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Spectral Evidences for the J-Aggregate Formation of a Non-Benzenoid Aromatic Dye, Dicyclohepta[5,6:b]pyrazino[2,3-g]quinoxaline-3,11-dione

Hitoshi TAKESHITA,* Akira MORI,* Tomohiro NAGAO,† and Toshihiko NAGAMURA†

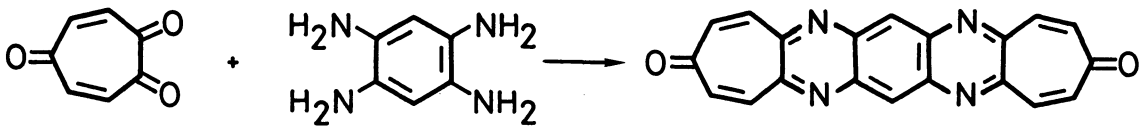
Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816

†Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816

The planar and symmetrically conjugated π-system, dicyclohepta-[5,6:b]pyrazino[2,3-g]quinoxaline-3,11-dione, showed a narrow and intense absorption band and resonance fluorescence in conc H_2SO_4 solutions as low as 10^{-7} M. These observations show the formation of the J-aggregate. A remarkable solvatochromism was also noticed in organic solvents (476 nm in $CHCl_3$ and 547 nm in DMF).

Intermolecular interactions of chromophores give specific absorption bands usually shifted from those of isolated monomeric compounds. Among them is there a J-band after Jelley[1] with narrow and intense absorption and resonance fluorescence. The J-aggregates play important roles in energy transfer or electron transfer reactions.[2] To the best of our knowledge, no compound but cyanines showed the J-band.[3] Now, we wish to show the formation of J-aggregates in acidic media with planar and symmetrical dicyclohepta[5,6:b]pyrazino[2,3-g]quinoxaline-3,11-dione (**1**).

The dye, **1**, was prepared by a condensation of p-tropoquinone (**2**) to 1,2,4,5-tetraaminobenzene (**3**)[4] in 45% yield. The symmetrical structure of **1** was assured by pertinent ^1H- and ^{13}C NMR spectral data.[5]



2 **3** **1**

As shown in Fig. 1, **1** showed a remarkable solvatochromism; the color was yellow in $CHCl_3$, orange in N,N-dimethylformamide (DMF), blue in trifluoroacetic acid (TFA), and green in conc H_2SO_4 and in a mixture of TFA and conc HCl (1:9).

The TFA solutions of **1** revealed a gradual change of color. The ^1H NMR spectrum of freshly-dissolved **1** in TFA-d exhibited sharp signals at δ=7.51 (4H, d, J=12.5 Hz), 8.35 (4H, d, J=12.5 Hz), and 9.68 (2H, s), however, after being kept for 1 d at

room temperature, the NMR signals became broadened and moved to the higher field (δ=7.0–7.7) which responded to its color change, from yellow to blue.

On the other hand, the chemical shifts of 1 did not change after standing for 1 d in $CDCl_3$ [δ=7.07(4H, dm, J=12.8 Hz), 7.91(4H, dm, J=12.8 Hz), and 9.12(2H, s)] and in D_2SO_4 [δ=6.77(2H, br s) and 7.3–7.8(8H, br)].

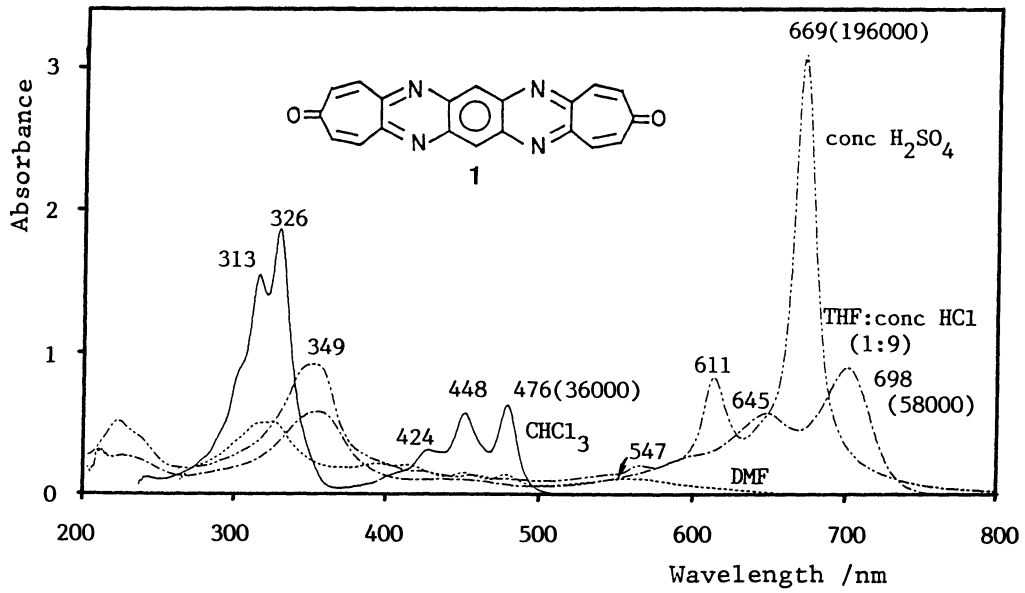


Fig. 1. The UV/vis spectra of 1 in various solvents (1.77×10^{-5} M).

