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Synthesis and Fluorescence of 2-pyrone Derivatives for Electroluminescence Devices

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Abstract: A convenient method of synthesizing 6-aryl- and 6-styryl-4-methylsulfanyl-2-oxo-2*H*-pyran derivatives through the reactions of various active methylene compounds with ketene dithioacetals and investigation of the fluorescence of the products in the solid state are described. The structure-activity relationships of various 2-pyrone derivatives and the effects of different aryl and styryl substituents on the aryl group were clarified. Materials which are strongly fluorescent in the primary colors (red, green, and blue) are the most important materials in the field of organic electroluminescence (EL). The 2-pyrone derivatives synthesized in this work emitted light at 447 ~ 620 nm in the solid state.

Key Words: *ketene dithioacetal, 2-pyrone, fluorescence, heterocycle, electroluminescence*

1. INTRODUCTION

The continuation of scientific progress means that new materials are constantly being developed. However, this can sometimes result in harm to the environment. The development of materials whose use results in a reduction in energy consumption has become increasingly urgent in recent years.[1] The use of fluorescent materials in organic synthesis can result in a reduction in power consumption and hence is an effective way of reducing environmental load. Fluorescent compounds have been applied in various types of high-sensitivity analysis.[2] Effective utilization of resources in analysis may result in a reduction in the quantity of waste material produced, which has an effect not only on the environment but also in economic terms, contributing to the building of a sustainable society. The development of environmentally friendly materials and technologies is urgent if we are to avoid contributing to the deterioration of the global environment.

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Organic electroluminescent (EL) materials which show fluorescence in the solid state have recently been the subject of attention.[3] Possible applications for these materials include replacement of liquid crystal displays, which are currently widely used.[4] Fluorescent dyes are currently of interest for various applications, such as emitters for electroluminescence devices in copy-prevention technologies, materials for collecting solar energy, fluorescent films for greenhouses, and fluorescent colorants for use in various fields.[2,5] Heteroaromatic compounds have been investigated because various fluorescent pigments may be designed based on these materials.[6] It is possible that the use of heterocycles will reduce environ-mental load by replacing the corresponding inorganic luminescent materials, many of which contain trace metals; in addition, heterocycles are relatively easy to dispose of.[6, 7, 8]

We previously investigated chemiluminescence reagents based on luminol, which allowed high-sensitivity analysis of enzymes and active oxygen.[7] That study was the start of our research into fluorescent organic compounds. Since then, we have synthesized many heterocyclic compounds

using ketene dithioacetals,[9] some of which showed fluorescence. One of these, a 2-pyrone derivative whose synthesis was first reported in 1976, showed strong fluorescence in the solid state.[10, 11] Coumarins, which are benzopyran derivatives in which a benzene ring is fused with a pyrone moiety, are known to show strong fluorescence in solution.[12] Chemical compounds which show fluorescence are generally polycyclic aromatic and multiaryl-substituted compounds;[13] thus, it was predicted that fluorescence would be observed in aryl 2*H*-pyran-2-one derivatives such as 6-phenyl-4-methylsulfanyl-2*H*-pyran-2-ones (Figure 1).

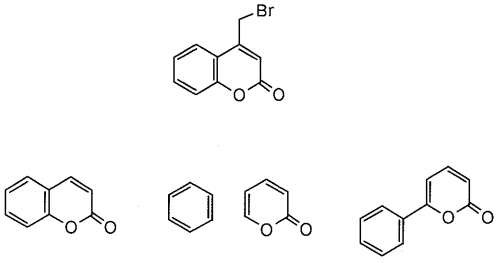


Figure 1

Several 4*H*-pyrone derivatives have already been shown to have interesting EL properties.[14] This suggested to us that 2-pyrones may show red EL, which has thus far proved very difficult to harness. First, we investigated 6-aryl- and 6-styryl-2*H*-pyran-2-ones, which show fluorescence in the solid state and have been the subject of attention as potential EL sources. Pyrones and fused pyrones are important in the design of luminescent materials for organic light-emitting diodes (OLED). In particular, 2-pyrones containing an aryl group at the 6-position have potential for use in optoelectronic devices such as displays, and continue to attract considerable interest in both synthetic and materials chemistry.[2] Komatsu *et al.* reported that the presence of a phenyl group at position 6 in 3,4,6-triphenyl-2-pyrones is important for fluorescence (Figure 2).[15]

In order to elucidate the structure-activity relationship of 2-pyrones containing functional groups at various positions, we synthesized and compared these compounds, which have been reported to show fluorescence in the solid state and have attracted attention as potential EL sources.

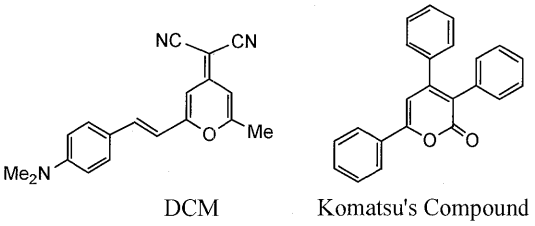


Figure 2

In 1976, it was reported that 2-pyrone derivatives might be easily obtained *via* the reaction of ketene dithioacetals with active methylene or methyl compounds in the presence of an appropriate base.[11] However, at that time, fluorescence was not among the observed chemical and physical properties of these pyrone derivatives.[16]

2. SYNTHESIS OF 2-PYRONES

The usefulness of ketene dithioacetal derivatives in the synthesis of heterocyclic compounds has already been reported by the author, who has hitherto demonstrated many examples.[9] Typical ketene dithioacetals used for this purpose are shown in Figure 3.

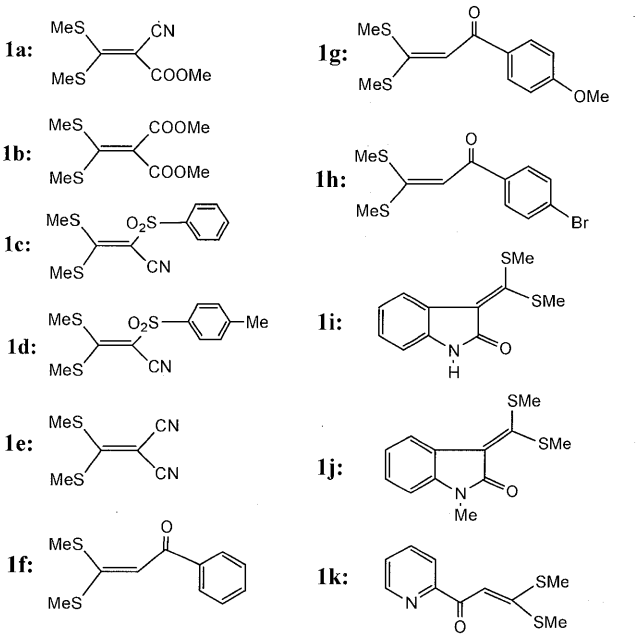


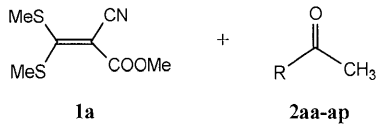
Figure 3

In this study, in order to elucidate structure-activity relationships for all substituents of the prepared 2-pyrone derivatives, and to clarify the effects of aryl groups with various substituents at

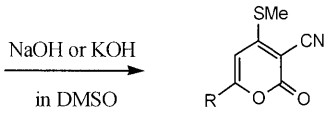
position 6, many more compounds were required compared to the previous study. Therefore, many new 2-pyrone derivatives were synthesized, and the method of synthesis was also slightly improved. A convenient method of producing 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles (**3aa-ap**) *via* the reaction of various methyl-ketones (**2aa-ap**) with ketene dithioacetal **1a** (methyl 2-cyano-3,3-bis(methylsulfanyl)acrylate) has been reported.[17b] These reactions occur smoothly in DMSO in the presence of potassium hydroxide as a base.

However, in this case the reaction was carried out in the presence of sodium hydroxide rather than potassium hydroxide to obtain a slightly better yield. The reaction of **2ai** with **1a** gave the desired product 6-(4-dimethylaminophenyl)-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (**3ai**) in 43% yield.[18a] In a manner similar, heteroaryl acetyl compounds **2ba-bg** were reacted with **1a** to give 6-heteroaryl-2-oxo-2*H*-pyran-3-carbonitriles **3ba-bg** in yields of 23 – 84% (see Scheme 1and 2).[17b, 19]

Scheme 1



1a **2aa-ap**

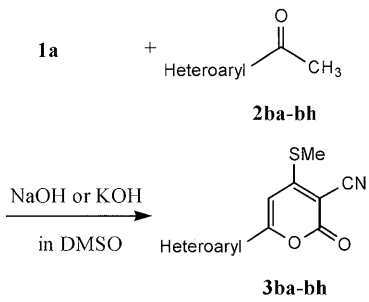


3aa-ap

R	Yield(%)	R	Yield(%)
3aa: C_6H_5	61(48)	**3ai**: C_6H_4-NMe_2(4)	43
ab: C_6H_4-OMe(2)	58	**aj**: C_6H_4-Br(4)	(42)
ac: C_6H_4-OMe(3)	64(35)	**ak**: C_6H_4-Cl(2)	65
ad: C_6H_4-OMe(4)	58	**al**: C_6H_4-Cl(4)	(42)
ae: C_6H_3-$(OMe)_2$(2,4)	33	**am**: C_6H_4-Ph(4)	88
af: C_6H_3-$(OMe)_2$(2,5)	27	**an**: C_6H_4-CN(4)	66
ag: C_6H_3-$(OMe)_2$(3,4)	(40)	**ao**: 1-naphthyl	58
ah: C_6H_2-$(OMe)_3$(3,4,5)	56	**ap**: 2-naphthyl	75

Benzalacetone derivatives **2ca-cf** also reacted with **1a** to give the corresponding 6-styryl-2-oxo-2*H*-pyran-3-carbonitriles **3ca-cf** in 26 – 45% yield.[17, 18a] The structures of these 2-pyrone derivatives resemble that of DCM: (4-(dicyano-methylene)-2-methyl-6-(4-*N*,*N*-dimethylaminostyryl)-4*H*-pyran), which is an interesting organic EL compound.

Scheme 2

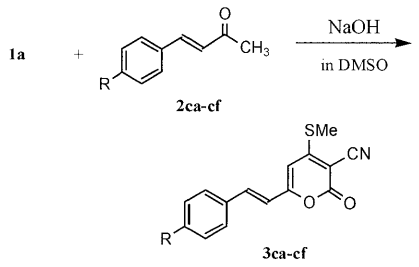


R	Yield(%)	R	Yield(%)
3ba: 2-pyridyl	(23)	**3be**: 2-benzothienyl	84
bb: 3-pyridyl	(58)	**bf**: 2-furyl	30
bc: 4-pyridyl	50	**bg**: 2-furyl-Me(5)	(44)
bd: 2-thienyl	68(44)		

This suggested that 2*H*-pyrans might also show useful EL and that the resulting fluorescence might be red (one of the most important properties in the field of EL). In fact, 6-(4-*N*,*N*-disubstituted styryl)-2-oxo-2*H* -pyran-3-carbonitriles **3cd-cf** did show red fluorescence in dichloromethane solution. The acetyl compounds 4-(*N*,*N*-disubstituted aminophenyl)but-3-en-2-ones (**2cd-cf**) also reacted with **1a** in a manner similar to that described for the preparation of **3aa**, and the corresponding 6-[2-(4-*N*,*N*-disubstituted aminophenyl)vinyl]-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles **3ca-cf** were obtained in 32, 26, and 29% yield, respectively (see Scheme 3).[18a]

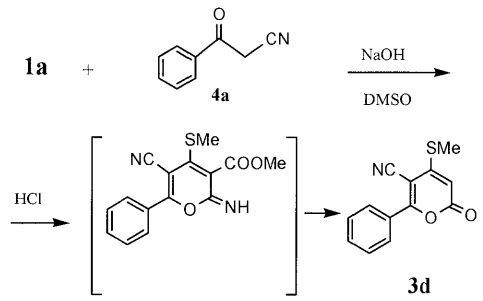
In contrast, 4-methylsulfanyl-6-phenyl-2-oxo-2*H*-pyran-5-carbonitrile (**3d**), which is a cyano-group positional isomer of **3aa**, was obtained *via* the reaction of benzoylacetonitrile (**4a**) with **1a** in the presence of sodium hydroxide in DMSO. However, the yield was very low (12%) (see Scheme 4).[16]

Scheme 3



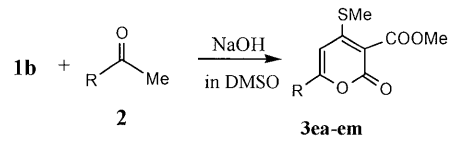
R	Yield(%)	R	Yield(%)
3ca: R=H	(35)	**3cd**: R=NMe_2	32
cb: R=Cl	(43)	**ce**: R=NEt_2	26
cc: R=OMe	(45)	**cf**: R=NPh_2	29

