 −76 ℃; IR 1740 cm^{-1}; ^{1}H NMR δ =0.88 (3H, t, J=6 Hz), 1.05−1.48 (28H, br m), 4.17 (2H, t, J=6 Hz), 7.04−7.60 (8H, m), and 8.65−8.75 (2H, m); MS m/z 557 (M^+).

Found: C, 73.26; H, 7.88; N, 7.31%. Anal. Calcd for $C_{34}H_{43}N_3O_2S$: C, 73.21; H, 7.77; N, 7.53%.

Preparation of 6a. After a mixture of 3, 4-di(p-ethoxyphenyl)-1, 2, 5-thiadiazole (**2b**) (1.00 g, 26 mmol) and ethyl gycinate hydrogen chloride (11 g, 78 mmol) in ethylene glycol (70 cm^3) was refluxed for 40h, precipitates were collected by filtration, washed with ethanol, and column-chromatographed with benzene as an eluant, affording **ω-hydroxyethyl 4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxylate (4g)** (0.27 g, 27%) and **4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine (6a)** (0.30 g, 31%). Recrystallization of **4g** from ethanol afforded orange prisms; mp 180−183 ℃; IR 3440, 1739 cm^{-1}; ^{1}H NMR δ =1.43 (3H, t, J=7 Hz), 1.44 (3H, t, J=7 Hz), 1.72 (1H, t, D_2O-ehanged, J =6 Hz), 3.64 (2H, m), 4.12 (2H, q, J=7 Hz), 4.14 (2H, q, J=7 Hz), 4.32 (2H, t, J=5 Hz), 7.06 (2H, dd, J=8 and 2 Hz), 7.08 (2H, dd, J=8 and 2 Hz), 7.57 (2H, dd, J=8 and 2 Hz), and 8.70 (2H, dd, J = 8 and 2 Hz); ^{13}C NMR δ = 14.8, 60.7, 63.6, 67.4, 114.6, 114.7, 126.1, 126.4, 128.6, 131.0, 131.9, 143.4, 149.7, 151.3, 158.4, 159.7, 161.4, and 167.5; MS

m/z 421 ($M^+ - CO_2$).

Found: C, 62.12; H, 4.90; N, 9.01%. Anal. Calcd for $C_{24}H_{23}N_3O_5S$: C, 61.92; H, 4.98; N, 9.03%.

Compound **6a** was recrystallized from ethanol, giving yellow prisms; mp 192−194 ℃; ^{1}H NMR δ =1.44 (6H, t, J=7 Hz), 4.12 (2H, q, J=7 Hz), 4.14 (2H, q, J=7 Hz), 7.04 (4H, dd, J=8 and 2 Hz), 7.92 (2H, dd, J=8 and 2 Hz), 8.57 (2H, dd, J=8 and 2 Hz), and 8.70 (1H, s); MS m/z 377 (M^+).

Found: C, 66.65; H, 4.93; N, 11.00%. Anal. Calcd for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13%.

Preparation of 6b. A mixture of ethyl ester and butyl derivative were prepared by the reaction of butoxy (**2c**) with ethyl glycinate hydrogen chloride in refluxing ethanol according to the procedure described in the preparation of **4a**. It was hydrolyzed as described in the hydrolysis of **4a**. Without purification, the crude carboxylic acid was pyrolyzed in glass tube oven at 200 ℃ for 30 min and the pyrolysate was chromatographed. The CH_2Cl_2-elution was evaporated and the residue was recrystallized.

4, 7-Di(p-butoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine (6b): Total yield 55%; orange prisms (ethanol): mp 116−149 ℃; ^{1}H NMR δ =1.00 (6H, t, J=6 Hz), 1.30−1.80 (8H, m), 4.08 (2H, t, J=6 Hz), 4.09 (2H, t, J=6 Hz), 7.04 (4H, dd, J=8 and 2 Hz), 7.09 (2H, dd, J=8 and 2 Hz), 8.57 (2H, dd, J=8 and 2 Hz), and 8.68 (1H, s); MS m/z 433 (M^+).

Found: C, 69.25; H, 6.28; N, 9.68%. Anal. Calcd for $C_{25}H_{27}N_3O_2S$: C, 69.16; H, 6.28; N, 9.48%.

Preparation of 8a and 8d. General procedure. After a mixture of **5** (0.3 mmol) and thionyl chloride (2 cm^3) was heated at 70 ℃ ror 2h, it was poured into an ice-cold conc. aqueous ammonia (20 cm^3) and stirred for 5h at room temperature. Precipitates were collected by filtration and recrystallized.

4, 7-Di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxamide (8a): Yield 88%; orange prisms (CH_2Cl_2): mp 252−253 ℃; IR 3374, 3200, 1656 cm^{-1}; ^{1}H NMR δ = 1.46 (3H, t, J=6 Hz), 1.49 (3H, t, J=7 Hz), 4.17 (2H, q, J=6 Hz), 5.60 (1H, br s, D_2O-exchanged), 7.05 (2H, dd, J=8 and 2 Hz), 7.15 (2H, dd, J=8 and 2 Hz), 7.49 (2H, dd, J=8 and 2 Hz), 7.72 (1H, br s, D_2O-exchanged), and 8.63 (2H, dd, J=8 and 2 Hz); MS m/Hz 420 (M^+).

