HETEROCYCLES, Vol. 84, No. 1, 2012, pp. 315 - 321. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 10th June, 2011, Accepted, 19th July, 2011, Published online, 22nd July, 2011
DOI: 10.3987/COM-11-S(P)33

SOLID-STATE FLUORESCENCE PROPERTIES AND CRYSTAL STRUCTURES OF 7-(DIETHYLAMINO)COUMARIN DERIVATIVES†

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Abstract – 7-(Diethylamino)-3-phenylcoumarin (**1**) gave strong emission band at 477 nm in the solid state when excited at 400 nm, but ethyl 2-[7-(diethylamino)-2-oxo-2*H*-1-benzopyran-3-yl]-4-thiazolecarboxylate (**2**) had no fluorescence in solid state. The crystal structures of **1** and **2** were analyzed by X-ray crystallography. The crystal of **1** had intermolecular C-H···O, C-H···N and C-H···π interactions and that of **2** had intermolecular C-H···O, π···π, and S···π interactions.

Materials containing a coumarin (2*H*-1-benzopyran-2-one) component have been useful in many fields such as fluorescence materials and laser dyes, nonlinear optical materials, photorefractive materials, photo resists, intermediates for drug synthesis, luminescence materials, and analytical reagents etc.[1] Although the fluorescence of the coumarin itself is weak, the introduction of substituent group into coumarin increase the fluorescence intensity. Recently, we have reported the synthesis and fluorescence properties of 7-diethylaminocoumarin derivatives as fluoroionohores accessible for analytical purposes in the fields of analytical and biological chemistry.[2] The crystal structure analyses of 7-diethylaminocoumarin,[3] 7-diethylamino-3-dimethylaminocoumarin,[4] methyl 4-(7-diethylamino-2oxo-2*H*-1-benzopyran-3-yl)-benzoate,[5] and cholesteryl 4-(7-diethylamino-2oxo-2*H*-1-benzopyran-3-yl)benzoate[6] have been reported.

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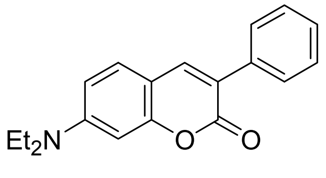
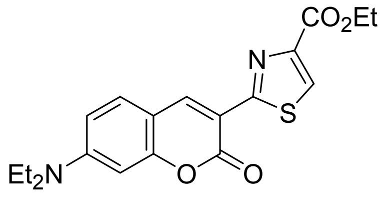
†Dedicated to Professor Dr. Albert Padwa on the occasion of his 75th birthday.

We now report the solid-state fluorescence properties and crystal structures of 7-(diethylamino)-3-phenyl-2*H*-1-benzopyran-2-one (**1**) and ethyl 2-[7-(diethylamino)-2-oxo-2*H*-1-benzopyran-3-yl]-4-thiazolecarboxylate (**2**) in order to elucidate the relationship between the solid-state fluorescence and molecular packing.



1



2

The structures of **1**[7] and **2**[8] were confirmed by X-ray crystallographic analysis as shown in Figure 1. Phenyl derivative (**1**) adopts a twisted conformation. The dihedral angle between the coumarin ring defined by C1–C9/O1/O2 and the phenyl ring defined by C14–C19 is 42.41(1)º. Thiazole derivative (**2**) adopts an almost flattened conformation. The thiazole ring defined by C14–C16/N2/S1 of **2** made angles of 2.31(4)º and 12.15(5)º with coumarin ring and ethoxycarbonyl plane defined by C17–C19/O3/O4, respectively.

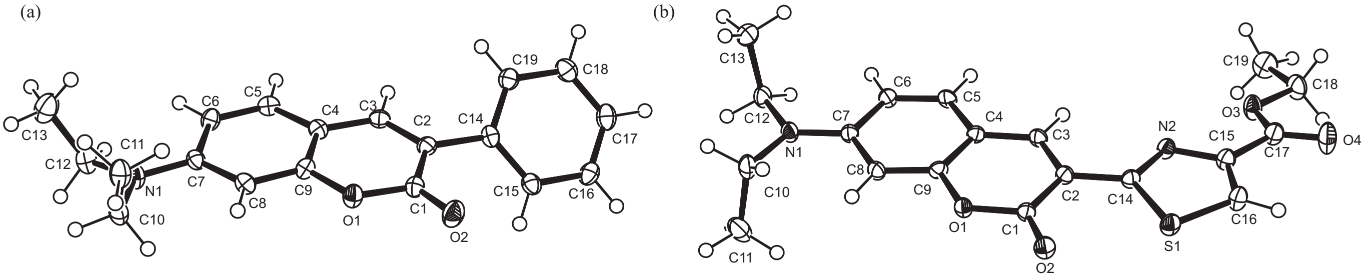


Figure 1. ORTEP diagrams of (a) **1** and (b) **2**, showing 50% probability displacement ellipsoids