Scheme 4



We expected methyl 6-aryl-2-oxo-2*H*-pyran-3-carboxylates (**3e**) and 3-sulfonyl-2-oxo-2*H*-pyran derivatives (**3h**) to show good fluorescence properties. 6-Aryl-2-oxo-2*H*-pyran-3-carboxylates **3ea-em** were obtained by reaction of **1b** with acetophenones **2aa**, **aj**, **ad**, **ag**, **ah**, **bb**, **ba**, **bh**, **bd**, **bf**, **cc**, **cg** in a manner similar to the synthesis of 6-aryl-4-methylsulfanyl-2*H*-pyran-2-ones (**3ea-em**) (see Scheme 5).[17, 20]

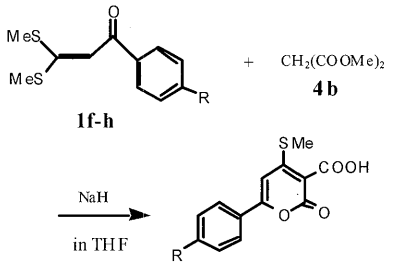
Scheme 5



R	Yield(%)	R	Yield(%)
3ea: C_6H_5	32	**3eg**: 3-pyridyl	34
eb: C_6H_4-Br(4)	59	**eh**: 2-pyridyl	48
ec: C_6H_4-OMe(4)	39	**ei**: 1-methylpyrrol-2-yl	7
ed: C_6H_3-OMe_2(3,4)	23	**ej**: 2-thienyl	42
ee: C_6H_3-O-CH_2-O(3,4)	37	**ek**: 2-furyl	25
ef: C_6H_2-$(OMe)_3$(3,4,5)	41	**el**: CH=CH-C_6H_4-OMe(4)	15
		em: CH=CH-C_6H_3-O-CH_2-O-(3,4)	17

We also attempted to synthesize 2*H*-pyran-2-one derivatives using α-oxoketene dithioacetals, which have been shown by Junjappa et al. to be versatile synthons for heterocyclic compounds.[9i] α-Oxoketene dithioacetals **1f-h** react with dimethyl malonate (**4b**) in THF in the presence of sodium hydride to give 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carboxylic acid (**3fa-hc**) in yields of 26 - 44%.[17] These products are formed by displacement of a methylsulfanyl group on the ketene dithioacetal, followed by cyclization and saponification when the reaction mixture is taken up in water (see Scheme 6).[20]

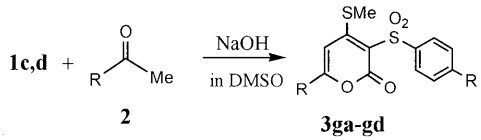
Scheme 6



R	Yield(%)
3fa: C_6H_5	34
fb: C_6H_4-OMe(4)	26
fc: C_6H_5	44

The synthesis of sulfonyl compounds was carried out *via* the reaction of sulfonyl ketene dithioacetals **1c**, **d** with **2**. Compound **1d** was allowed to react with **2aa** in DMSO in the presence of sodium hydroxide, followed by treatment with hydrochloric acid to give the desired 3-phenylsulfonyl-2-oxo-2*H*-pyran (**3ha**) in 61% yield. The other sulfonyl compounds (**3hb-hd**) were synthesized *via* the reaction of **1c** and **1d** with **2aa** and **2ab** under the same reaction conditions (see Scheme 7).[16]

Scheme 7

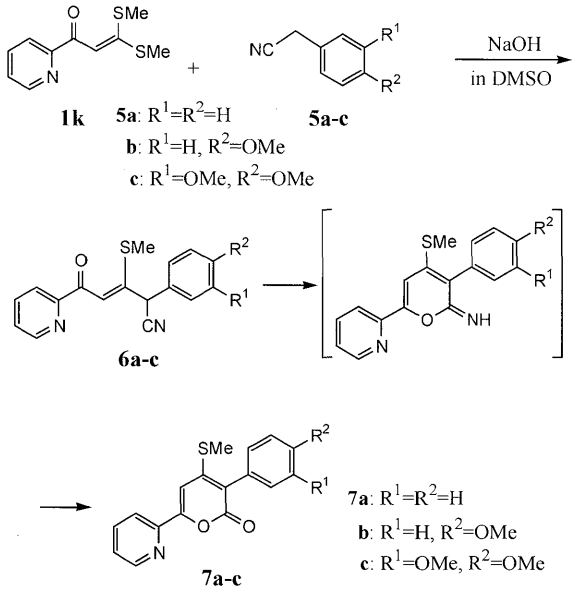


R	R	Yield(%)
3ga: C_6H_5	H	61(48)
gb: C_6H_4-OMe(4)	H	58
gc: C_6H_5	Me	64(35)
gd: C_6H_4-OMe(4)	Me	58

The α-oxoketene dithioacetal, 3,3-bis(methylsulfanyl)-1-pyrid-2-yl-2-propenone (**1k**), is also a

very interesting synthon and is used for synthesis of heterocycles bearing a 2-pyridyl group.[21] The reaction of **1k** with arylacetonitriles **5a-c** in the presence of powdered sodium hydroxide in DMSO, followed by treatment with hydrochloric acid, gives the corresponding 3-aryl-4-methylsulfanyl-6-pyrid-2-yl-2-oxo-2*H*-pyrans (**7a-c**) in practical yields. These 2-pyrone derivatives show strong fluorescence in the solid state (see Scheme 8).[19]

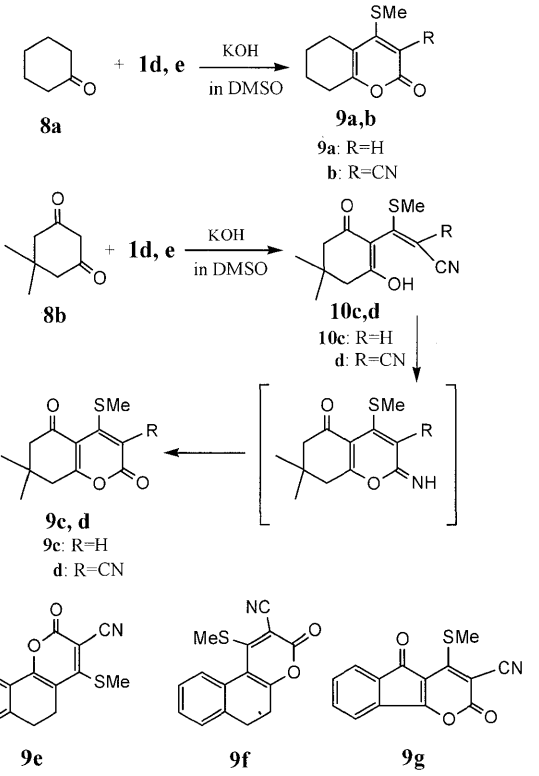
Scheme 8



Another series of compounds which are of considerable chemical and pharmacological importance are fused 2-pyrones. In particular, benzofused 2-pyrones, well-known coumarin derivatives which are widely distributed in nature, have been the subject of extensive reviews.[22]

Cyclic active methylene compounds also react smoothly with ketene dithioacetals in the presence of the appropriate base and solvent. Ketene dithioacetal **1a** reacts with **8a** to give the corresponding fused 2-pyrone **9a** in poor yield.[23] The reaction of cyclohexanone **8a** with **1e** in DMSO in the presence of potassium hydroxide gives the corresponding fused 2-pyrone derivative **9b** in 20% yield.[11] When dimedone (**8b**) is allowed to react with **1a**, the displacement product (**10**) of the methylsulfanyl group on **1a** is obtained in good yield. Treatment of **10** under acidic conditions affords the corresponding 2-pyrone derivatives **9c** and **9d**. In a similar manner, compounds **9e**, **9f**, and **9j** are obtained from the corresponding active methylene compounds (1-tetralone, 2-tetralone, 1,3-indandione) and ketene dithioacetal **1a** (See Scheme 9).[11, 24]

Scheme 9

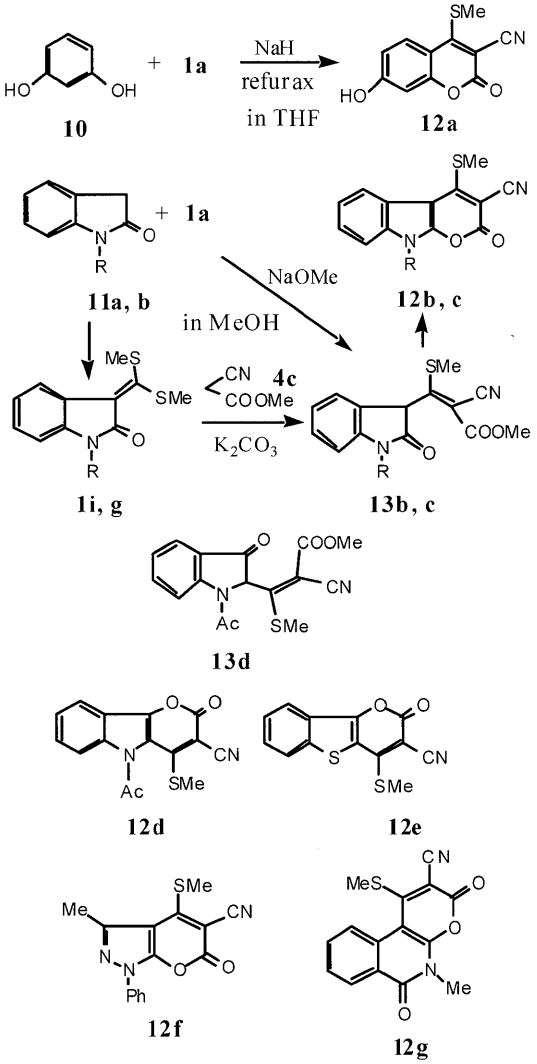


Ketene dithioacetal **1b** reacts with resorcinol (**10**) in the presence of sodium hydride in THF to give 4-methylsulfanyl-7-hydroxycoumarin-3-carbonitrile (**12a**) in 80% yield.[25] The methylsulfanyl group at the 4-position on the pyran ring is highly reactive toward nucleophiles such as amines and active methylene compounds, giving the corresponding 4-substituted coumarin derivatives in satisfactory yields.[25]

The reaction of **1i**, **j** with methyl cyanoacetate (**4b**) in THF the presence of sodium hydride gives the corresponding displacement products **13b**, **c** in good yields.[26, 27] Compounds **13b**, **c** are also prepared by the reaction of oxindoles **11a**, **b** with **1a**. When these compounds (**13b**, **c**) are heated at 200°C, cyclized pyrano[2,3-*b*]indole derivatives **12b**, **c** are obtained in good yields. Similarly, fused 2-pyrone derivatives **12d** and **e** are prepared by this method.[27] Junjappa *el al.* have also reported a similar reaction which gives pyrano[2,3-*c*]pyrazole derivatives (**12f**).[28] These fused 2-pyrone derivatives may also be synthesized by the reaction of ketene dithioacetals with the corresponding active

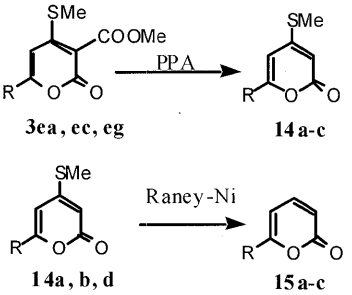
methylene heterocyclic compounds in the presence of a base. The reaction of 1-acetylindoxyl with **1a** in the presence of sodium hydride in THF under reflux conditions proceeds smoothly to yield the corresponding displacement product (**13d**), which converts to pyrano[3,2-*b*]indole (**12d**) under heating at 200°C.[29] In a similar manner, compounds **12e** and **g** were synthesized by reaction of the corresponding heterocyclic compounds with **1a** in good yields (see Scheme 10).[29, 30] Kakehi *et al.* have also reported that the reaction of 3,3-bis(methylsulfanyl)methylene-2,3-dihydroindolizin-2-ones with active methyl compounds in the presence of triethylamine under reflux afforded 4-alkylsulfanyl-3-cyano-2*H*-pyrano[2,3-*d*]indolizin-2-one derivatives.[31]

Scheme 10



Some 6-aryl- and 6-styryl-2*H*-pyrones are known in the form of natural products, including phenylcoumalin (**15a**),[32] paracotoin (**15c**),[33] 4-methoxyphenylcoumalin (**17a**),[33b] methoxyparacotoin (**17d**),[32a] and anibine.[33b] The deesterified products **14a-c** (6-aryl-4-methyl-sulfanyl-2*H*-pyran-2-ones) are easily prepared by treatment of **3ea**, **ec**, and **eg** with polyphosphoric acid (PPA) at 100°C. Finally, desulfurization of **14a-c** is easily effected using Raney nickel to afford the desired compounds **15a-c** (6-aryl-2*H*-pyran-2-ones) in 42, 45, and 49% yield, respectively (see Scheme 11).[19b]

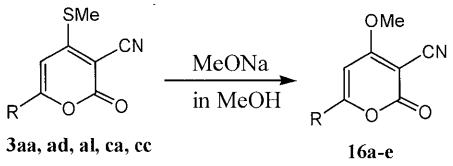
Scheme 11



14a: R=C_6H_5, mp 135°C, 80%
b: R=C_6H_4-OMe(4), mp 61°C, 33%
c: R=3-pyridyl, mp 182°C, 91%
15a: R=C_6H_5, mp 68°C, 42%
b: R=C_6H_4-OMe(4), mp 98°C, 45%
c: R=C_6H_3-O-CH_2-O-(3,4), mp 150°C, 49%

