Unusual Fluorescent Properties of 3,4,6-Triphenyl-α-pyrones

Keisuke Hirano, Satoshi Minakata, and Mitsuo Komatsu*
Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

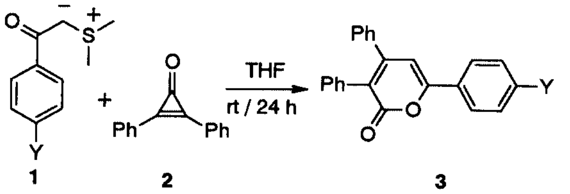
(Reveived September 22, 2000; CL-000880)

Novel fluorophores, 3,4,6-triphenyl-α-pyrone derivatives, were synthesized and their spectroscopic properties have been investigated. In the solid state they show intense greenish-yellow fluorescence, but not in solution. It is concluded that the 6-phenyl group is fixed at an angle of about 26° to the pyrone plane in the solid state by molecular packing and this fixation is required for this unique fluorescent property.

The α-pyrone structure is one of basic skeletons found in natural products and is also well-known as a dye in yellow flowers.[1,2] This chromophore has been known to be biologically active since Corey carried out Diels–Alder reaction between the diene portions of α-pyrone and dienophiles.[3] It was recently found that a low molecular weight α-pyrone functions as an inhibitor for HIV-protease, which makes this compound of even more interest from the biological point of view.[4] However only a few reports have appeared in which the α-pyrone derivatives are used as functional materials.

Recently we found that some α-pyrone derivatives show intense fluorescence, but only in the solid state. Fluorescence has been a major topic of recent research for photofunctional materials, and has found wide application in a variety of fields, such as photochemistry, laser chemistry, fluorescent probes, electroluminescence devices and related areas.[5] In this paper, we report the synthesis of the novel functional fluorophores, derivatives of 3,4,6-triphenyl-α-pyrone, and their unusual spectroscopic properties.

The title compounds were synthesized using sulfonium ylides.[6] The sulfonium ylides **1** were prepared in situ from the corresponding sulfonium salts followed by reactions with diphenylcyclopropenone **2** to give the desired compounds **3**.



1 **2** **3**

The results are summarized in Table 1. In the case where Y was NO_2, the yield of **3e** was slightly lower than those of the other derivatives. It is assumed that nucleophilicity of the sulfonium ylide **1c** toward **2** is weak because of the presence of the electron-withdrawing substituent. The α-pyrone derivatives thus synthesized were yellow solids and emitted a greenish yellow fluorescence. The only exception was **3f** which appeared orange and emitted a reddish fluorescence.

The absorption spectra of the α-pyrone derivatives were measured in dichloromethane and acetonitrile. The absorption maxima in acetonitrile showed a slight blue shift by about a few nm, compared with those in dichloromethane. Pyrones **3d** and **3f** whose Y groups were electron-donating, were red-shifted, compared with **3a** and **3b**. Based on the above, we conclude that the intramolecular charge-transfer occurs from an electron-releasing group to the lactone moiety which is enrolled as an electron-withdrawing group. However, pyrone **3e** whose Y group was a nitro group, showed a red shift in its absorption band, compared with that of **3d**. It is assumed that elongated conjugation by the nitro group affects this spectrum change.

Table 1. Characterization and absorption maxima of α-pyrones

No.	Y	Yield %	mp °C	λ_{abs} / CH_2Cl_2 nm	λ_{abs} / CH_3CN nm
3a	H	87	184	356	357 (+1)[a]
3b	Cl	67	184	358	355 (-3)
3c	Ph	69	203	368	364 (-4)
3d	MeO	82	179	370	365 (-5)
3e	NO_2	60	228	378	371 (-6)
3f	Et_2N	73	219	425	421 (-4)

[a] λ_{abs} (CH_3CN) – λ_{abs} (CH_2Cl_2).

Interestingly, the α-pyrone derivatives did not emit fluorescence in solutions at all. Only a few reports have appeared in which such a type of fluorescent property is expressed, so far as we are aware. Tris(8-hydroxyquinolino)aluminum (Alq_3), which is used in electroluminescence devices showed a largely similar phenomenon in which an intense fluorescence was observed in the solid state and only weak one in solution.[7] Evaporated films of the α-pyrone derivatives on glass plates were prepared and their spectroscopic properties were investigated. The results are listed in Table 2. Compared with the solution properties, these evaporated films showed a slight red-shift in their absorption maxima, but tendency of the shift by Y was similar to that in solutions. These films all showed fluorescence properties and their large Stokes shifts of about 150 nm were assumed to be caused by contributions of intermolecular interactions. The relative fluorescence intensity was evaluated in the solid state with excitation at 380 nm using Alq_3 as the

Table 2. Absorption and fluorescence maxima of α-pyrones in evaporated films

No.	λ_{abs} nm	λ_{fl}[a] nm	SS[b] nm	$\Delta\lambda_{abs}$[c] nm	Relative intensity	(λ_{fls})[d] (nm)
3a	371	528	157	15	3.2	(471)
3b	365	519	154	7	1.3	(479)
3c	375	528	153	7	3.1	(512)
3d	375	522	147	5	1.4	(521)
3e	388	540	156	10	0.1	(537)
3f	429	570	141	4	1.2	(552)

[a] Excited at λ_{abs}. [b] Stokes shift (λ_{fl} - λ_{abs}). [c] λ_{abs} - λ_{abs} (CH_2Cl_2). [d] The intensity of Alq_3 was set to 1 (λ_{fl} = 495). Excited at 380 nm.