Found: C, 62.58; H, 4.89; N, 13.19%. Anal. Calcd for $C_{22}H_{20}N_4O_3S$: C, 62.84; H, 4.79; N, 13.33%.

4, 7-Diphenyl-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxamide (8d): Yield 66%; green prisms (ethanol): mp 220−223 ℃; IR 3384, 3320, 3200, 1670 cm^{-1}; ^{1}H NMR δ =5.80 (1H, br s, D_2O-exchanged), 7.45−7.70 (8H, m), 7.80 (1H, br s, D_2O-exchanged), and 8.45 −8.70 (2H, m); MS m/z 332 (M^+).

Found: C, 65.00; H, 3.86; N, 16.82%. Anal. Calcd for $C_{18}H_{12}N_4OS$: C, 65.00; H, 3.64; N, 16.84%.

Preparation of 8b, 8c, 8e, and 8f. Typical procedure. A mixture of **4a** (100 mg, 0.2 mmol), cetylamine (200 mg, 2 mmol), and 2-hydroxypyridine (20 mg, 0.2 mmol) was heated at 100 ℃ for 3h, cooled to room temperature, chromatographed using CH_2Cl_2 as an eluante, and recrystallized from ethanol, giving **N-cetyl-4, 7-di(p-ethoxyphenyl)-1, 2, 5-**

thiadiazolo[3, 4-c]pyridine-6-carboxamide (8b) as orange needles: Yield 66%; mp 150—152 ℃; IR 3278, 3126, 1649 cm^{-1}; ^{1}H NMR δ =0.85 (3H, t, J=7 Hz), 1.20—1.50 (28H, m), 1.45 (3H, t, J=7 Hz), 1.49 (3H, dd, J=7 Hz), 3.42 (2H,q, J=7 Hz), 4.12 (2H, q, J=7 Hz), 4.15 (2H,q, J=7 Hz), 7.03 (2H, dd, J=8 and 2 Hz), 7.11 (2H, dd, J=8 and 2 Hz), 7.45 (2H, dd, J=8 and 2 Hz), 8.00 (1H, br s, D_2O-exchanged), and 8.65 (2H, dd, J=8 and 2 Hz); MS m/z 664 (M^+).

Found: C, 70.61; H, 8.09; N, 8.52%. Anal. Calcd for $C_{38}H_{52}N_4O_3S$: C, 70.77; H, 8.13; N, 8.69%.

Compounds, **8c, 8e,** and **8f**, were similarly prepared and their physical and spectral properties are given below.

N-Hexyl-4, 7-di(p-ethoxyphenyl)-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxamide (8c): Yield 79%; orange needles (ethanol); mp 172—174 ℃; IR 3284, 1648 cm^{-1}; ^{1}H NMR δ =0.90 (3H, t, J=6 Hz), 1.25—1.50 (6H, m), 1.45 (3H, t, J=7 Hz), 1.49 (3H, t, J=7 Hz), 1.54—1.68 (2H, m), 3.43 (2H, q, J=6 Hz), 4.11 (2H, q, J=6 Hz), 4.14 (2H, q, J=7 Hz), 7.03 (2H, dd, J=8 and 2 Hz), 7.10 (2H, dd, J=8 and 2 Hz), 7.45 (2H, dd, J=8 and 2 Hz), 8.00 (1H, t, D_2O-exchanged, J=5 Hz), and 8.63 (2H, dd, J=8 and 2 Hz); MS m/z 504 (M^+).

Found: C, 66.74; H, 6.58; N, 11.03%. Anal. Calcd for $C_{28}H_{32}N_4O_3S$: C, 66.64; H, 6.39; N, 11.10%.

N-Cetyl-4,7-diphenyl-1, 2, 5-thiadiazolo[3, 4-c]pyridine-6-carboxamide (8e): Yield 62%; greenish yellow needles (ethanol): mp 132—134 ℃; IR 3294, 1651 cm^{-1}; ^{1}H NMR δ = 0.87 (3H, t, J=6 Hz), 1.25 (26H, br s), 1.62 (2H, q, J=6 Hz), 3.43 (2H, q, J=7 Hz), 7.46 —6.60 (8H, m), 8.14 (1H, t, D_2 O-exchanged, J=5 Hz), and 8.58—8.65 (2H, m); MS m/z 556 (M^+).

Found: C, 73.10; H, 8.09; N, 9.83%. Anal. Calcd for $C_{34}H_{44}N_4OS$: C, 73.34; H, 7.97; N, 10.06%.

N-Hexyl-4,7-diphenyl-1,2,5-thiadiazolo[3, 4-c]pyridine-6-carboxamide (8f): Yield 69%; greenish yellow needles (ethanol): mp 148—150 ℃; IR 3294, 1651 cm^{-1}; ^{1}H NMR δ = 0.88 (3H, t, J=7 Hz), 1.20—1.60 (8H, br m), 3.40 (2H, q, J=6 Hz), 7.45 (5H, s), 7.55—7.65 (3H, m), 8.08 (1H, br s, D_2O-exchanged), and 8.45—8.60 (2H, m); MS m/z 416 (M^+).

Found: C, 69.35; H, 5.76; N, 13.37%. Anal. Calcd for $C_{24}H_{24}N_4OS$: C, 69.20; H, 5.81; N, 13.45%.

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