Electron-donating and accepting substituents are recognized as molecular subunits that confer non-linear optical properties due to their high polarizability. These molecules not only exhibit optical properties but also display diverse pharmacological activities. The high fluorescence of 2*H*-pyrone derivatives is due to the presence of an electron-withdrawing group at the 3-position and an electron-donating group at the 4-position. The electron-donating properties of alkoxy and amino groups at the 4-position of 2-pyrone are stronger than that of a methylsulfanyl group. If an alkoxy and an amino group can be introduced at the 4-position of a 2-pyrone, the synthesis of 2-pyrone derivatives with very high fluorescence may be possible. Displacement reactions of **3aa**, **ad**, **al**, **ca**, and **cc** with methoxide in methanol occurred smoothly to give 4-methoxy-6-phenyl-2-oxo-2*H*-pyran-3-carbonitriles (**16a-e**) in good yields (see Scheme 12).[17, 19b] However, treatment of **3da**, **dc**, **dd**, and **dm** with sodium methoxide in methanol gave the deesterified products **17a-d** (see Scheme 13).[19b]

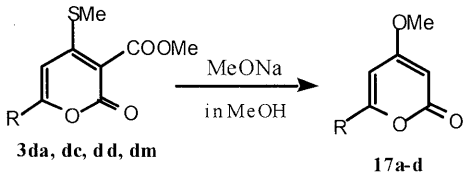
Scheme 12



3aa, ad, al, ca, cc → **16a-e**

a: C_6H_5
b: C_6H_4-OMe(4)
c: C_6H_4-Cl(4)
d: -CH=CH-C_6H_4
e: -CH=C-C_6H_4-OMe(4)

Scheme 13

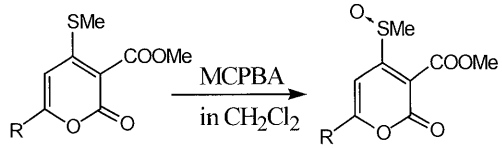


3da, dc, dd, dm → **17a-d**

a: C_6H_5
b: C_6H_4-OMe(4)
c: C_6H_3-$(OMe)_2$(3,4)
d: CH=CH- C_6H_3-O-CH_2-O-(3,4)

4-Methylsulfanyl-2*H*-pyrones are also very important electrophilic reagents for preparation of 4-substituted 2-pyrones and fused-pyrone derivatives. However, displacement of the methylsulfanyl groups in compounds **3ea-em** with amine or active methylene compounds was not successful. In order to obtain the various 4-substituted 2*H*-pyran-2-one derivatives, activation of the methylsulfanyl group was necessary. It is known that nucleophilic displacement of alkylsulfonyl (SO_2Me) or alkylsulfinyl (SOMe) groups occurs more rapidly than that of alkylsulfanyl groups. Treatment of **3ea** with 30% hydrogen peroxide in acetic acid gives the sulfinyl derivative **18a** in 84% yield.[19b] Compound **18a** may also be prepared by oxidation of **3ea** with 3-chloroperoxybenzoic acid (MCPBA) in dichloromethane in 92% yield. Compounds **18b-f** are obtained in a similar manner (see Scheme 14). The 4-methylsulfinyl group in **18a-f** is smoothly displaced with methoxide anion to give 4-methoxy derivatives **19a-e**, in which compounds **19a**, **b** are readily converted to **17a** and **b** (see Scheme 15)[17].

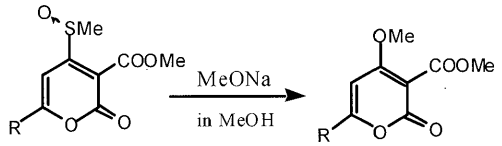
Scheme 14



3da, dc, dd, de, df, dl → **18a-f**

a: C_6H_5
b: C_6H_4-OMe(4)
c: C_6H_3-$(OMe)_2$(3,4)
d: C_6H_3-O-CH_2-O(3,4)
e: C_6H_2-$(OMe)_3$(3,4,5)
f: CH=CH-C_6H_4-OMe(4)

Scheme 15

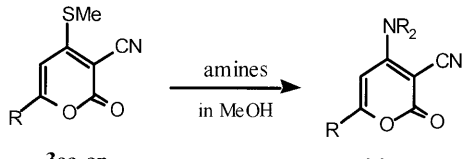


18a-f → **19a-e**

a: C_6H_5
b: C_6H_4-OMe(4)
c: C_6H_3-O-CH_2-O(3,4)
d: C_6H_2-$(OMe)_3$(3,4,5)
e: CH=CH-C_6H_4-OMe(4)

Next, we will describe the synthesis of 4-amino-6-aryl-2-oxo-2*H*-pyrane derivatives. We previously reported the synthesis of 4-amino-6-aryl-2-oxo-2*H*-pyran-3-carbonitriles by displacement reaction of 4-methylsulfanyl-2*H*-pyran-3-carbonitriles (**3**) with various amines in methanol under reflux. Various 4-amino-6-aryl-2-oxo-2*H*-pyrane derivatives (**20a-y**) were prepared by this method (see Scheme 16). Compounds **18a**, **b** were allowed to react with amines (methylamine, benzylamine, dimethylamine, pyrrolidine) under refluxing methanol to give 4-amino-6-aryl-2-oxo-2*H*-pyran-3-carboxylic acid methyl esters **21a-f** in good yields (see Scheme 17).[17]

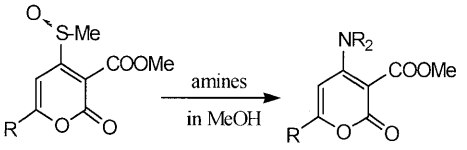
Schemes 16



3aa-ap **20a-y**

R	NR_2
a: C_6H_5	dimethylamino
b: C_6H_5	pyrolidino
c: C_6H_5	morphorino
d: C_6H_4-OMe(3)	dimethylamino
e: C_6H_4-OMe(4)	dimethylamino
f: C_6H_4-OMe(4)	pyrolidino
g: C_6H_4-OMe(4)	morpholino
h: C_6H_4-OMe(4)	thiomorpholino
i: C_6H_4-OMe(4)	phenethylamino
j: C_6H_3-$(OMe)_2$(2,5)	morpholino
k: C_6H_3-$(OMe)_2$(3,4)	morpholino
l: C_6H_4-NMe_2(4)	dimthylamino
m: C_6H_4-NMe_2(4)	pyrolidino
o: C_6H_4-NMe_2(4)	morpholino
p: C_6H_4-NMe_2(4)	thiomorpholino
q: C_6H_4-Br(4)	pyrrolidino
r: C_6H_4-Cl(2)	morpholino
s: C_6H_4-Cl(4)	pyrrolidino
t: C_6H_4-C_6H_5(4)	pyrrolidino
u: 1-naphthyl	pyrrolidino
v: 1-naphthyl	morpholino
w: 2-thienyl	pyrrolidino
x: 2-thienyl	morpholino
y: 2-benzothienyl	piperidino

Schemes 17



18a, b **21a-f**

R	NR_2
a: C_6H_5	methylamino
b: C_6H_5	benzylamino
c: C_6H_5	dimethylamino
d: C_6H_4-OMe(4)	methylamino
e: C_6H_4-OMe(4)	dimethylamino
f: C_6H_4-OMe(4)	pyrrolidino

A disadvantage of this reaction is its long reaction time. We attempted a simple method for 4-amino-2-pyrone synthesis by direct reaction of 2-pyrones with amines, without solvent, under heating at 100°C for 5 – 10 minutes. This reaction gave a separable mixture of the desired 4-amino-2-

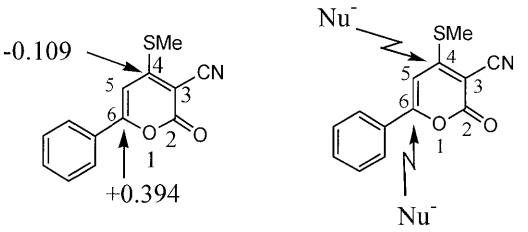
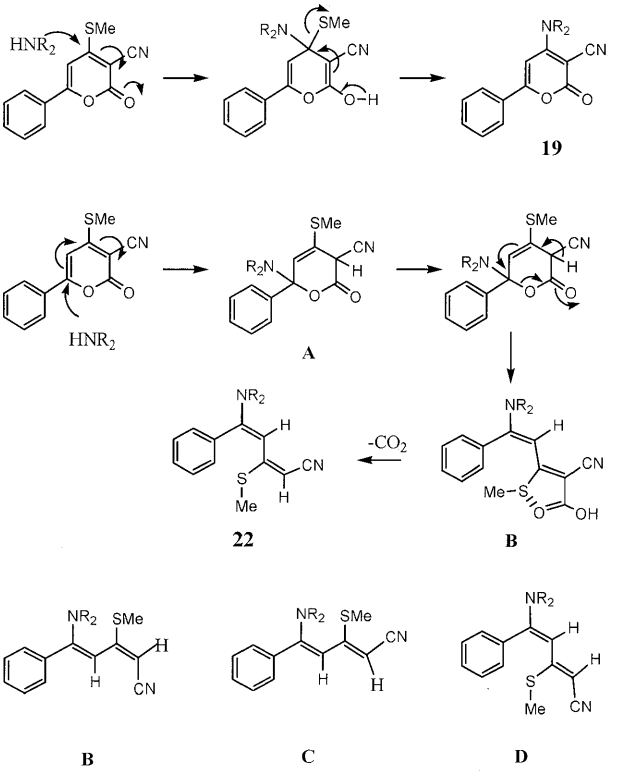


Figure 4

Scheme18



pyrone derivatives (**12a-z**) and butadiene derivatives (**22a-n**) (see Table 1). Analysis by IR, UV, NMR and mass spectroscopy and elemental analysis showed that the structure of these butadienes was 2E,4E-3-methylsulfanyl-5-amino-5-arylpenta-2,4-dienenitrile (**22a-n**). One of the products (**22b**) was also subjected to X-ray crystallographic analysis. The reaction pathway is shown in Scheme 18. As shown in Figure 4, attack of 2-pyrones by amines occurs at position 4 or 6, according to simple molecular orbital calculations.[17]

In the field of organic EL, red fluorescence is the most desirable type; DCM: (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran) and other 4*H*-pyran derivatives are important red-fluorescent materials (see Figure

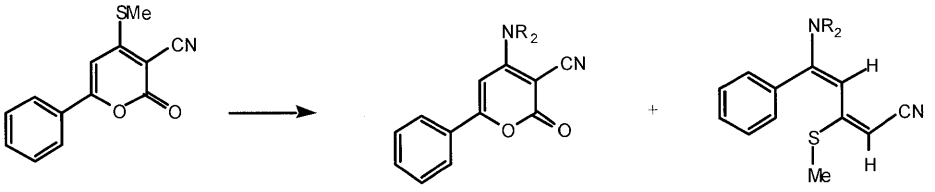
2).[14] As the structure of compound **23h**, which bears both (4-*N*,*N*-dimethylaminophenyl)styryl and active methylene groups on a pyran ring, is very similar to that of DCM, this compound was predicted to show red fluorescence.

To prepare **23h**, we synthesized 2-pyrone derivatives bearing an active methylene group at the 4-position by the displacement of the 4-methylsulfanyl group.The reactions of **3aa**, **ad**, **ai**, **bd**, and **cd** with methyl or ethyl malonates (**4c**, **d**) in the presence of potassium carbonate in DMSO gave the corresponding dialkyl 3-cyano-6-phenyl- or 6-styryl-2-oxo-2*H*-pyran-4-ylmalonates (**23a-h**) in 72-97% yields, respectively (shown in Table 2).[17, 19a)]

Similarly, dialkyl 3-methoxycarbonyl-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates (**23i-m**) were readily obtained from 6-aryl-4-sulfinyl-2*H*-pyran-2-ones (**18a**, **b**, **d**) and active methylene compounds (**4b**,**d**) in good yields (shown in Table 3).[17] In contrast, the reactions of **3aa**, **d**, **e**, **g**, and **i** with methyl or ethyl acetyl acetates (**4c**, **f**, **g**) under the same reaction conditions did not give the corresponding displacement products like **23a-m**.

The products of these reactions were determined by spectroscopic (IR, UV, NMR, and MS) and elemental analysis to be 8-hydroxy-3-phenyl-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylates (**24a-h**) (Table 4).

