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Structural Requirement for the J-Aggregate Formation in Dicyclohepta[5,6:b]-pyrazino[2,3-g]quinoxaline-3,11-diones and Related Compounds

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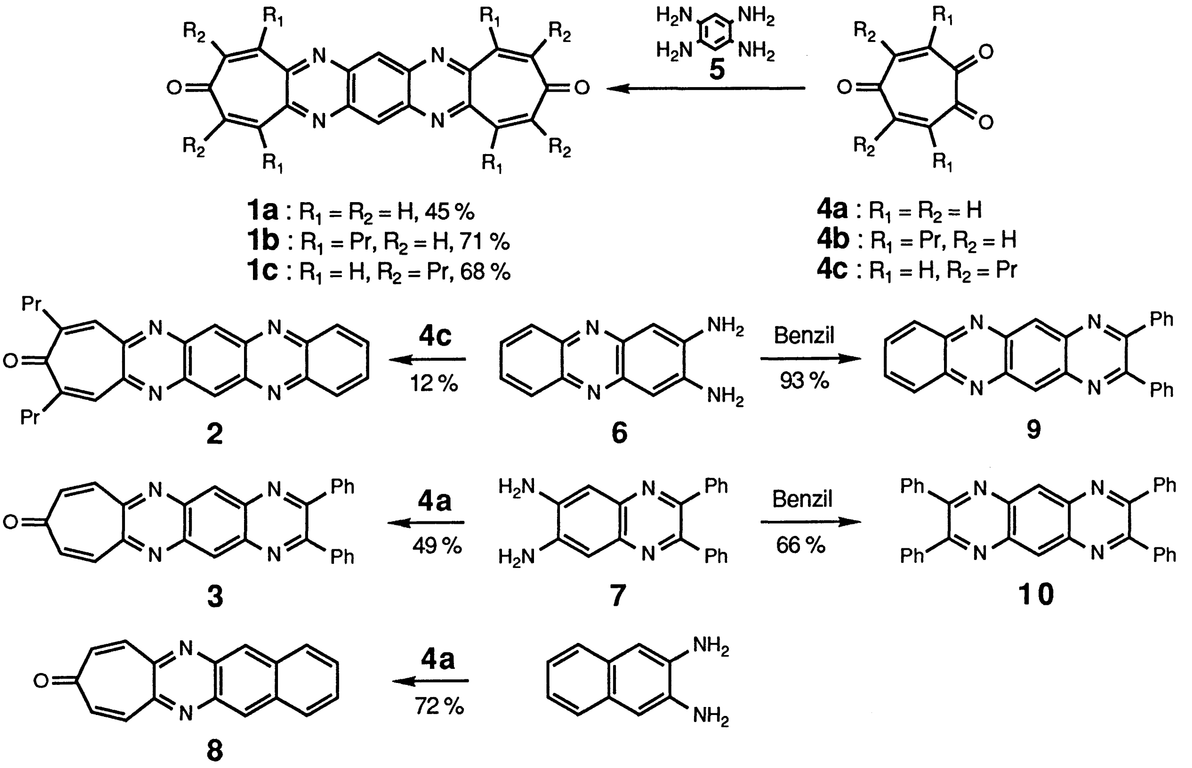
Two tetrapropyl derivatives of dicyclohepta[5,6:b]pyrazino-[2,3-g]quinoxaline-3,11-dione and 9,11-dipropylcyclohepta[5,6]pyrazino[2,3-b]phenazin-10-one, revealed the J-band in conc H_2SO_4. On the other hand, 2,3-diphenylcyclohepta[b]pyrazino[2,3-g]quinoxalin-9-one formed a non-J-aggregate, but benzo[g]cyclohepta[b]quinoxalin-9-one formed no aggregate. A pyrazinoquinoxaline framework is required for the aggregation.

Recently, we reported the J-aggregate formation of a planar symmetrical non-benzenoid aromatic dye, dicyclohepta[5,6:b]pyrazino[2,3-g]quinoxaline-3,11-dione (**1a**) in acidic media.$^{1)}$ This was the first example of the J-aggregate formation other than the cyanine dyes.$^{2)}$ In this paper, we will describe the preparation of the derivatives (Scheme 1) and the modified systems of **1** to know the structural requirement to the J-aggregation in these systems.

The 1,5,9,13- and 2,4,10,12-tetrapropyl derivatives (**1b** and **1c**) of **1**, 9,11-dipropylcyclohepta[5,6]pyrazino[2,3-b]phenazin-10-one (**2**), and 2,3-diphenylcyclohepta[b]pyrazino[2,3-g]quinoxalin-9-one (**3**)$^{3)}$ were prepared by the condensation of 3,7-dipropyl- and 4,6-dipropyl-3,6-cycloheptadiene-1,2,5-triones (**4b** and **4c**) with 1,2,4,5-tetraaminobenzene (**5**) and corresponding diaminoquinoxalines (**6**$^{4)}$ and **7**$^{5)}$).

