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Molecular stacking and solid state spectra of 2,5-bis(1-aza-1-cycloalkyl)-3,6-dicyanopyrazines and their X-ray crystal structures

Kazuko Shirai[a], Masaru Matsuoka[*,b], Shinya Matsumoto[a,*], Motoo Shiro[c]

[a]*Faculty of Education and Human Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[b]*Laboratory of Material Science, Kyoto Women's University, 35 Kitahiyoshi-cho, Imakumano, Higashiyama-ku, Kyoto 605-8501, Japan*
[c]*X-Ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akisima, Tokyo 196-8666, Japan*

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Abstract

Solid state absorption and fluorescence spectra of 2,5-bis(1-aza-1-cycloalkyl)-3,6-dicyanopyrazines were correlated in terms of intermolecular π–π interactions with their differences in molecular stacking evaluated by X-ray structure analyses and MOPAC methods.

Keywords: 2,5-Diamino-3,6-dicyanopyrazine; Solid state spectra; X-ray structure analysis; Intermolecular π–π interactions; Molecular stacking; Fluorescence quenching

1. Introduction

Almost all functionalities of organic materials for electronics and photonics are induced by π-electron based intermolecular interactions. Interactions including intermolecular π–π interactions, dipole–dipole interactions, and characteristics of molecular stacking are very significant with respect to their special functionalities in the solid state. Dye molecules have a large π-conjugated planar structure and are thus valuable candidates for organic functional materials [1]. Correlation between the solid state chemistry of dye molecules and their molecular structures in the solid state is of current interest with regard to their functionality in crystals and aggregates. Such correlations include large color changes in the solid state [2–5], solid state topochemical reactivities [6], nonlinear optical properties [7], and solid state fluorescence properties [8–11]. Many of these functionalities are caused by intra- and intermolecular π–π interactions of dye molecules in the solid state. Solid state absorption and fluorescence spectra of dye chromophores and their spectral shift from the solution to the solid state could be correlated with the intermolecular π–π interactions in crystals and vapor deposited thin films [12].

* Corresponding author. Tel.: +81-45-339-3366; fax: +81-45-339-3345.
E-mail address: smatsu@edhs.ynu.ac.jp (S. Matsumoto).
* Deceased.

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In our previous paper, fluorescence quenching of 2,5-bis(*N*,*N*-dialkylamino)-3,6-dicyanopyrazines in the solid state gave rise to valuable information about intermolecular π–π interactions; the stronger the intermolecular π–π interactions in the solid state, the stronger the fluorescence quenching, but these differences were not observed in the solution [13]. Conformational analyses of the 2,5-bis(*N*,*N*-dialkylamino)-3,6-dicyanopyrazines were conducted by the MOPAC methods [14], and their optimized structures were correlated with their molecular stacking behaviors and their spectral changes in the solid state [13].

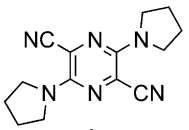
In this paper, we report the correlation between the solid state spectral properties and X-ray crystal structures of 2,5-bis(pyrrolidino- and piperidino)-3,6-dicyanopyrazines, in terms of their molecular stacking and intermolecular π–π interactions.

2. Results and discussion

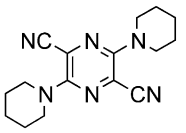
2,5-Bis(pyrrolidino)-3,6-dicyanopyrazine **1** and 2,5-bis(piperidino)-3,6-dicyanopyrazine **2** have been synthesized by the cycloalkylation of 2,5-diamino-3,6-dicyanopyrazine [12]. Their structures, absorption and fluorescence spectra in chloroform, vapor deposited thin films and the powder state are shown in Table 1. The difference in absorption maximum (λ_{max}) between the solution and solid state is denoted as $\Delta\lambda$, and the corresponding difference in the fluorescence maximum (F_{max}) as ΔF. The physical appearance of the compounds in the solid state, and their $\Delta\lambda$ and ΔF values are compared with their substituent effects.