Table 1. Synthesis of 4-Amino-6-phenyl-2-oxo-2*H*-pyrano-3-carbonitriles and 5-Amino-5-phenyl-3-methylsulfanylpenta-2,4-diennitriles



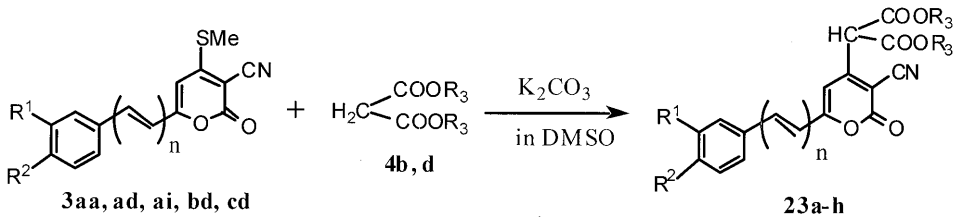
3 **20a, b, d, e, l, g m, q, s, ba-be** **22a-n**

Entry	Aryl	Amines	**20**	Yield (%)	mp (℃)	**22**	Yield (%)	mp (℃)
1	C_6H_5	dimethylamine	**a**	46	251-253	**a**	35	112-113
2	C_6H_5	pyrrolidine	**b**	52	287-289	**b**	38	137-139
3	C_6H_4-OMe(4)	dimethylamine	**d**	40	194-196	**c**	44	103-105
4	C_6H_4-OMe(4)	pyrrolidine	**e**	51	259-260	**d**	30	132-134
5	C_6H_4-OMe(4)	thiomorpholine	**g**	38	218-220	**e**	22	104-106
13	C_6H_4-NMe_2(4)	dimethylamine	**l**	38	265-267	**f**	47	121-123
14	C_6H_4-NMe_2(4)	pyrrolidine	**m**	44	270-271	**g**	51	123-125
12	C_6H_4-Br(4)	pyrrolidine	**q**	55	282-284	**h**	29	142-144
10	C_6H_4-Cl(4)	pyrrolidine	**s**	46	288-290	**i**	14	140-141
6	C_6H_4-OMe(2)	dimethylamine	**ba**	10	206-208	**j**	72	94-95
7	C_6H_4-OMe(2)	pyrrolidine	**bb**	39	244-246	**k**	41	146-148
8	C_6H_3-$(OMe)_2$(2,4)	dimethylamine	**bc**	25	236-239	**l**	57	108-109
9	C_6H_2-$(OMe)_3$(3,4,5)	pyrrolidine	**bd**	55	222-224	**m**	33	110-112
11	C_6H_4-Cl(2)	dimethylamine	**be**	56	176-178	**n**	39	129-130

[a] All reaction were carried out in a system of **1** (10 mmol) and amine (100 mmol). Reaction were carried out at 100℃ for 5-10 min.

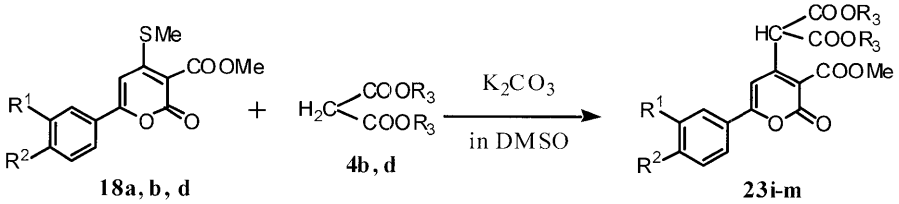
[b] All yields were isolated yields.

Table 2. Synthesis of Dialkyl 3-Cyano-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates



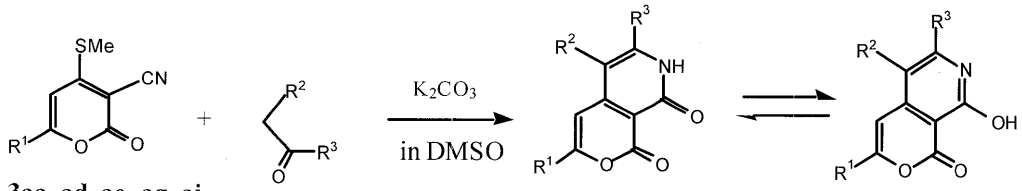
No.	R^1	R^2	R^3	n	Yield(%)	mp(°C)	Appearance
23a	H	H	Me	0	97	159-160	pale yellow needles
b	H	H	Et	0	82	158-159	pale yellow needles
c	H	OMe	Me	0	81	182-183	yellow needles
d	H	OMe	Et	0	72	194-198	pale yellow needles
e	H	NMe_2	Me	0	77	198-199	red needles
f	H	NMe_2	Et	0	74	194-198	red needles
g	thienyl		Me	0	83	174-175	yellow needles
h	H	NMe_2	Me	1	84	200-202	black red needles

Table 3. Synthesis of Dialkyl 3-Methoxycarbonyl -6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates

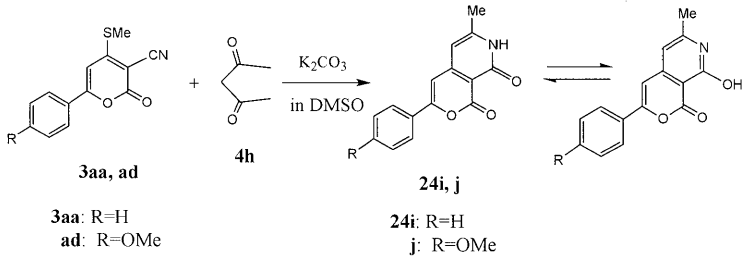


No.	R^1	R^2	R^3	Yield(%)	mp(°C)	Appearance
23i	H	H	Me	88	120-121	yellow needles
j	H	H	Et	80	80-90	yellow needles
k	H	OMe	Me	90	120-121	yellow needles
l	H	OMe	Et	79	89-92	yellow needles
m	-O-CH_2-O-		Me	53	143-146	yellow needles

Table 4. Synthesis of 1*H*-Pyrano[3,4-*c*]pyridines



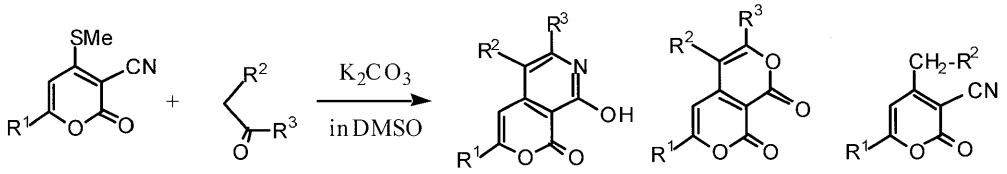
No.	R^1	R^2	R^3	Yield (%)	mp (℃)
24a	C_6H_5	COOMe	Me	46	>300
b	C_6H_4-OMe(4)	COOMe	Me	52	296-297
c	C_6H_5	COOEt	Me	40	295-297
d	C_6H_4-OMe(4)	COOEt	Me	51	287-288
e	C_6H_3-$(OMe)_2$(2,4)	COOEt	Me	38	298-299
f	C_6H_3-$(OMe)_2$(3,4)	COOEt	Me	38	303-304
g	C_6H_4-NMe_2(4)	COOEt	Me	44	298-299
h	C_6H_4-OMe(4)	SO_2-C_6H_4-Me(4	Me	55	260-270



In the NMR spectra of **24a-h**, the hydroxy protons at position 8 appear at 12.0 – 12.5 ppm due to hydrogen bonding with the C=O group; however, in the case of **24i** and **j**, the hydroxy protons are not seen in the ^{1}H-NMR spectra due to strong hydrogen bonding. In the final step of this reaction, the reaction mixture was acidified with 10% HCl solution, and the intermediates (**3**) were treated with concentrated HCl to give separable mixtures of **24**, **25**, and **26**, which were easily separated due to their differential solubilities in solvents such as dichloromethane, DMF, and ethanol (see Table 5). The structures of these compounds were determined by spectroscopic (IR, NMR, UV, and MS) and elemental analysis. The reaction pathways are shown in Scheme 19.[17]

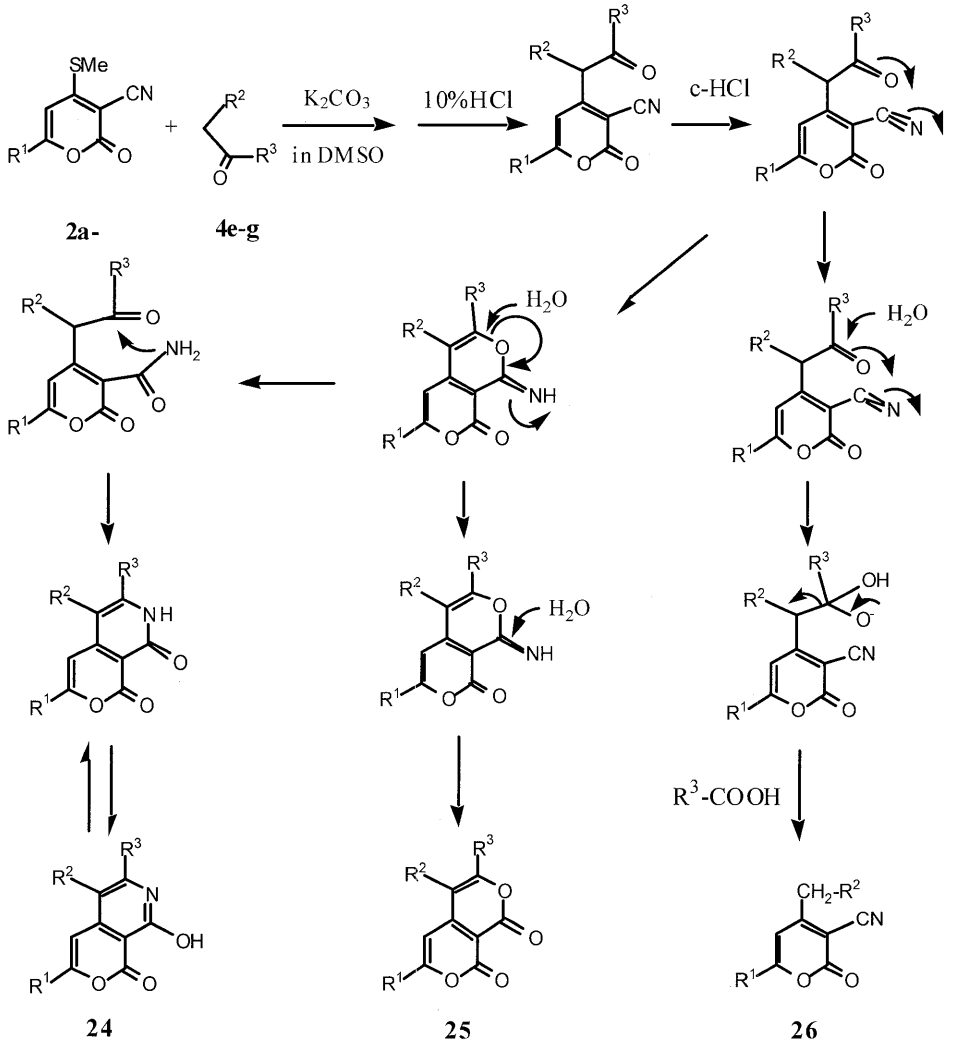
The above reaction of 2-pyrones with active methylene compounds in the presence of potassium carbonate proceeds initially by carbon nucleophilic attack at position 4, followed by displacement of the methylsulfanyl group to give the corresponding 4-substituted 2-pyrone derivatives (see Scheme 19).

Table 5. Synthesis of 1*H*-Pyrano[3,4-*c*]pyridines



Entry	R^1	R^2	R^3	**24** Yield(%)	**25** Yield(%)	**26** Yield(%)
1	C_6H_5	COOMe	Me	**24a** 10	-- --	**26a** 60
2	C_6H_5	COOEt	Me	**24c** 12	**25a** 11	**26b** 36
3	C_6H_4-OMe(4)	COOEt	Me	**24d** 30	**25b** 21	**26c** 22
4	$C_6H_3(OMe)_2$(3,4)	COOEt	Me	-- --	**25c** 14	**26d** 45
5	C_6H_4-NMe_2(4)	COOEt	Me	**24g** 9	-- --	**26e** 2
6	C_6H_5	COOEt	Ph	-- --	**25d** 11	**26b** 69
7	C_6H_4-OMe(4)	COOEt	Ph	-- --	**25e** 14	**26c** 43
8	C_6H_5	SO_2-C_6H_4-Me(4)	Me	-- --	-- --	**26f** 66
9	C_6H_4-OMe(4)	SO_2-C_6H_4-Me(4)	Me	**24h** 22	-- --	**26g** 18

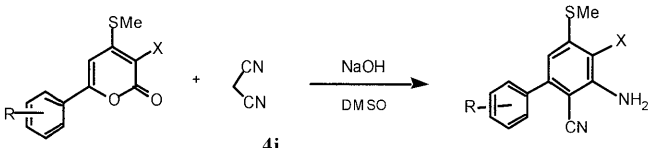
Scheme 19. Reaction Pathway



Ram *et al.* reported the synthesis of biaryl compounds by reaction of 2-pyrone derivatives (**3**) with malononitrile in the presence of potassium hydroxide.[35] This reaction proceeds initially by carbanion attack at position 6 with ring opening followed by ring transformation to yield biaryl compounds. While this reaction allows convenient synthesis of polyfunctionalized biaryl compounds, the yield is low. We re-examined our reaction conditions to increase the product yield.