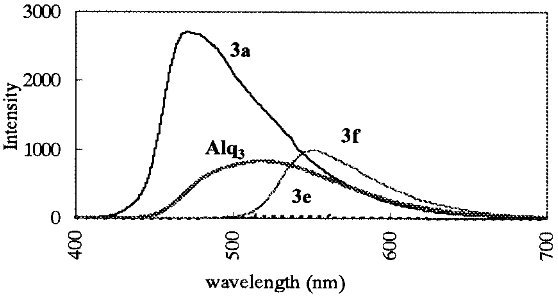
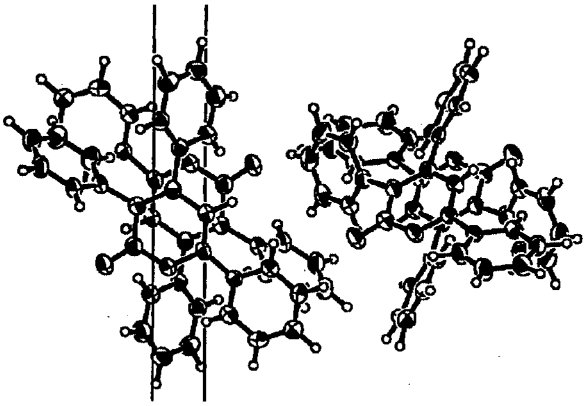


Figure 1. Comparison of fluorescent intensity of α-Pyrones with that of Alq$_3$ at the powder form

reference. Some α-pyrone derivatives showed more intense fluorescence than Alq$_3$ as shown in Figure 1. Therefore these compounds are of considerable promise for use in EL applications instead of Alq$_3$.

X-ray structure analysis was performed on **3a** and Figure 2 shows the molecular packing diagram.[8] Two phenyl groups at the 3- and 4-positions were twisted from the plane of the pyrone ring about 50°. On the other hand, the other one at 6-position is also twisted out of the pyrone plane by only 26°. This figure clearly showed that the free rotation of the 6-phenyl group was blocked because of the rather short intermolecular distance between molecules. Based on these results, it is assumed that the behavior of the phenyl group is relevant to the unusual fluorescent properties observed, i.e. emission only in the solid state.



Figue. 2. Molecular packing diagram of **3a**

This suggests that the phenyl group is fixed at an angle of about 26° to the pyrone plane in the solid state by molecular packing and the path of fluorescence was thus increased. On the other hand, in solution, the free rotation of the 6-phenyl group provides a path for non-radiative decay, and, hence, the α-pyrone derivatives do not fluoresce, when in solution.

In summary, novel fluorophores, α-pyrone derivatives, were synthesized and their spectroscopic properties were investigated. An electron-donating substituent on the 6-phenyl group, Y, causes a red-shift in the absorption and a fluorescent maximum. The unusual property of fluorescence only in the solid state can be explained by the fact that the 6-phenyl group is fixed at an angle of about 26° to pyrone plane by the molecular packing, which caused intense fluorescence in the solid state. Fluorescent material in the solid state has potential for use as a fluorescent pigment and in EL devices. These issues are currently under investigation.

References and Notes

1 R. A. Hill, "Progress in the Chemistry of Organic Natural Products"; Speringer-Verlag, Weinheim-New York (1986); Vol. 49, pp. 1–78.

2 L. A. Collect, M. T. Davies-Coleman, and D. E. A. Rivett, *Prog. Chem. Org. Nat. Prod.*, **75**, 181 (1998).

3 E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, **48**, 5373 (1983).

4 D. L. Romero, P. R. Menninen, F. Han, and A. G. Romero, *J. Org. Chem.*, **64**, 4980 (1999).

5 K. Araki, T. Mutai, Y. Shigematsu, M. Yamada, T. Nakajima, S. Kuroda, and I. Shimano, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 613.

6 Y. Hayashi and H. Nozaki, *Tetrahedron*, **27**, 3085 (1971).

7 C. W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.*, **51**, 913 (1987).

8 X-ray crystallographic data : $C_{23}H_{16}O_2$, MW = 324.38, yellow, prismatic, monoclinic, space group $P2_1/c$ (#14), a = 18.267(4) Å, b = 20.298(5) Å, c = 8.975(3) Å, β = 90.01 (3)°, V = 3327(1) Å^3, Z = 8, D_c 1.295 g/cm^3, $F(000)$ = 1360.00, μ(Mo Kα) = 0.81 cm^{-1}, graphite monochromated Mo Kα (λ = 0.71069 Å), T = 23 °C, Final discrepancy factor: R = 0.062 and R_w = 0.105 This crystal consists of crystallographically independent two molecules in the asymmetrical unit. The structure was solved by direct method (MITHRIL90).