The C-C and C-O bond lengths of the coumarin ring of **1**[9] and **2**[10] are similar to those of 7-diethylaminocoumarin[3] and distinct from those of coumarin itself.[11] The C7-N1 bond lengths of **1** and **2** are close to that (1.376(5) Å)[4] of 7-diethylamino-3-dimethylaminocoumarin and Csp^2-Nsp^2 planar bond length [1.355 Å].[12] The respective deviations of each atom from the least squares plane defined by C7/C10/C12/N1 atoms are within the range of -0.002–0.005(1) Å for **1** and -0.001–0.003 Å for **2**, respectively. This means that the diethylamino group substituted at C-7 position effects on the conjugation system of coumarin. The two ethyl groups of diethylamine group are *syn* for **1** and *anti* for **2** with respect to one another.

There are some intermolecular C-H···O hydrogen bonds of **1**[13] and **2**[14] as shown in Figure 2 and 3. The H···O distances of **1** and **2** are similar to those of methyl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl)benzoate (2.49–2.88 Å)[5] and cholesteryl 4-(7-diethylamino-2oxo-2*H*-1-benzopyran-3-yl)benzoate (2.40–2.66 Å).[6] Intermolecular C-H···N hydrogen bonds is observed in **1** as shown in Figure 2. The H···N distance[13] of **1** is shorter to that [2.91 Å][15] of 2,2'-bi-2-imidazoline.