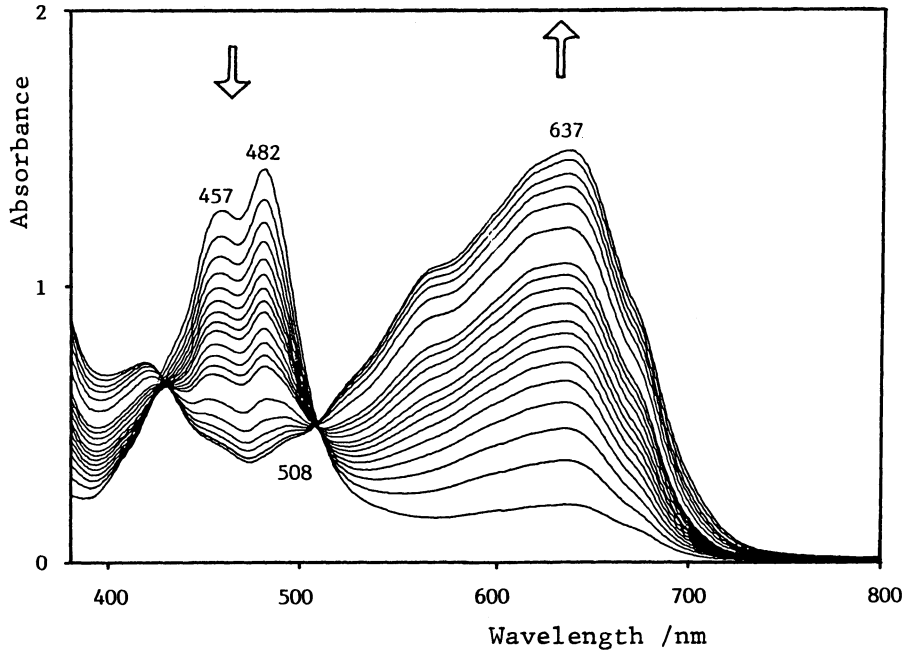


Fig. 2. The time-dependent UV/vis spectra of 1 in TFA (3.75×10^{-5} M).

Times, in min, are 1, 4, 7, 10, 13, 16, 19, 22, 25, 30, 35, 40, 45, 65, 85, 105, 125, 155, and 185.

Since an equilibration process of protonation and deprotonation must be quite rapid, such phenomena, the high-field shift and broadening of signals, should be due to intermolecular interactions of the π-systems of planar molecule **1**. The high-field shift indicated formation of an ordered structure having an increased anisotropy from neighboring molecules in proximity. The time-dependent UV/vis absorption spectra in TFA also showed informative results: the absorption band at 637 nm, broader than that in conc H_2SO_4, gradually increased and those at 457 and 482 nm, monomer bands, decreased with a neat isosbestic point at ca. 508 nm (Fig. 2). The molar extinction coefficient (ε) at 637 nm was 1.52 x 10^5 $M^{-1}cm^{-1}$. Since quantitative amount of **1** was recovered by dilution, neutralization, and filtration, these must be best explained in terms of the aggregation.

In conc H_2SO_4 solution, the narrow and intense absorption appeared at 669 nm immediately after the dissolution even to the concentration of 10^{-7} M: the half-width of the absorption was 201 cm^{-1} and its absorption coefficient was 1.96 x 10^5 M^{-1} cm^{-1}. Furthermore, an additional band appeared at 611 nm (Fig. 1).

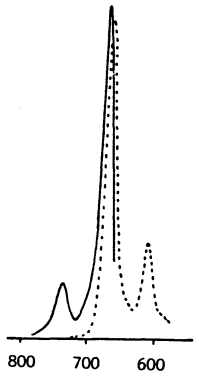
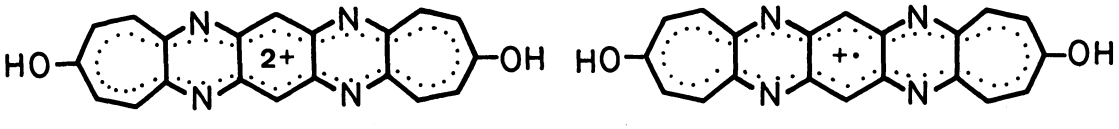


Fig. 3. The fluorescence spectrum of **1** in conc H_2SO_4 (1 x 10^{-6} M).
(———): Fluorescence and
(------): Excitation spectra

Next, in a fluorescence spectrum of **1** in conc H_2SO_4, the strong emission bands appeared at 675 and 740 nm as shown in Fig. 3, which behaved as mirror image of the absorption spectrum. The Stokes loss for the main band was only ca. 130 cm^{-1}, characteristic of J-aggregates. These luminescence properties closely resembled those of the fluorescence from J-aggregates of cyanine dyes.[3] Therefore, the above-described spectral properties of **1** is explained by the J-aggregate formation.