Compound **3a** was allowed to react with malononitrile (**4i**) in DMSO in the presence of powdered sodium hydroxide at room temperature for 5 hours. The reaction mixture was then poured into a large amount of water, precipitating the product, and was stirred at room temperature for about 12 hours until no more precipitate was formed. The product was recrystallized from methanol to give colorless needles, mp 240 – 242°C, in 85% yield. The structure of this compound was determined to be 4-amino-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (**27a**), which was spectrosco-pically identical to the compound prepared by Ram. Other new biphenyl compounds (**27b-g**) were synthesized in 73 – 90% yields by reaction of the corresponding 4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles (**3aa, ab, ad, ae ah ai, an**) with **4i** under similar conditions. In the reactions of **3ea**, **ec**, and **ee** with **4i**, 3-aminobiphenyl-4-carboxylates **27h-j** were also obtained in 74 – 80% yield (see Table 6 and Scheme 20).[19b]

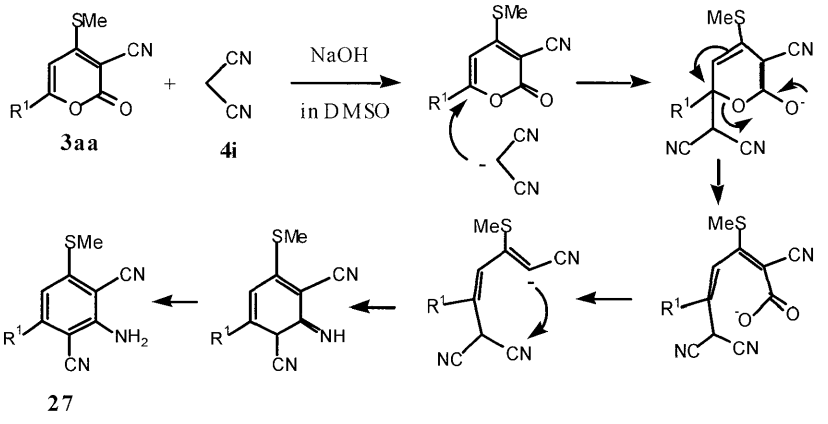
Table 6. Synthesis of Biaryl Derivatives from 2-Pyrones



3aa, ab, ad, ae, ah, ai, an, ea, ec, ee + **4i** → **27a-j**

No.	Aryl	X	Yield(%)	Appearance	mp (°C)
27a	C_6H_5	CN	85	colorless needles	240-242
b	C_6H_4-OMe(2)	CN	76	colorless needles	216-219
c	C_6H_4-OMe(4)	CN	99	colorless needles	212-213
d	C_6H_3-$(OMe)_2$(2,4)	CN	85	coloroless prisms	259-261
e	C_6H_2-$(OMe)_3$(3,4,5)	CN	90	colorless leaflets	263-265
f	C_6H_4-NMe_2(4)	CN	73	pale yellow needles	257-259
g	C_6H_4-(CN)(4)	CN	94	colorless needles	312-314
h	C_6H_5	COOMe	80	colorless needles	138-140
i	C_6H_4-OMe(4)	COOMe	68	colorless needles	124-126
j	C_6H_3O-CH_2-O-	COOMe	74	colorless needles	182-184

Scheme 20. Reaction Pathway



Merocyanines are dipolar chromophores which generally consist of two parts, a basic heterocycle with electron-donating ability, such as dihydropyridine or dihydroquinoline, and an acidic heterocycle with electron-accepting terminal groups such as rhodanines.[1)] Although heterocycles of many types have been used as the acidic moiety in merocyanine dyes, there are no such dyes, to our knowledge, which incorporate acidic heterocycles such as 2-pyrone derivatives as a terminal group. Here, we describe the synthesis of new merocyanine dyes with a pyran-2-one ring incorporated into the methine chain. 2-Pyrones containing both an electron-donating methylsulfanyl group and an electron-withdrawing cyano group are important and versatile synthetic starting materials for construction of merocyanine dyes.

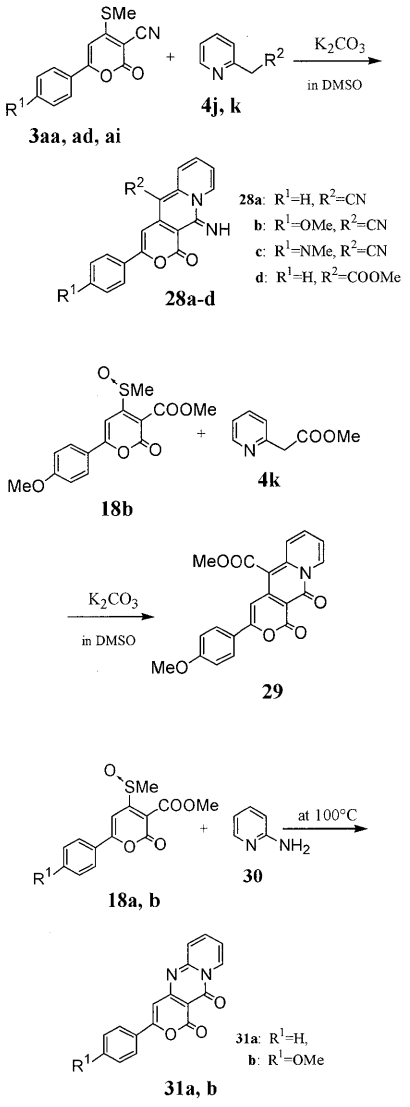
Basic dihydro-heterocyclic compounds, such as 1,2-dihydropyridines with an exocyclic double bond, are obtained by the action of a base on the appropriate quaternized heterocycles. These heterocycles react at the exocyclic double bond with electrophilic reagents such as ethoxymethylenes to give the corresponding 2- or 4-pyridinylidene derivatives.[2f)] This method has been conveniently applied to the preparation of various merocyanines.

Certain types of quinolizine attract much attention due to their valuable pharmacological properties. They are also used as synthetic intermediates and as additives for photographic materials and dyes. The reaction of 2-pyridylacetonitrile (**4j**) with **3aa** produces the pyrano[4,3-*b*]quinolizine **28a**, which is presumably formed by an addition-elimination mechanism. Compounds

28b-d were also easily prepared by reaction of **3ad** and **ai** with **4j**, **k** under the same reaction conditions. Compound **18b** also reacts with **4k** in the presence of potassium carbonate in DMSO to give **29** in 82% yield. Reaction of **18a**, **b** with 2-aminopyridine (**30**) under heating at 100°C occurred smoothly to give 2-phenylpyrano[3,4-*d*]pyrido[1,2-*a*]pyrimidines (**31a**, **b**) in 86 and 82% yields, respectively (see Scheme 21).[24]

The reaction of 2-picolinium methiodide (**32a**) with **3aa** in the presence of potassium carbonate as a base in dichloromethane at room temperature

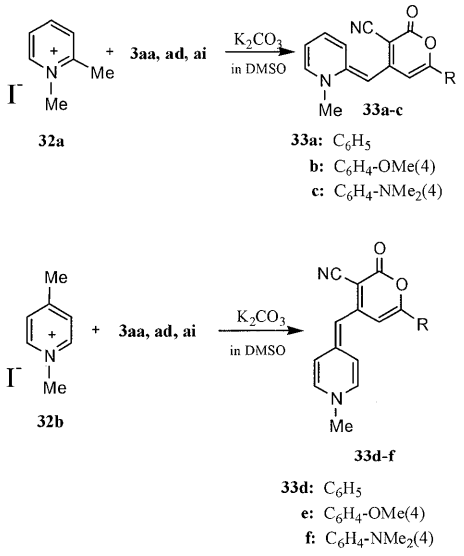
Scheme 21



gave the desired merocyanine dye (**33a**) as a reddish- violet product in 64% yield. In this reaction, the yield was increased by using dimethylsulfoxide as a solvent (87%). Compound **32a** also reacted smoothly with **3ad** and **c** to give the corresponding compounds **32b** and **ai** in 92 and 70% yields, respectively. The reaction of 1,4-dimethylpyridinium iodide (**32b**) with **3aa**, **ad**, and **ai** under the same reaction conditions also proceeded smoothly to give the corresponding merocyanine dyes **33a-c** in 61, 81, and 90% yields, respectively (see Scheme 22).

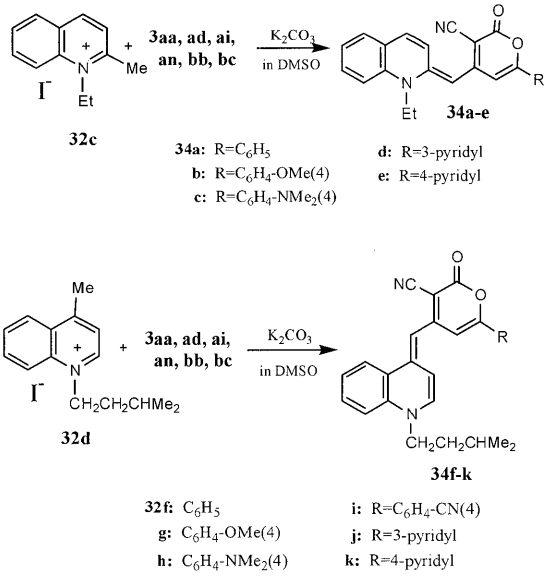
In a similar manner, the reaction of quinaldine ethyl iodide (**32c**) and lepidine isoamyl iodide (**32d**) with pyrone derivatives **3aa**, **ad**, **ai**, **an**, **bb**, **bc** gave

Scheme 22



the corresponding merocyanine dyes (**34a-k**) in good yields (see Scheme 23).[24]

Scheme 23



3. Fluorescence of 2-Pyrones

An efficient fluorescence measurement method was considered necessary for obtaining the fluorescence intensities of 2-pyrone derivatives in the solid state. It is easy to screen for fluorescence in the solid state by irradiation with a hand-held UV lamp (254 nm). Samples of the compound to be examined were placed on filter paper and irradiated with a UV lamp, and fluorescence was determined by visual examination. The resulting fluorescence intensities were divided into six categories. The fluorescence of Al_3-quinoline was defined as the standard, and on this basis, the fluorescence of the prepared 2-pyrone derivatives was determined.

Next, secondary evaluation was carried out by fluorophotometer. Measurements of absorption and fluorescence spectra were carried out in ethanol and dichloromethane solution and in the solid state at room temperature. The spectroscopic properties of the compounds—absorption maxima (λ_{max}), molar absorption (ε), fluorescence maxima (λ_{max}), and relative fluorescence intensities (RI)—are listed in Table 7.

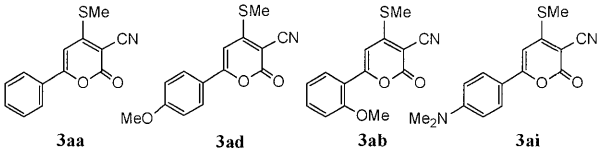
Table 7. Spectral Data of 6-Aryl-4-methylsulfanyl-2*H*-pyrones (3aa-pp, bd-bg, ga, gd)

				UV λmax(log ε)	Fluorescence (ethanol)				Fluorescence (solid)			
No.	position 3	position 4	position 6	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	ϕ	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
3aa	CN	SMe	C_6H_5	328(4.24)				0.00	358	480	122	1.54
3ab	CN	SMe	C_6H_4-OMe(2)	387(4.35)				ND	357	493	136	1.67
3ac	CN	SMe	C_6H_4-OMe(3)	369(4.29)				ND	350	495	145	1.16
3ad	CN	SMe	C_6H_4-OMe(4)	395(4.45)				0.00	297	536	239	1.23
3ae	CN	SMe	C_6H_3-$(OMe)_2$(2,4)	400(4.60)				ND	297	534	237	0.57
3af	CN	SMe	C_6H_3-$(OMe)_2$(2,5)	402(4.28)				ND	303	531	228	0.71
3ag	CN	SMe	C_6H_3-$(OMe)_2$(3,4)	402(4.39)	402	491	89	0.01>	294	551	257	0.76
3ah	CN	SMe	C_6H_2-$(OMe)_3$(3,4,5)	391(4.33)	392	520	128	0.01>	295	502	207	0.28
3ai	CN	SMe	C_6H_4-NMe_2(4)	465(4.58)				ND	301	608	307	0.15
3aj	CN	SMe	C_6H_4-Br(4)	337(4.33)				0.00	304	518	214	0.76
3ak	CN	SMe	C_6H_4-Cl(2)	354(4.18)				ND	296	491	195	0.68
3al	CN	SMe	C_6H_4-Cl(4)	336(4.34)				0.00	364	492	128	1.29
3am	CN	SMe	C_6H_4-Ph(4)	388[c]				ND	326	509	183	1.11
3an	CN	SMe	C_6H_4-CN(4)	332(4.12)				ND	0.00	0.00	-	0.00
3ao	CN	SMe	1-naphthyl	371(4.22)	269	457	188	0.01>	303	498	195	0.66
3ap	CN	SMe	2-naphthyl	370(4.17)				0.00	342	516	174	2.01
3bd	CN	SMe	2-thienyl	415(4.30)				ND	309	563	254	0.84
3be	CN	SMe	2-benzothienyl	408(4.40)				ND	298	543	245	0.37
3bf	CN	SMe	2-furyl	395(4.42)				ND	323	546	223	0.59
3bg	CN	SMe	2-furyl-Me(5)	404(4.47)				ND	298	521	223	0.21
3ea	COOMe	SMe	C_6H_5	360(4.18)				ND	299	475	176	6.31
3ec	COOMe	SMe	C_6H_4-OMe(4)	386(4.41)				ND	295	483	188	3.94
3ga	phenylsulfonyl	SMe	C_6H_5	339(4.28)				ND	297	460	163	0.51
3gd	tolylsulfonyl	SMe	C_6H_4-OMe(4)	387(4.54)				ND	294	508	214	11.27

[a] Stoke's Shift = Em max(nm) - Ex max(nm).
[b] Relative intensity of fluorescence in solid state, using Alq_3 as a standard.
[c] insufficient solubility.
[d] amorphus
[e] Relative intensity of fluorescence in dichloromethane($1.0x10^{-5}$M), using DCM as a standard.