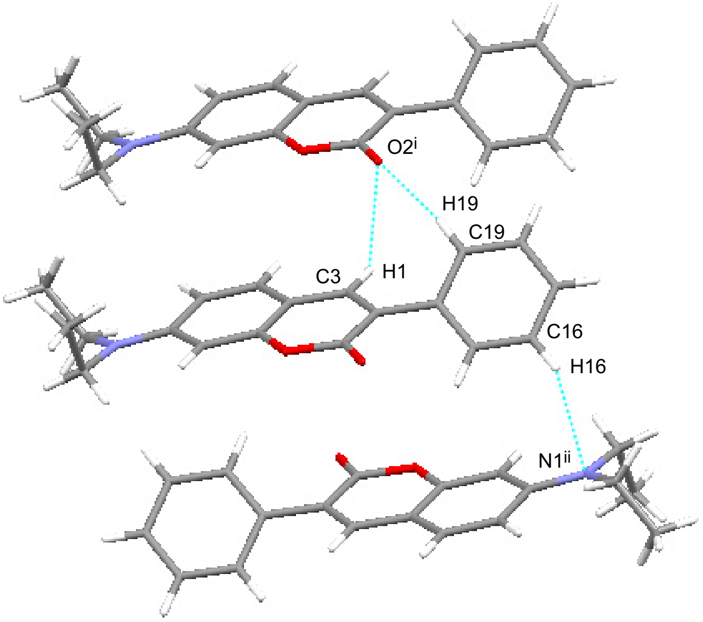


Figure 2. Intermolecular C-H···O and C-H···N interactions of **1**

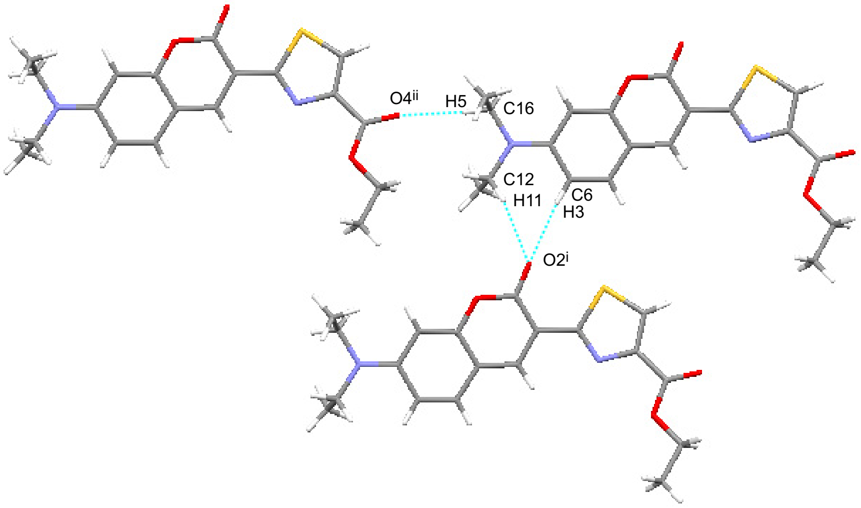


Figure 3. Intermolecular C-H···O interactions of **2**

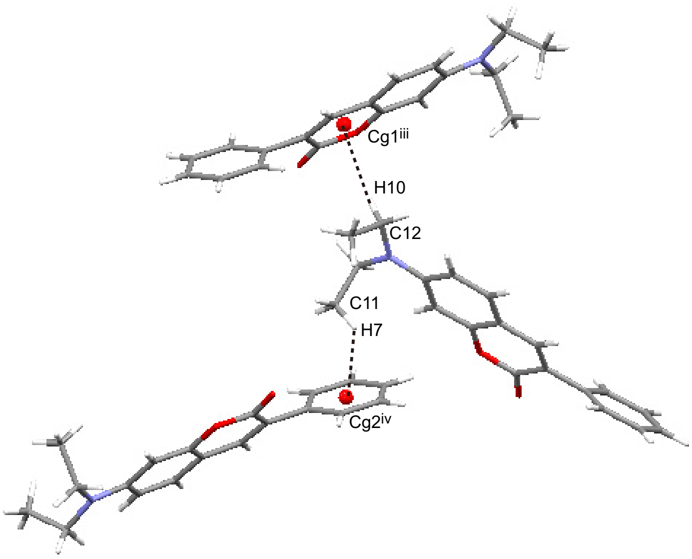


Figure 4. Intermolecular C-H···π interactions of **1**

Intermolecular C–H···π interactions are observed in **1**, as shown in Figure 4. The distances between H10 and the centroid (Cg1^{iii}) (Symmetry code: (iii) x, 1/2-y, 1/2+z) of the pyrane ring (C1–C4/C9/O1) and between H7 and the centroid (Cg2^{iv}) (Symmetry code: (iv) 1-x, 1/2+y, 1/2-z) of the benzene ring (C16–C19) are 2.691 and 3.133 Å, respectively, which are similar to the intermolecular C–H···π interaction [2.835, 3.079 Å] observed in cholesteryl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl)benzoate.[6]

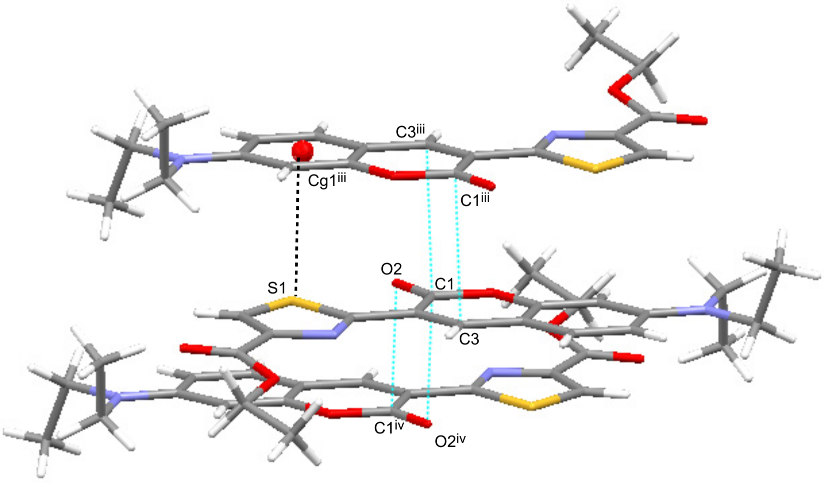


Figure 5. Intermolecular S···π and π···π interactions of **2**

Intermolecular π···π interactions between the coumarin planes of **2** are observed in Figure 5. The distances between intermolecular coumarin planes are 3.288(2) Å for C1···C3^{i} and 3.064(2) Å for

C1···O2[i] (symmetry codes: (iii) -x, 2-y, 1-z, (iv) 1-x, 2-y, 1-z), which is within the range associated with π···π interaction [3.3-3.8 Å].[16,17] Interestingly intermolecular S···π contact (3.372 Å) between S1 atom and the centroid of benzene ring (C4–C9) of **2** is observed.

Figure 6 illustrates the fluorescence spectral behavior of **1** and **2** in $CHCl_3$ (1.0 x 10^{-5} M) and in the solid state. Coumarin derivatives (**1** and **2**) in $CHCl_3$ solution gave a strong emission band around 464 nm (when excited at 400 nm) for **1** and 480 nm (when excited at 452 nm) for **2**, respectively. The emission intensity of **2** was larger than that of **1**. Interestingly, phenyl derivative (**1**) gave a strong emission band at longer wavelength (477 nm) in the solid state when excited at 400 nm but thiazole derivative (**2**) had no fluorescence in solid state.