The colors of **1b** and **1c** in solutions were similar to **1a**; yellow in $CHCl_3$, blue in trifluoroacetic acid (TFA), and green in conc H_2SO_4, but the color changes in acids were faster than **1a**. The electronic spectra of **1b**, **1c**, and **1a** were mutually very similar as shown in Fig. 1: there observed a narrow and strong absorption at 681 nm (ε 133000) with the half-width ($W_{1/2}$) of 512 cm^{-1} for **1b** and at 682 nm (138000) with $W_{1/2}$ of 602 cm^{-1} for **1c**. The ^1H NMR spectrum of **1c** in TFA-d appeared at higher fields (δ=1.09, 1.5-1.8, 2.7-3.0, 7.31, and 7.59) than in $CDCl_3$ (δ=1.04, 1.70, 2.80, 7.85, and 9.00), while the spectral change of **1b** in TFA-d was slower than that of **1c**, and it was gradually moving to higher fields than that in $CDCl_3$ (δ=1.09, 1.77, 3.19, 7.06, and 9.04). The strong emission bands in conc H_2SO_4 appeared at 687 nm for **1b** and 691 nm for **1c**, showing a small Stokes loss of 128 cm^{-1} and 191 cm^{-1}, respectively. The color of **1b** in non-oxidizing trifluoro-



Scheme 1.

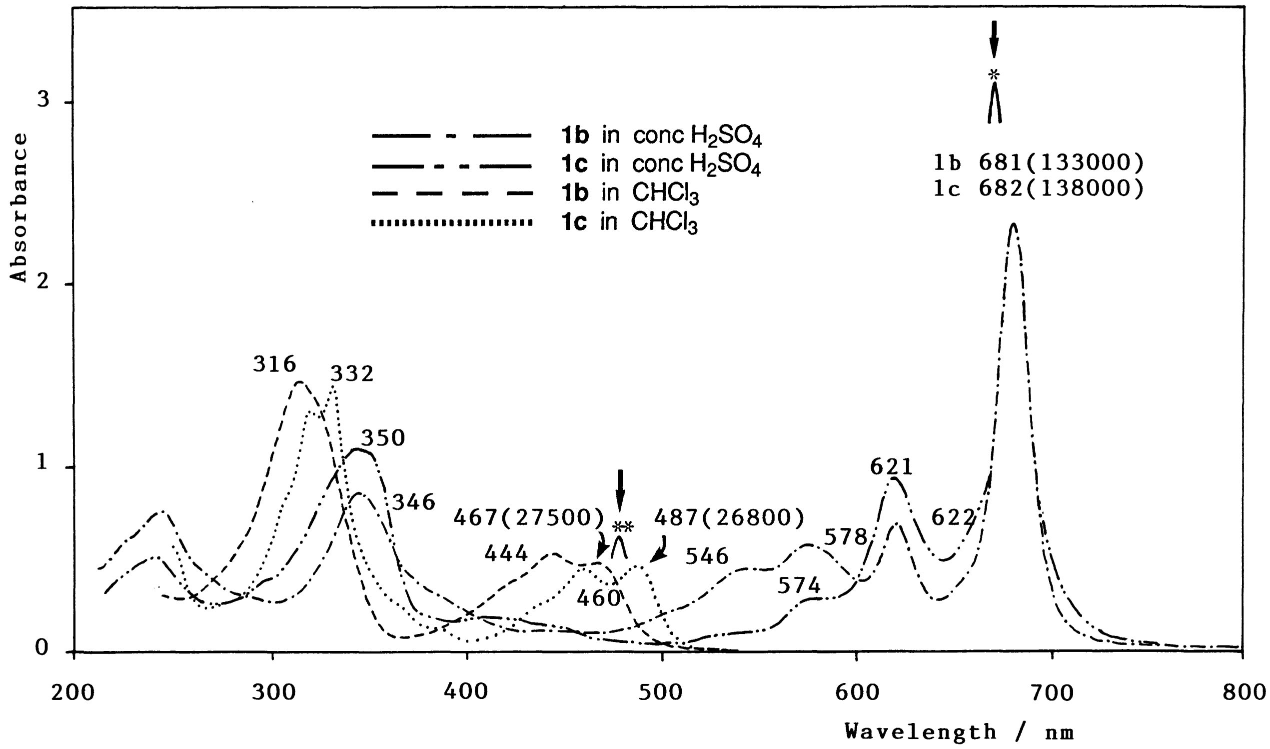


Fig. 1. Electronic spectra of **1** (1.77 x 10^{-5} M).

* the longest absorption maximum of **1a** in conc H_2SO_4 (669 nm; ε=196000)

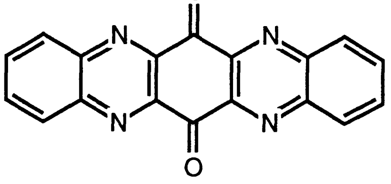
** the longest absorption maximum of **1a** in $CHCl_3$ (476 nm; ε=36000) methanesulfonic acid (CF_3SO_3H) was blue, and it showed a sharp absorption at 679 nm (187000) and a narrow and strong emission band at 681 nm. Therefore, it was concluded that both **1b** and **1c** formed the J-aggregates in conc H_2SO_4, and a contribution of a radical cation to the blue coloration in CF_3SO_3H or in conc H_2SO_4 was eliminated.