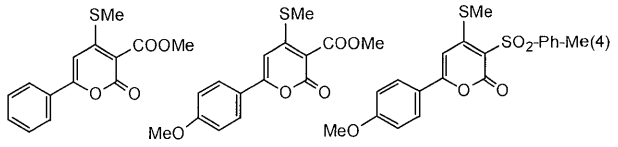
Materials which fluoresce strongly in the three primary colors (red, green and blue) are the most important materials in the field of organic EL. The light emission regions for red, green and blue (RGB) are 440 nm, 550 nm, and 630 nm, respectively. Although these colors are each of considerable importance, blue fluorescent materials are the most basic electroluminescent compounds, and red fluorescent materials are the most difficult to synthesize. In comparison with the spectroscopic properties of 4-methylsulfanyl-2-oxo-6-phenyl-2*H*-pyran-3-carbonitriles (**3aa-gd**), both the absorption and fluorescence maxima of 2-pyrones bearing electron-rich aryl groups showed longer wavelength shifts, together with an increase in molar absorption. The aryl group at the 6-position on 2-pyrone derivatives also has an important effect on fluorescent properties. The fluorescence of 6-methyl-2-oxo-2*H*-pyran-3-carbonitrile was found to be very weak, and compounds **9a-g** and **12a-g** also

showed very weak fluorescence. Among 6-phenyl-2-pyrone derivatives, compounds with electron-donating groups on the phenyl group (**3ad**, **ag**, **ai**) showed stronger fluorescence. Compound **3aa**, which contains an unsubstituted phenyl group at the 6-position, showed the strongest fluorescence among 4-methylsulfanyl-2*H*-pyrone derivatives, and emitted light in the shortest wavelength region (480 nm). The light emission region is shifted to the long-wavelength side if a methoxy group is introduced as an electron-donating group on the phenyl group. Compound **3ad**, containing a methoxy group at 4-position of the phenyl group, emitted light at 536 nm, which is 56 nm further toward the red side than **3aa**. Partitioning of the localized conjugated system between the pyrone ring and the methoxy group at the 2-position on phenyl group due to steric hindrance (**3ab**) resulted in a small shift to the long-wavelength side. A weak electronic effect due to a methoxy group in the meta-position results in no shift (**3ac**). The fluorescence maximum of 6-(4-dimethylamino-phenyl)-2-oxo-2*H*-pyran-3-carbonitrile (**3ai**) was 608 nm (RI = 0.15) which results in fluorescence close to the target red region. Red light emission around 620 – 640 nm is required for light-emitting materials in EL devices (see Figure 5, 6 and 7).



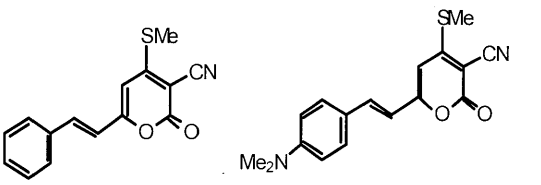
3aa RI=1.54 Ex=358, Em=480 nm
3ad RI=1.23 Ex=297, Em=536 nm
3ab RI=1.67 Ex=357, Em=493 nm
3ai RI=0.15 Ex=301, Em=608 nm

Figure 5



3ea RI=6.31 Ex=299, Em=475 nm
3ec RI=3.91 Ex=295, Em=483 nm
3gd RI=11.27 Ex=294, Em=508 nm

Figure 6



3ca RI=0.39 Ex=323, Em=541 nm
3cd RI>0.01 Ex=342, Em=699 nm

Figure 7

Compound **3an**, which contains a cyano group as an electron-withdrawing substituent on the phenyl group, did not emit fluorescent light, as expected. Electron-deficient heteroaryl compounds such as 6-pyrid-3-yl-2-pyrone (**3ba-bc**) also proved to be very weak light emitters.

Naphthyl (**3ao**, **ap**) and heteroaryl derivatives (**3bd-bg**) also showed strong fluorescence, as shown in Table 7. The light-emitting region of **3ao** (498 nm) was shifted by 18 nm compared to **3aa** due to the twisted nature of the molecule, which results in steric hindrance between the naphthyl and the pyranyl group. The light emission region is shifted toward the long-wavelength side, even if the aromatic substituent at the 6-position is an electron-rich heterocyclic compound. In particular, in the case of 6-thien-2-yl-2*H*-pyran-2-one (**3bd**) and 6-fur-2-yl-2*H*-pyrones **3be** and **3bg**, light is emitted at 563, 546, and 521 nm, respectively. Styryl-2*H*-pyrone derivatives, in which a double bond is introduced between the aryl group at the 6-position and the pyrone ring, emit light further on the long-wavelength side (see Table 7).

6-Styryl-3-cyano-4-methylsulfanyl-2*H*-pyrone (**3ca**) emits at 563 nm, while the methoxy derivative **3cc** emits light at 563 nm (RI = 0.84). The light emission of amino styryl compounds **3cd-cf** was not as strong in the solid state. However, **3cf** emitted light at 610 nm (RI = 0.88) in dichloro-methane as a non-polar solvent, and the fluore-scence intensity was stronger than that of DCM (4-(dicyanomethylene)-2-methyl-6-(4-*N*,*N*-dimethyl-aminostyryl)-4*H*-pyran). As explained earlier, the most important contributor to fluorescence in pyrone derivatives is the presence of an aryl or a styryl group at the 6-position (see Table 8 and

Figure 7).

The next most important influence on the fluorescence of 2-pyrone derivatives is the presence of an electron-donating substituent at the 4-position and an electron-withdrawing substituent at the 3-position. Compounds with an electron-donating substituent at the 4-position showed strong light emission. It is considered that the presence of sulfur atoms in a compound generally results in weakened fluorescence; for this reason, compounds in which the methylthio group at the 4-position is substituted with an alkoxy or amino group are expected to show strong fluorescence. In fact, alkoxy and amino derivatives did show considerably stronger fluorescence than methylsulfanyl compounds. The oxo-2*H*-pyran-3-carbonitriles (**3aa-ap**) show stronger intensity than the corresponding 4-methylsulfanyl compounds, and their light-emission regions show a 40 -50 nm blue shift. The 4-amino compound **20a** is a typical blue-fluorescent material (447 nm), as shown in Table 9 and Figure 8 and 9.

Another important factor in fluorescence properties is the presence and positioning of a cyano group in the pyrone ring. Almost all 6-aryl-2-oxo-2*H*-pyran-3-carbonitrile derivatives showed fluorescence in the solid state, as shown in Table 7. However, 2-oxo-6-phenyl-2*H*-pyran-5-carbonitrile (**3d**) shows no fluorescence at all. It is probable that the positioning of the electron-deficient group is an important determinant of electroluminescence in 2-pyrone derivatives. The presence of an ester or sulfonyl group at the 3-position was also effective in causing fluorescence in the solid state, and the fluorescence obtained was stronger than that of the corresponding cyano compounds. In particular, the fluorescence of sulfonyl compound **3gd** was 9.2 times more intense than that of the cyano derivative **3ad** (see Figure 8).

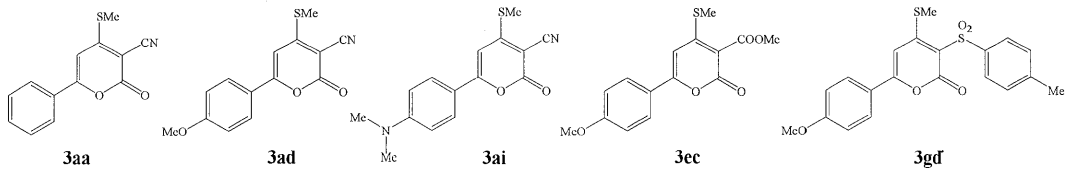
The electron-withdrawing effect is not the only cause of this phenomenon. According to the detailed structural analysis of **8ea** carried out by X-ray crystallography, the intramolecular non-bonded S...O (SMe...COOMe) distance is 2.735 Å which is shorter than the sum of the van der Waals distances for O and S (3.25Å). This result implies that there is strong molecular stacking due to the planar nature of the molecule. Similar strong interactions have been reported for other compounds, with lengths in the range 2.41 – 2.78 Å. The non-bonding O=C-MeO $\cdots$ O=C (COOMe... C=O) interaction can also be observed in ORTEP; this distance is 2.713 Å. The eight central atoms, S(18), C(7), C(8), C(9), C(10), C(11), C(12), and C(14), are almost planar. The results of X-ray crystallographic analysis show the results of X-ray crystallographic analysis that there is strong molecular stacking. The molecules are stacked along the *c*-axis due to the π–π interaction force.

Table 8. Spectral Data of 4-Methylsulfanyl-6-styryl-2*H*-pyrones (3ca, cc-cf)

			UV λmax(log ε	Fluorescence (dichloromethane)				Fluorescence (solid)			
No.	position 4	position 6	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	R.I.[c]	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
3ca	SMe	styryl	395[c]				ND	323	541	218	0.39
3cc	SMe	-CH=CH-C_6H_4-OMe(4)	415 (4.30)				ND	309	563	254	0.84
3cd	SMe	-CH=CH-C_6H_4-NMe_2(4)	513 (4.67)	541	610	69	0.77	342	699	357	0.01>
3ce	SMe	-CH=CH-C_6H_4-NEt_2(4)	529 (4.69)	554	612	58	0.88	346	705	359	0.01>
3cf	SMe	-CH=CH-C_6H_4-NPh_2(4)	502 (4.19)	573	620	47	0.03	349	645	296	0.01>

Table 9. Spectral Data of 4-Alkoxy- and 4-Amino-2*H*-pyrones (16a, b, 20a-y, 21a-f)

				UV λmax(log ε)	Fluorescence (ethanol)				Fluorescence (solid)			
No.	position 3	position 4	position 6	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	ϕ	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
16a	CN	OMe	C_6H_5	320 (4.18)				ND	367	472	105	2.88
16b	CN	OMe	C_6H_4-OMe(4)	376 (4.49)	301	603	302	0.01>	375	487	112	5.14
20a	CN	NMe_2	C_6H_5	310 (4.35)	361	447	86	0.01>	361	447	86	1.50
20b	CN	pyrrolidino	C_6H_5	308 (4.36)				ND	304	478	174	0.91
20c	CN	morpholino	C_6H_5	315 (4.41)				ND	371	455	99	3.08
20d	CN	NMe_2	C_6H_4-OMe(3)	324 (4.25)	303	476	174	0.01>	303	476	173	0.92
20e	CN	NMe_2	C_6H_4-OMe(4)	332 (4.42)	376	475	99	0.01>	376	475	99	6.90
20f	CN	pyrrolidino	C_6H_4-OMe(4)	331 (4.41)	268	462	194	0.01>	369	453	84	4.27
20g	CN	morpholino	C_6H_4-OMe(4)	336 (4.43)				ND	374	475	101	4.60
20h	CN	thiomorpholino	C_6H_4-OMe(4)	339 (4.47)				0.00	373	474	101	4.14
20i	CN	phenethylamino	C_6H_4-OMe(4)	346 (4.42)	311	424	113	0.01>	370	461	91	4.34
20j	CN	morpholino	C_6H_3-$(OMe)_2$(2,5)	364 (4.15)				ND	371	509	138	3.05
20k	CN	morpholino	C_6H_3-$(OMe)_2$(3,4)	358 (4.25)				ND	296	497	201	5.52
20l	CN	NMe_2	C_6H_4-NMe_2(4)	400 (4.57)	352	500	252	0.57	294	517	223	9.90(5.72[d])
20m	CN	pyrrolidino	C_6H_4-NMe_2(4)	396 (4.64)	391	480	89	0.70	373	537	164	3.86
20o	CN	morpholino	C_6H_4-NMe_2(4)	409 (4.54)	425	515	90	0.01>	322	606	284	1.08
20p	CN	thiomorpholino	C_6H_4-NMe_2(4)	410 (4.57)	307	582	275	0.45	295	582	287	0.43
20q	CN	pyrrolidino	C_6H_4-Br(4)	315 (4.42)				ND	363	516	153	1.45
20r	CN	morpholino	C_6H_4-Cl(2)	298 (4.17)				ND	303	466	163	0.78
20s	CN	pyrrolidino	C_6H_4-Cl(4)	314 (4.38)				ND	369	481	112	2.84
20t	CN	pyrrolidino	C_6H_4-Ph(4)	328 (4.56)				ND	352	479	127	1.28
20u	CN	pyrrolidino	1-naphthyl	320 (4.30)				ND	359	470	111	1.38
20v	CN	morpholino	1-naphthyl	324 (4.33)				ND	361	472	111	1.43
20w	CN	pyrrolidino	2-thienyl	336 (4.36)				ND	369	486	117	2.51
20x	CN	morpholino	2-thienyl	343 (4.57)	263	449	186	0.01>	375	461	116	6.99
20y	CN	piperidino	2-benzothienyl	349 (4.45)				ND	369	494	125	1.81
21a	COOMe	methylamino	C_6H_5	314 (4.26)				ND	296	437	141	3.51
21b	COOMe	benzylamino	C_6H_5	305 (4.28)				ND	272	445	173	0.96
21c	COOMe	NMe_2	C_6H_5	303 (4.28)				ND	272	453	181	0.27
21d	COOMe	methylamino	C_6H_4-OMe(4)	341 (4.38)				ND	270	453	183	1.46
21e	COOMe	NMe_2	C_6H_4-OMe(4)	321 (4.41)				ND	258	457	199	9.81
21f	COOMe	pyrrolidino	C_6H_4-OMe(4)	311 (4.46)				ND	265	466	201	3.87