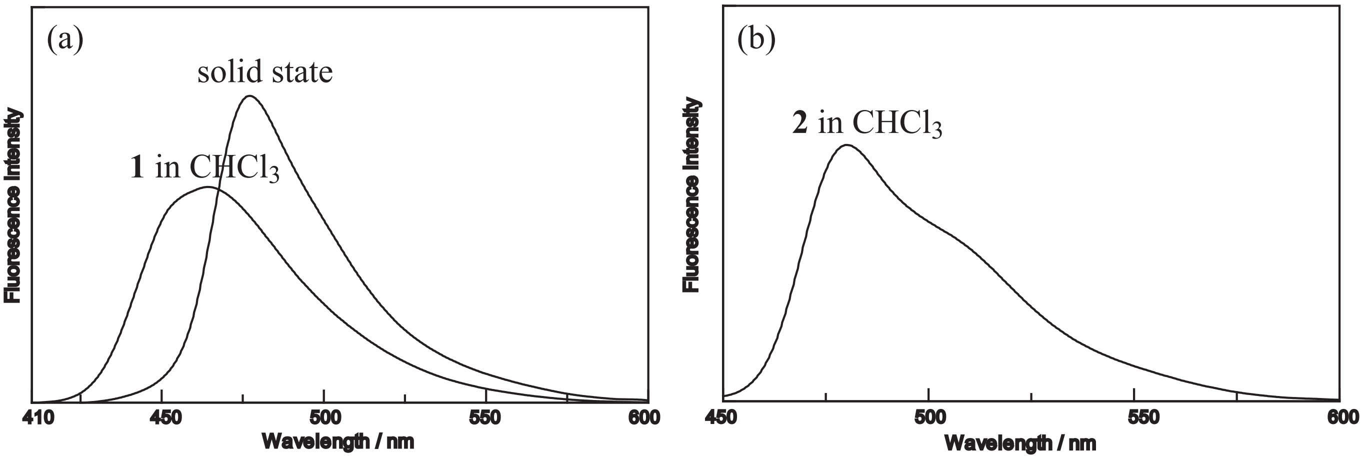


Figure 6. Fluorescence spectra of (a) **1** in $CHCl_3$ (1.0 x 10^{-5} M) and solid state and (b) **2** in $CHCl_3$ (1.0 x 10^{-5} M) at room temperature

The strong emission at longer wavelength of **1** would be explained on the intermolecular interaction between the coumarin rings by the formation of C-H···π interaction in the crystal state. While no fluorescence of **2** in solid state might be explained on the intermolecular interaction between the coumarin rings by the formation of π···π and S···π interactions in the crystal state. In conclusion, the solid-state fluorescence properties of 7-diethylaminocoumarin derivatives were dependent on the molecular arrangement in the crystals.

ACKNOWLEDGEMENT

This work was performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices (Institute for Materials Chemistry and Engineering, Kyushu University)".