There are small structural differences between **1** and **2**; **1** has 5-membered pyrrolidine rings but **2** has 6-membered piperidine rings. Both have intramolecular charge-transfer chromophoric systems [12] and the difference in λ_{max} of 34 nm from **1** to **2** can be attributed to the difference in the electron donating properties of the amino groups which is supported by the increase in the molar absorptivity (ε_{max}) value from **2** (4000) to **1** (5630). The optimized structures calculated by the MOPAC AM1 and PM3 methods of **1** and **2** indicate that these two dyes have similar planar π-conjugation systems including the amino nitrogen atoms. It is difficult to explain the differences in their absorption spectra by electronic effects and/or

Table 1
Visible absorption and fluorescence properties of dyes **1** and **2** in solution and in the solid state



1



2

Dye No.	λ_{max}/nm		$\Delta\lambda$[b]/nm	F_{max}/nm[c]			ΔF[e]/nm	Appearance of crystals
	$CHCl_3$ (ε)	Film[a]		$CHCl_3$ (intensity)	Film[a]	Powder (intensity)[d]		
1	526 (5630)	461[f] 596	−65 70	596 (840)	647	680 (610)	51 (film) 84 (powder)	Dark purplish red
2	492 (4000)	417 566	−75 74	597 (430)	594	633 (8230)	−3 (film) 36 (powder)	Bright red

[a] Vapor deposited thin film.
[b] $\Delta\lambda = \lambda_{max}$ (solid)− λ_{max} (solution).
[c] Excited at λ_{max} in solution and in the film, respectively.
[d] Relative intensity of the solid state fluorescence in the powder state.
[e] $\Delta F = F_{max}$ (solid) $- F_{max}$ (solution).
[f] Shoulder.

the optimized structures. The X-ray crystal data showed differences in the bond length between the ring-carbon and the amino-nitrogen atom; i.e. 1.348 Å for **1** and 1.379 Å for **2**. Similar differences were also observed between the ring-carbon cyano-carbon bond length; 1.422 Å for **1** and 1.449 Å for **2**. These results indicated that **1** has stronger intramolecular charge-transfer chromophoric system than **2**, predicting a bathochromic shift of λ_{max} and hyperchromic effects of ε_{max} value from **2** to **1**.

Single crystals of **1** and **2** were obtained from mixtures of ethanol and ether (1:1), by slow evaporation of the solvent. To elucidate the molecular structure and packing modes of **1** and **2** in the crystals, X-ray crystal structure analyses were carried out. The crystallographic parameters are summarized in Table 2. The space group of **1** is $C2/c$ and that of **2** is $P2_1/n$, although both crystals belong to the same monoclinic system. The final R was 0.045 for **1** and 0.039 for **2**, respectively. The calculated density is 1.332 for **1** and 1.287 for **2**, respectively.

From these X-ray analyses, molecular stacking of **1** was found to be much stronger than that of **2**, indicating that **1** has stronger intermolecular interactions than **2**. Molecular overlap in the paired molecules of **1** and **2** is illustrated in Fig. 1.

Table 2
Crystallographic parameters of dyes **1** and **2**

Dye	**1**	**2**
Chemical formula	$C_{14}H_{16}N_6$	$C_{16}H_{20}N_6$
Molecular weight	268.32	296.37
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Lattice parameters		
a/Å	21.197 (5)	5.349 (1)
b/Å	5.683 (1)	16.140 (3)
c/Å	12.138 (2)	9.077 (2)
β/°	113.83 (1)	102.56 (1)
V/Å^3	1337.5 (5)	764.9 (3)
Z	4	2
Calculated density/Mg m^{-3}	1.332	1.287
μ/cm^{-1}	15.95	15.22
Observed reflections	1291	1537
R	0.045	0.039
Rw	0.067	0.062
Goodness of fit	1.31	1.36

The upper drawings are the side-view and the lower ones are the front-view of the π-plane. The intermolecular atomic distance between the amino-nitrogen and the cyano-carbon in charge-transfer characters is 3.340 Å in the perpendicular direction for **1**, but that of **2** in a slightly translocated direction is 3.400 Å. The molecular structure of **1** has a chair form whereas **2** has a dumbbell form and the molecular stacking behavior of these dyes differs slightly; thus **1** is oriented in the perpendicular direction to attain intermolecular charge-transfer interatomic interaction, but **2** is translocated a little to avoid steric interactions between the six-membered piperidine moieties. As a result, intermolecular π–π interactions of **1** are proposed to be stronger than those of **2**. The calculated density of the crystal of **1** is found to be higher than that of **2**.

Molecular arrangements are shown in Fig. 2 on the *ac* and the *bc* plane for **1** and **2**, respectively. Dye **1** molecules are parallel with each other along the *a*-axis to form a two-dimensional layer parallel to the *ab* plane. Between the adjacent layer, the molecules are alternatively twisted by about 85° along the *c*-axis. On the other hand, molecular arrangement of dye **2** is different. The molecules are arranged in a typical herringbone fashion as shown in Fig. 2(b). As a result, the solid state absorption spectra of **1** and **2** differ significantly. The relative magnitudes of the splitting of the two bands differ considerably [8], as does the appearance of the crystals. Thus solid **1** is dark purplish-red but solid **2** is bright-red, as described in Table 1.