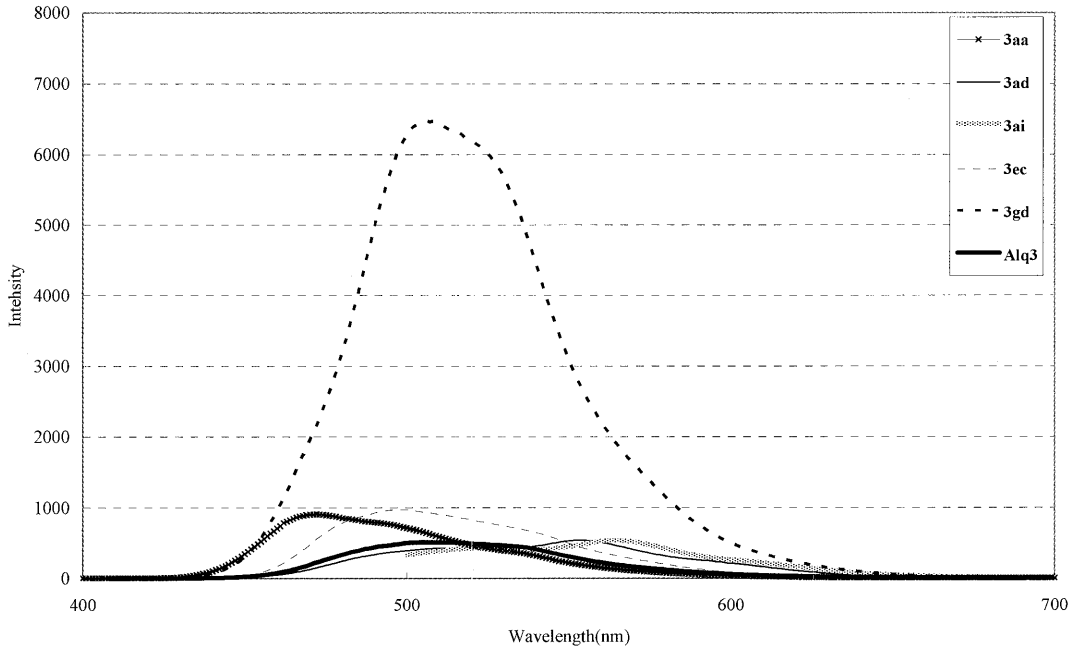


Figure 8. Fluorescence Spectra of 2*H*-Pyrone Derivatives (3aa, 3ad, 3ai, 3ec, 3gd)

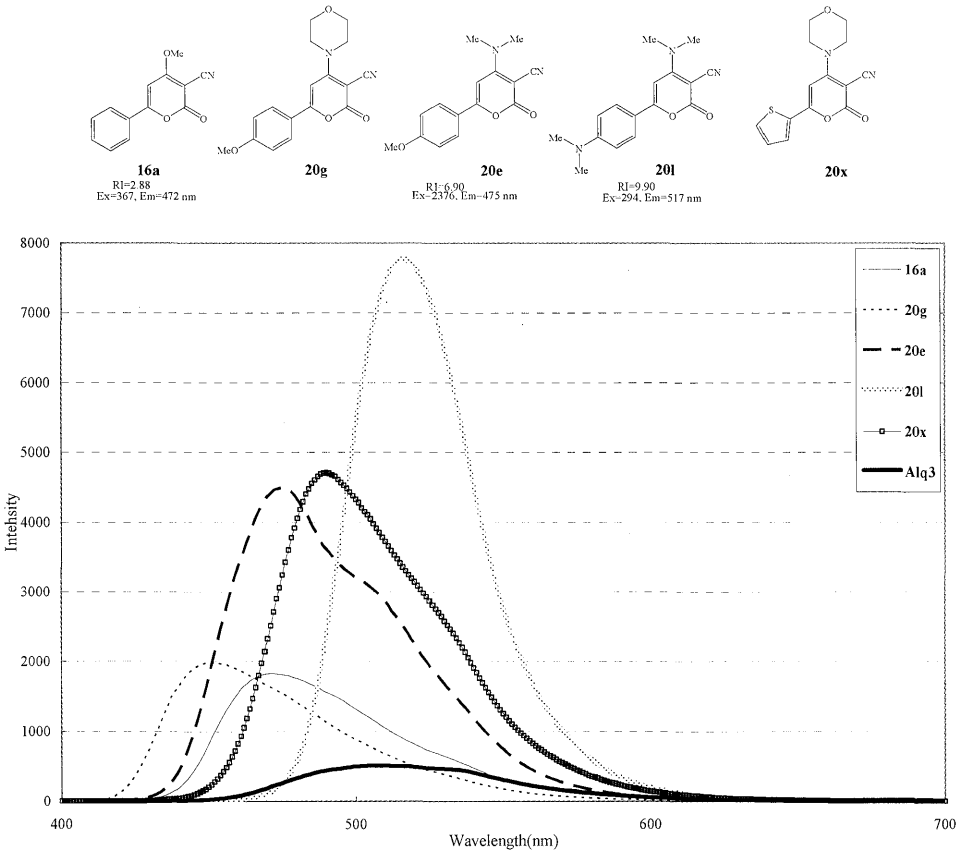


Figure 9. Fluorescence Spectra of 2*H*-Pyrone Derivatives (16a, 20g, 20e, 20l, 20x)

The shortest intermolecular distance is 3.345 Å for O(13)···C(5), which is similar to the distance observed (3.26 Å) in the charge transfer (CT) complex tetrathiafulvalene (7,7,8,8-tetracyano-*p*-quinodimethane).[35]

Pyrone derivatives **20a-m** showed almost no fluorescence in solution, although they showed strong fluorescence in the solid state. However, 4-dimethylamino-6-(4-dimethylaminophenyl)-2-oxo-2*H*-pyran-3-carbonitrile (**20l**), 6-(4-dimethyl-aminophenyl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (**20p**), and 6-(4-dimethyl- aminophen-yl)-4-pyrrolidino-2-oxo-2*H*-pyran-3-carbonitrile (**20q**), showed strong fluorescence in ethanol as well as in the solid state, with fluorescent quantum yields of 0.57, 0.45, and 0.70, respectively. These compounds are used as fluorescence materials for an oxalate chemiluminescence system.[36] Detailed structural analysis of **20l** was carried out by X-ray crystallography. The shortest intermolecular distance in **20l** was 3.120 Å between O(13) and N(37). In addition, because the intermolecular distances for O(13)···C(32) and O(13)···C(38) were 3.236 Å and 3.293 Å, respectively, intermolecular π interactions are possible. Moreover, it is thought that the array of molecules resembles a CT complex, because the intermolecular distance in a CT complex is 3.21 Å, and that there are very strong π-electron interactions, because the shortest intramolecular distance is 3.120 Å. The dimethyl-amino group at the 6-position of the phenyl group and the dimethylamino group at the 4-position of the pyrone ring are thought to be near-planar structures, to account for their torsion angles. However, it appears that there is a twist of approximately 10 degrees between the pyrone ring and the phenyl ring bearing the dimethylamino group. Moreover, **20l** has a structure that enables easy intramolecular charge movement, as shown in Figure 10 and 11, and it is thought that this is due to the presence of a betaine structure. This is likely to be one of the causes of its strong fluorescence.

Finally, we describe the structure-activity relationships of these fluorescent 2-pyran derivatives.

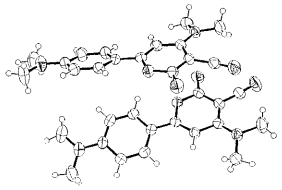


Figure 10. Asymmetric unit of 20l

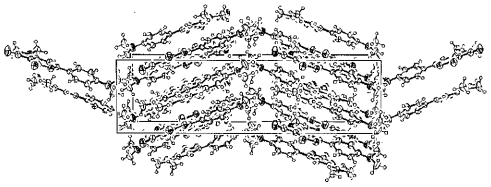


Figure 11. Molecular packing diagram of 20l

The aryl group at the 6-position on the pyrone ring that showed strong fluorescence was twisted at the angle of pyrone ring and 25 degrees.[15] It is thought that this angle is an important factor in fluorescence, and this is supported by the X-ray (ORTEP) findings that the structure that takes the minimum energy in the ground state has a twist of 25 degrees.

These results agree well with MOPAC and Stokes shift calculations, as shown in Tables 7 and **8**. The optimized molecular structures of **3ea** and **20l** were calculated using MOPAC; these structures are shown in Figures 12 and 13.

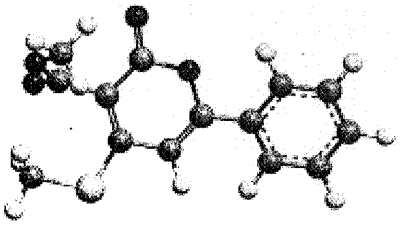


Figure 12. Structure of 8ea caluculated by MOPAC/AM1

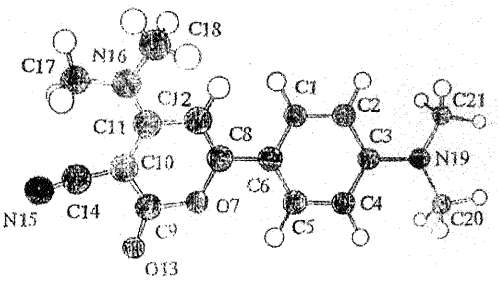
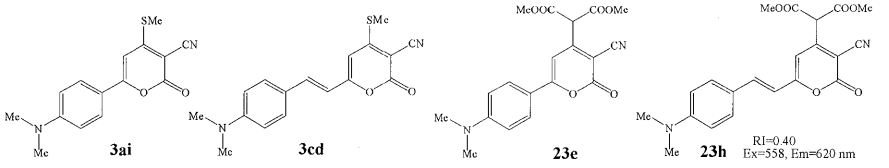


Figure 13. Structure of 20l caluculated by MOPAC/AM1

The new 2-pyrone derivatives dialkyl 3-cyano-6- phenyl-2-oxo-2*H*-pyran-4-yl malonates (**23a-h**) and alkyl 3-cyano-6-phenyl-2-oxo-2*H*-pyran-4-yl-acetates (**23i-m**), which were easily prepared by the reaction of 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles with active methylene compounds in the presence of potassium carbonate, show fluorescence emission radiation. Compounds **23a-m**, which are substituted at the 4-position, show a small bathochromic shift and stronger fluorescence emissions than those of compound series **3** in the solid state (see Table 10).

In particular, the light-emitting region of compound **23h** in dichloromethane was 620 nm, which means that this is a typical red-fluorescent compound (see Figure 14). Compounds **7e**, **f** also showed red fluorescence in ethanol solution and can be used as fluorescence reagents in an oxalate chemiluminescence system.