REFERENCES AND NOTES

1. Y. Tian, E. Akiyama, Y. Nagase, A. Kanazawa, O. Tsutsumi, and T. Ikeda, *Macromol. Chem. Phys.*, 2000, **201**, 1640.
2. H. Takechi, Y. Oda, N. Nishizono, K. Oda, and M. Machida, *Chem. Pharm. Bull.*, 2000, **48**, 1702.
3. D. S. Yufit, M. A. Kirpichenok, Y. T. Struchkov, L. A. Karandashova, and I. I. Grandberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 802.
4. H. Takahashi, H. Takechi, K. Kubo, and T. Matsumoto, *Acta Cryst.*, 2005, **E61**, o3041.
5. H. Takechi, K. Kubo, H. Takahashi, and T. Matsumoto, *Acta Cryst.*, 2006, **E62**, o3826.
6. H. Takechi, K. Kubo, H. Takahashi, and T. Matsumoto, *J. Oleo Sci.*, 2007, **56**, 195.
7. Crystal data for **1**, $C_{19}H_{19}NO_2$, monoclinic, $P2_1/c$, $a = 6.3599(18)$ Å, $b = 17.257(5)$ Å, $c = 13.520(4)$ Å, $\beta = 93.1306(14)^\circ$, $V = 1481.6(7)$ Å^3, $Z = 4$, $M_r = 293.36$, $D_x = 1.315$ Mgm^{-3}, $\mu = 0.849$ cm^{-1}, T = 123(1) K, refinement on F^2 (*SHELXL97*), $R[F^2 > 2\sigma(F^2)] = 0.0727$, $wR(F^2) = 0.2236$, $S = 1.111$.
8. Crystal data for **2**, $C_{19}H_{20}N_2O_4S$, triclinic, $P\bar{1}$, $a = 7.3832(15)$ Å, $b = 9.476(2)$ Å, $c = 14.024(4)$ Å, $\alpha = 84.329(10)^\circ$, $\beta = 77.505(9)^\circ$, $\gamma = 67.101(8)^\circ$, $V = 882.3(4)$ Å^3, $Z = 4$, $M_r = 372.44$, $D_x = 1.402$ Mgm^{-3}, $\mu = 2.111$ cm^{-1}, T = 123(1) K, refinement on F^2 (*SHELXL97*), $R[F^2 > 2\sigma(F^2)] = 0.0456$, $wR(F^2) = 0.1180$, $S = 1.075$.
9. Selected geometric parameters (Å, º) of **1**, O1-C1 1.389(2), O1-C9 1.373(2), O2-C1 1.210(3), N1-C7 1.371(3), N1-C10 1.459(3), N1-C12 1.454(3), C1-C2 1.462(3), C2-C3 1.357(3), C3-C4 1.421(3), C4-C5 1.407(3), C4-C9 1.395(3), C5-C6 1.367(3), C6-C7 1.426(3), C7-C8 1.402(3), C8-C9 1.384(3), C7-N1-C10 120.6(2), C7-N1-C12 122.8(2), C10-N1-C12 116.5(2), C1-C2-C14-C15 43.4(3).
10. Selected geometric parameters (Å, º) of **2**, O1-C1 1.3804(19), C1-C2 1.449(2), C2-C3 1.367(2), C3-C4 1.407(2), C4-C5 1.415(2), C4-C9 1.404(2), C5-C6 1.365(2), C6-C7 1.428(2), C7-C8 1.418(2), C8-C9 1.373(2), N1-C7 1.360(2), N1-C10 1.465(2), N1-C12 1.466(2), C2-C14 1.457(2), C15-C16 1.365(3), S1-C14 1.7416(19), S1-C16 1.6993(19), N2-C14 1.317(2), N2-C15 1.373(2), C7-N1-C10 121.96(16), C7-N1-C12 122.47(16), C10-N1-C12 115.57(14), N2-C15-C17-O(3) -8.0(2), C18-O3-C17-C15 -175.31(16), C17-O3-C18-C19 175.86(18), N2-C15-C17-O3 -8.0(2).
11. E. Gavuzzo, F. Mazza, and E. Giglio, *Acta Cryst.*, 1974, **B30**, 1351.
12. D. R. Lide, '*Handbook of Chemistry and Physics, 81st ed.*', CRC Press, Boston, 2000.
13. Hydrogen bond geometry of **1**, $H1\cdots O2^{i}$: 2.622 Å, $C3\cdots O2^{i}$: 3.343(2) Å, $C3\text{-}H1\cdots O2^{i}$: 133º, $H19\cdots O2^{i}$: 2.654 Å, $C19\cdots O2^{i}$: 3.561(3) Å, $C19\text{-}H19\cdots O2^{i}$: 160º, $H16\cdots N1^{ii}$: 2.739 Å, $C16\cdots N1^{ii}$: 3.473(3) Å, $C16\text{-}H16\cdots N1^{ii}$: 135º. (i) x-1, y, z, (ii) 1-x, -y, 1-z.

14. Hydrogen bond geometry of **2**, $H3\cdots O2^{i}$: 2.419 Å, $C6\cdots O2^{i}$: 3.356(2) Å, $C6-H3\cdots O2^{i}$: 169°, $H11\cdots O2^{i}$: 2.495 Å, $C12\cdots O2^{i}$: 3.540(2) Å, $C12-H11\cdots O2^{i}$: 143°, $H5\cdots O4^{ii}$: 2.426 Å, $C10\cdots O4^{ii}$: 3.384(2) Å, $C10-H5\cdots O4^{i}$: 163°. (i) x, y-1, z, (ii) x, y-1, 1+z.
15. C. J. Brennan and V. McKee, *Acta Cryst.*, 1999, **C55**, 1492.
16. C. K. Prout, T. Morley, I. J. Tickle, and J. D. Wright, *J. Chem. Soc., Perkin Trans. 2*, 1973, 523.
17. H. Takahashi, H. Takechi, K. Kubo, and T. Matsumoto, *Heterocycles*, 2007, **72**, 123.