In conclusion, significant differences between the absorption and fluorescence properties of **1** and **2** in the solid state are caused by the differences in their molecular stacking and arrangement; in dye **1**, ΔF values in the film and powder are larger than those of **2** (51 and 84 nm for **1**, −3 and 36 nm for 2) indicating much stronger stabilization of **1** in the aggregated or solid state. The relative strengths of fluorescence in the solid state are also supported by the stronger intermolecular π–π interactions of **1** compared to **2** (610 for **1** and 8230 for **2**). The reverse occurs in solution (840 for **1** and 430 for **2**), as shown in Table 1. It was found that fluorescence quenching in the solid state is

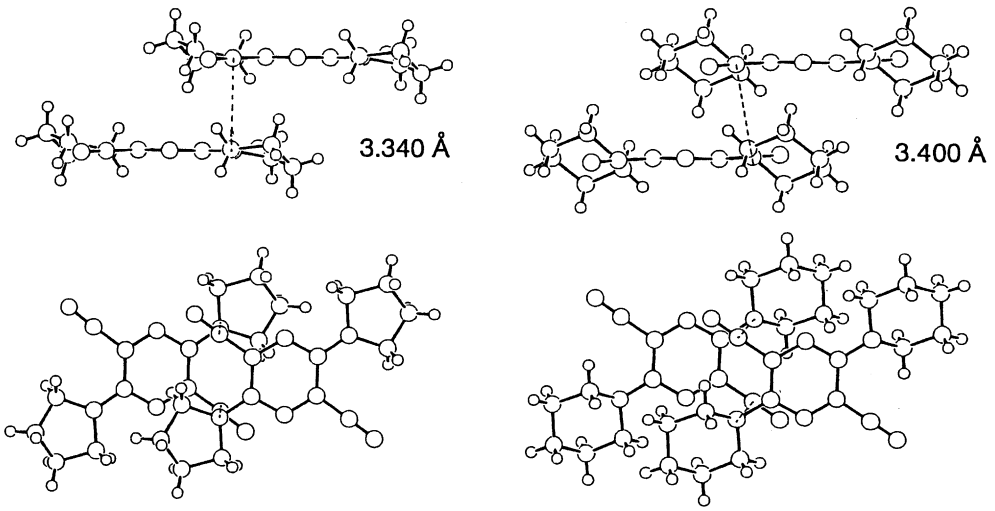


Fig. 1. Overlap of two dye molecules for **1** and **2** in the crystal state. The upper drawings are side-views and the lower ones are front-views of π-planes of these dyes.

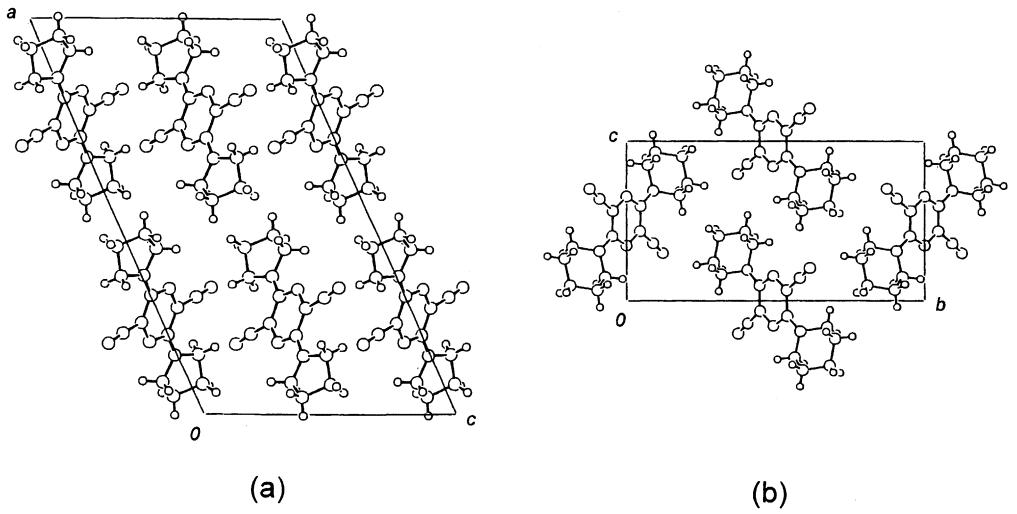


Fig. 2. Molecular arrangements of dyes **1** (a) and **2** (b) in the crystalline state.

potentially a useful method for evaluating intermolecular π–π interactions of fluorescent dyes.