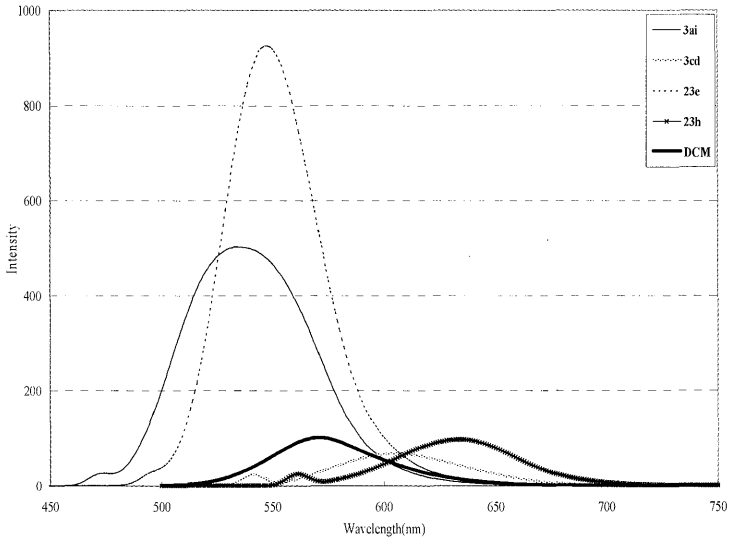


Figure 14. Fluorescence Spectra of 3ai, 3cd, 23e and 23h

The fluorescence emissions of fused pyrones such as compounds **24** and **25** were analyzed. The 1*H*-pyrano[3,4-*c*]pyridin-1-one derivatives **24a-j** exhibited moderately strong fluorescent radiation in the solid state, while the 1*H*,8*H*-pyrano[3,4-*c*]-pyran-1,8-dione derivatives (**25a-e**) did not show appreciable fluorescence emission (see Table 11 and 12). As seen in the case of compound **3**, 3-phenyl pyrano[3,4-*c*] pyridin-1-ones bearing electron-donating groups (such as methoxy groups) on the phenyl group showed strong fluorescence. For example, ethyl 8-hydroxy-3-(2,4-dimethoxyphenyl)-6-methyl-1-oxo-1*H*-pyr-ano[3,4-*c*]pyridine-5-carboxylate (**24e**) showed fluorescence at 490 nm in the solid state with a relative intensity of 4.88. The reason for the increased fluorescence in these compounds appears to be the packing system, which is based on flat molecules and strong -C=O ··· H-O- hydrogen bonding. This suggests that it may be possible to develop other fused 2*H*-pyrone derivatives which show fluorescence. Biaryl derivatives **27a-j** showed weak fluorescence emission in the solid state. The substituent on the aryl group at position 6 of 2-pyrone derivatives also has a strong influence on fluorescent expression. Among 2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile compounds (**3aa-ai**), derivatives bearing an electron-donating group on the phenyl group showed stronger fluorescence intensity than other compounds; in contrast, 6-(4-cyanophenyl)-2-oxo-2*H*-pyran-3-carbonitrile (**3an**), bearing an electron-withdrawing group on the aryl group, showed no fluorescence. Similarly, 4-methyl-sulfanyl-6-pyridyl-2-oxo-2*H*-pyran-3-carboni-triles **3ba-bc** and methyl 4-methylsulfanyl-2-oxo-6-pyridyl-2*H*-pyran-3-carboxylates **3eg**, **ef** also showed very weak fluorescence in solution and in the solid state.

However, 3-phenyl-6-pyrid-2-yl-2*H*-pyran-2-ones bearing an aryl group rather than a cyano group at position 3 (**7a-c**) showed fluorescence in the solid state, although the fluorescence of these 2-pyrone derivatives in ethanol was not so strong. At present, the reason for this fluorescence is not known, but it is not simply due to the presence of electron-withdrawing and electron-donating substituents on the 2-pyrone ring. The fluorescence intensity of **7a** was 7.02 times stronger than that of AlQ_3. The difference between the Em_{max} values in the solid state and in solution indicates the effect of molecular stacking on the fluorescence spectra. The introduction of an electron-donating substituent in the aryl moiety results in a bathochromic shift in the absorption maximum (λ_{max}) together with a very small increase in ε_{max} in UV spectrum.

Table 10 . Spectral Data of Dialkyl 6-Aryl-2*H*-pyran-4-ylmalonates (23a-l)

				UV λmax(log ε)	Fluorescence (dichloromethane)				Fluorescence (solid)			
No.	R^1	R^2	n	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	R.I.[c]	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
23a	C_6H_5	Me	0	372 (4.35)				ND	337	479	142	7.51
23b	C_6H_5	Et	0	324 (4.40)				ND	306	461	155	4.77
23c	C_6H_4-OMe(4)	Me	0	372 (4.35)				ND	331	510	169	1.72
23d	C_6H_4-OMe(4)	Et	0	339 (4.44)				ND	332	507	175	2.16
23e	C_6H_4-NMe_2(4)	Me	0	488 (4.78)	493	547	54	7.82	296	610	314	0.70
23f	C_6H_4-NMe_2(4)	Et	0	379 (4.56)				ND	345	591	246	0.07
23g	2-thienyl	Me	0	348 (4.40)				ND	267	527	260	2.47
23h	C_6H_4-NMe_2(4)	Me	1	539 (4.70)	570	634	64	1.06	558	620	62	0.40
23i	C_6H_5	Me	-	352 (4.27)				ND	336	470	134	4.16
23j	C_6H_5	Et	-	347 (4.36)				ND	341	472	131	3.24
23k	C_6H_4-OMe(4)	Me	-	380 (4.37)				ND	337	477	140	6.74
23l	C_6H_4-OMe(4)	Et	-	381 (4.25)				ND	332	479	147	4.20

Table 11. Spectral Data of 1*H*-Pyrano[3,4-*c*]pyridines (24a-j)

				UV λmax(log ε	Fluorescence (dichloromethane)				Fluorescence (solid)			
No.	R^1	R^2	R^3	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	R.I.[c]	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
24a	C_6H_5	COOMe	Me	346 (5.23)				ND	345	462	117	1.23
24b	C_6H_4-OMe(4)	COOMe	Me	366 (4.60)				ND	335	468	133	3.93
24c	C_6H_5	COOEt	Me	349 (4.25)				ND	340	460	120	3.99
24d	C_6H_4-OMe(4)	COOEt	Me	372 (4.36)				ND	339	496	157	2.45
24e	C_6H_3-$(OMe)_2$(2,4)	COOEt	Me	377 (4.51)				ND	336	490	154	4.88
24f	C_6H_3-$(OMe)_2$(3,4)	COOEt	Me	273 (4.43)				ND	343	495	152	2.08
24g	C_6H_4-NMe_2(4)	COOEt	Me	434 (4.61)	441	515	74	0.01>	331	540	209	0.36
24h	C_6H_4-OMe(4)	SO_2-C_6H_4-Me(4)	Me	372 (4.15)				ND	345	493	148	3.40
24i	C_6H_5	H	Me	347 (4.39)				ND	319	468	149	0.22
24j	C_6H_4-OMe(4)	H	Me	363 (4.57)				ND	337	495	158	0.40

Table 12. Spectral Data of 1*H*-Pyrano[3,4-*c*]pyrones (25a-e) and Pyranyl acetates (26a-g)

				UV λmax(log ε	Fluorescence (dichloromethane)				Fluorescence (solid)			
No.	R^1	R^2	R^3	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	R.I.[c]	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
25a	C_6H_5	COOEt	Me	359 (4.30)				ND	337	457	120	0.82
25b	C_6H_4-OMe(4)	COOEt	Me	395 (4.43)				ND	343	472	129	1.38
25c	C_6H_3-$(OMe)_2$(3,4)	COOEt	Me	404 (4.48)				ND	341	542	201	0.14
25d	C_6H_5	COOEt	Ph	354 (4.40)				ND	337	476	139	0.62
25e	C_6H_4-OMe(4)	COOEt	Ph	400 (4.54)				ND	337	531	194	0.51
26a	C_6H_5	COOMe	Me	370 (4.22)				ND	348	474	126	1.00
26b	C_6H_5	COOEt	Me	359 (4.32)				ND	322	482	160	8.72
26c	C_6H_4-OMe(4)	COOEt	Me	359 (4.54)				ND	342	513	171	2.32
26d	C_6H_3-$(OMe)_2$(3,4)	COOEt	Me	386 (4.91)				ND	347	567	220	0.15
26e	C_6H_4-NMe_2(4)	COOEt	Me	471 (4.80)				ND	343	612	269	0.04
26f	C_6H_5	SO_2-C_6H_4-Me(4)	Ph	359 (4.13)	476	531	55	0.01>	342	464	122	5.20
26g	C_6H_4-OMe(4)	SO_2-C_6H_4-Me(4)	Ph	388 (4.37)				ND	340	497	157	0.08

Table 13. Spectral Data of 3-Aryl-4-methylsulfanyl-6-pyridyl-2*H*-pyrones (7a-c)

				UV λmax(log ε	Fluorescence (ethanol)				Fluorescence (solid)			
No.	position 3	position 4	position 6	nm (ethanol)	Ex max(nm)	Em max(nm)	SS[a]	ϕ	Ex max(nm)	Em max(nm)	SS[a]	R.I.[b]
7a	C_6H_5	SMe	2-pyridyl	360 (4.08)	282	439	157	0.01	349	474	125	7.02
7b	C_6H_4-OMe(4)	SMe	2-pyridyl	371 (4.12)	279	462	183	0.02	349	503	154	1.49
7c	C_6H_3-$(OMe)_2$(3,4)	SMe	2-pyridyl	369 (4.13)	284	435	151	0.15	340	529	189	0.25

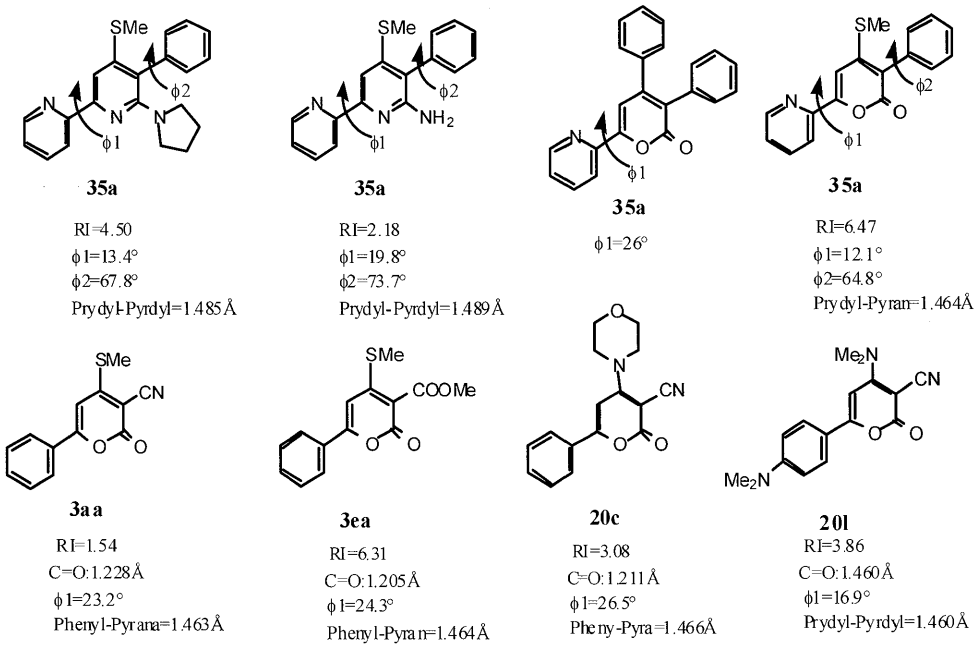


Figure 15

It has been reported that the twist angles between the two pyridyl groups in bipyridyl derivatives has a significant effect on fluorescence in the solid state. (see Table 13). The twist angles between pyridyl and pyranyl groups on the 3-phenyl-6-pyridy-2*H*-pyran-2-one (**7a**), which showed the strongest fluorescence was 12.1 degrees. This angle was the smallest among 2*H*-pyrone derivatives and pyridyl heterocycles such as **3aa**, **3ea**, **7a**, **20c**, **20l**, and **35a-c** (Figure 15). The fluorescence intensity is strongly affected by the twist angle between the pyridyl or/and aryl groups and the pyranyl group. Molecular stacking is an important factor in the expression of strong fluorescence.

Fused 2-pyrone derivatives **9a-g**, **12a-g**, **25a-d**, all except **24a-h,** showed either no fluorescence or very weak fluorescence in the solid state. This implies that fused pyrone derivatives may undergo radiation. However, methyl 8-hydroxy-6-methyl-1-oxo-3-phenyl-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate derivatives **24a-j** did show fluorescence in the solid state. This is the first example of fluorescence in fused 2-pyrone derivatives. Compounds **26a-g** also emitted light in the solid state.

Because compounds **28a-d** have a =N-H···O=C structure which includes a powerful hydrogen, we expected that these compounds would show strong fluorescence. Although the research was unfinished, these compounds did in fact show strong fluorescence. This means that strong fluorescence may also be expected in quinolizine derivatives.

In certain styryl derivatives described earlier, the introduction of an ethenyl group into 6-aryl-2*H*-pyrones was also expected to result in red shift. We attempted to synthesize merocyanine dyes with a pyrone ring incorporated into the methane chain. However, the resulting merocyanine dyes (**34a-k**) did not show fluorescence in the solid state, nor in solution (e.g. dichloromethane).

Ketene dithioacetals, which are polar ethylenic compounds containing both electron-withdrawing and electron-donating groups in the same ethylene group, were demonstrated to be useful electrophilic reagents for synthesis of 2-pyrone derivatives bearing both electron-withdrawing and electron-donating groups, as described above. It is expected that the fluorescent pigments synthesized in this work will be of future use in many different fields, and that this research will contribute toward a reduction in environmental damage.

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