Contrary to that in TFA, the aggregation in conc H_2SO_4 was very rapid, and the absorption and luminescence spectra did not show any time-dependence. Therefore, the acidity of the media is playing a fundamental role in the aggregate formation.

The observations may be explained as follows: the neutral **1** is a sort of extended quinone but not peripherally-conjugated aromatic derivative, while the dicationic species (1^{2+}) generated by the protonation of **1** can be expressed as a fully-conjugated aromatic peripheral 22π derivative. The stabilized electron-withdrawing tropylium moiety and the electron-releasing pyrazine moiety in the dication will facilitate the intermolecular dipole interactions to favor the complexation, the aggregation.



1^{2+} $1^{+\bullet}$

Furthermore, since a cation radical was conceived, the ESR spectra of **1** in conc H_2SO_4 and in TFA were measured: no ESR signal was detected in conc H_2SO_4 below 10^{-4}

M. This eliminated a possible responsibility of the cation radical ($1^{+\cdot}$) to the green coloration. At higher concentrations, i.e., 3.7×10^{-3} M, the ESR spectrum of **1** (g=2.003) in conc H_2SO_4 solution was observed as shown in Fig. 4. It showed the hyperfine structure due to four equivalent nitrogen atoms (a_N=5.5 G), which suggested that the ESR spectrum is attributable to cation radicals of **1**. However, no hyperfine structure due to proton (a_H) was resolved even employing very small modulation width (0.02 G) and a weak microwave power (4×10^{-4} W). The a_H values were expected to be smaller than a_N from the results of cation radicals for related heteroaromatics.[6] This result was probably due to the exchange broadening between cation radicals and diamagnetic molecules in aggregates. On the contrary, no ESR signal was observed in TFA.

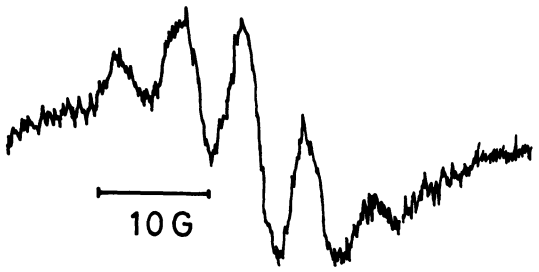


Fig. 4. The ESR spectrum of $1^{+\cdot}$ at room temperature (3.7×10^{-3} M; 9.426 GHz and 100 kHz modulation).

In conclusion, the exhibitions of narrow and strong bands in the absorption and fluorescence spectra, the broad ESR signals, and the high-field shifted NMR signals with the peak-broadening all together confirmed the formation of aggregates in acidic media. The observed spectral properties in conc H_2SO_4 indicated the formation of typical J-aggregates. In TFA solutions J-like aggregates presumably formed.

Although the aggregation numbers are unknown at the present stage, this has constituted the first J-aggregates in a simple cyclic π-system. Related aspect of this study is in progress.[7]

References

1) E. E. Jelley, Nature, 138, 1009 (1936); 139, 631 (1937).
2) e.g., H. Kuhn, Pure Appl. Chem., 53, 2105 (1981).
3) e.g., A. H. Herz, Adv. Colloid Interface Sci., 8, 237 (1977).
4) 1,2-Diaminobenzene is known to condense with **2**. See S. Itô, Y. Shoji, M. Hirama, H. Takeshita, and K. Takahashi, Tetrahedron Lett., 1975, 1075.
5) The NMR spectra were measured with a JEOL GSX 270H Spectrometer, and the chemical shifts were expressed in δ values. The ESR spectrum was taken with a JEOL JES-FEIX Spectrometer. The UV/vis spectra were measured with a Hitachi U-3200 Spectrophotometer. The fluorescence spectra were determined by a Hitachi 650-10S Fluorescence Spectrophotometer.
6) T. -S. Lin and J. Retsky, J. Phys. Chem., 90, 2687 (1986).
7) We are deeply indebted to Professor Teiichiro Ogawa, Kyushu University, for the use of a fluorescence spectrophotometer and to Dr. Masao Hayashi, Kyushu University, for arrangement to obtain ESR spectra. Also, we wish to thank The Ministry of Education, Science, and Culture for a financial assistance through a Grant-in-Aid to A. M. (No. 60470025).

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