2.1. Experimental

Dyes **1** and **2** were previously synthesized and characterized in our laboratory [12]. Single crystals of dyes **1** and **2** were obtained from a mixture of ethanol and ether (1:1) by slow evaporation of the solvent. The diffraction data were collected on a Rigaku R-axis IV with an imaging plate area detector using graphite-monochromated Mo$K\alpha$ radiation to a maximum 2θ value of 55° at −120 C°. The camera length was set to be 105 mm from the crystal. A total of 29 ($\Delta\varphi = 6°$) and 25 ($\Delta\varphi = 4°$) images were collected using an oscillation technique for **1** and **2**, respectively. An absorption correction was not applied and a correction for secondary extinction was applied in both dyes. The structures were solved by the direct

method SIR97 [15] and expanded using DIRDIF94 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the teXsan program package [17].

References

[1] Matsuoka M. The chemistry of special dyes for electro-optical applications. The Journal of the Society of Dyers and Colourists 1989;105:167–73.

[2] Philpott MR. Theory of molecular polaritons. Application to the reflection spectra of anthracene, 1,5-bis(dimethylamino)pentamethinium perchlorate, and some other cationic dye crystals The Journal of Chemical Physics 1971; 54(5):2120–9.

[3] Daehne L. Self-organization of polymethine dyes in thin solid layers. The Journal of the American Chemical Society 1995;117:12855–60.

[4] Endo A, Matsumoto S, Mizuguchi J. Interpretation of the near-IR absorption of magnesiumphthalocyanine complexes in terms of exciton coupling effects. Journal of Physical Chemistry A 1999;103:8193–9.

[5] Matsumoto S, Tokunaga W, Miura H, Mizuguchi J. Interpretation of the solid-state spectra of tetrathiabenzoquinone derivatives from the standpoint of intermolecular interactions. Bulletin of the Chemical Society of Japan 2001;74(3):471–7.

[6] Kim JH, Matsuoka M, Fukunishi K. Selective topochemical photodimerization of styryldicyanopyrazines in the solid state. Journal of Chemical Research (S) 1999:132–3.

[7] Matsuoka M, Oshida A, Mizoguchi A, Hattori Y, Nishimura A. Molecular design of quinoid dyes for 3rd order NLO materials. Nonlinear Optics 1995;10:109–14.

[8] Shirai K, Jaung JY, Matsuoka M, Fukunishi K. Structure and spectral properties of dicyanopyrazine fluorescence dyes. Journal of Society of Photographic Science and Technology of Japan 1998;61(5):261–7.

[9] Kim JH, Shin SR, Matsuoka M, Fukunishi K. Self-assembling of aminopyrazine fluorescent dyes and their solid state spectra. Dyes and Pigments 1998;39(4):341–57.

[10] Kim JH, Shin SR, Matsuoka M, Fukunishi K. Self-assembling of aminopyrazine fluorescent dyes and their solid state spectra, part 2. Dyes and Pigments 1999;41(3):183–91.

[11] Shirai K, Matsuoka M, Fukunishi K. New syntheses and solid state fluorescence of azomethine dyes derived from diaminomaleonitrile and 2,5-diamino-3,6-dicyanopyrazine. Dyes and Pigments 2000;47(1-2):107–15.

[12] Shirai K, Yanagisawa A, Takahashi H, Fukunishi K, Matsuoka M. Syntheses and fluorescent properties of 2,5-diamino-3,6-dicyanopyrazine dyes. Dyes and Pigments 1998;39(1):49–68.

[13] Shirai K, Matsuoka M, Fukunishi K. Fluorescence quenching by intermolecular π–π interactions of 2,5-bis(*N*,*N*-dialkylamino)-3,6-dicyanopyrazines. Dyes and Pigments 1999;42(1):95–101.

[14] Stewart JJP. MOPAC version 6, QCPE #455 revised as version 6.01 by Hirano T. JCPE Newsletter 1991;2:26.

[15] Altomare A, Burla MC, Camalli M, Cascarano G, Giacovazzo C, Guagliardi A, Moliterni AGG, Polidori G, Spagna R. A new tool for crystal structure determination and refinement. Journal of Applied Crystallography 1999;32:115–9.

[16] Beurskens PT, Admiraal G, Beurskens G, Bosman WP, de Gelder R, Israel R, Simts JMM. The DIRDIF-94 program system. Technical report of the crystallography laboratory. The Netherlands: University of Nijmegen; 1994.

[17] Crystal structure analysis package, Molecular structure corporation 1985&1992.