The color changes (yellow in $CHCl_3$ and greenish blue in conc H_2SO_4) of **2** were also similar to **1**. The electronic spectrum of **2** showed a band at 682 nm (86500) with the $W_{1/2}$ of 1067 cm^{-1}. The strong emission band appeared at 689 nm. These behaviors were characteristic of the J-aggregates.[1,2] Thus, one of the tropone rings may be replaced by the benzene ring.[6]

The tetracyclic compound (**3**) was yellow in $CHCl_3$ and gradually altered from red to blue in TFA. In conc H_2SO_4, the color changed from blue to green with an isosbestic point at 721 nm. The ^1H NMR spectrum in TFA-d behaved as same as **1** and **2**. These results strongly suggested an aggregate formation of **3**. However, it was hardly assignable as the J-aggregate since **3** revealed no emission band in conc H_2SO_4.[1,2]

Next, benzo[g]cyclohepta[b]quinoxalin-9-one (**8**), 2,3-diphenylpyrazino[2,3-b]phenazine (**9**), and 2,3,6,7-tetraphenylpyrazino[2,3-g]quinoxaline (**10**) were prepared; **8** was yellow in $CHCl_3$, greenish yellow in TFA, and red in conc H_2SO_4, indicating no aggregate formation. While the color of **9** was yellow in $CHCl_3$, it changed from red to purple in TFA, and was green in conc H_2SO_4, the colors of **10** were yellow in $CHCl_3$, red in TFA, and green in conc H_2SO_4. The ^1H NMR signals of **9**[7] in TFA-d shifted slowly to the higher field, whereas those of **8** and **10** did not. Thus, the compounds containing no pyrazinoquinoxaline skeleton did not form aggregates to indicate a requirement for the aggregation, but the heterocyclic system was not sufficient for J-aggregation.

Finally, we attempted to prepare 5,7,12,14-tetraazapentacenes from the reactions between **5** and **6** and o-benzoquinones to study a role of a tropone nucleus for a J-aggregate formation.[8] However, every synthetic effort has failed due to instability of the products.[9] In this regard, Fox and Voynick[10] have already observed that acidic solutions of 5,7,12,14-tetraazapentacene-6,13-quinone (**11**) caused a redox photochromism by an intense blue coloration upon irradiations. They explained this color change as the formation of a diprotonated, four-electron-reduced salt (**12**). It is noteworthy that, although 5,7,12,14-tetraazapentacene derivatives were unstable, the pentacyclic troponoids, **1** and **2**, isoelectronic with tetraazapentacenes, were quite stable even in conc H_2SO_4.



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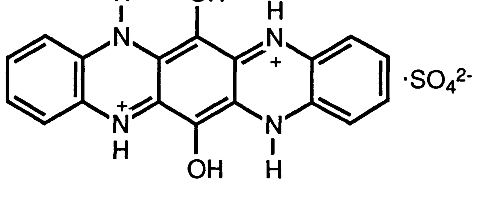

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Thus, the tropone ring played an important role not only to form the J-aggregate but also to stabilize the polycyclic system.

Further investigations on the other aggregation species are now in progress.

References

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2) e.g., A. H. Herz, Adv. Colloid Interface Sci., 8, 237 (1977).

3) All new compounds had satisfactory elemental analyses and spectral data. The selected spectral data were shown below.

1b: Orange crystals, mp 247 °C (decomp); ^{1}H NMR ($CDCl_3$) 1.09(12H, t, J=7.3 Hz), 1.77(8H, sext, J=7.3 Hz), 3.19(8H, t, J=7.3 Hz), 7.06(4H, s), and 9.04(2H, s); ^{13}C NMR ($CDCl_3$) 14.2(4C), 23.3(4C), 39.1(4C), 129.3(2C), 137.1(4C), 139.7(4C), 150.0(4C), 150.4(4C), and 188.9(2C).

1c: Reddish yellow crystals, mp 250 °C (decomp); ^{1}H NMR ($CDCl_3$) 1.04(12H, t, J=7 Hz), 1.70(8H, sext, J=7 Hz), 2.80(8H, t, J=7 Hz), 7.85(4H, s), and 9.00(2H, s); ^{13}C NMR ($CDCl_3$) 14.3(4C), 22.9(4C), 38.3(4C), 128.9(2C), 136.7(4C), 141.0(4C), 149.8(4C), 150.6(4C), and 188.3(2C).

2: Red crystals, mp 250 °C (decomp); ^{1}H NMR ($CDCl_3$) 1.05(6H, t, J=7.3 Hz), 1.70 (4H, sext, J=7.3 Hz), 2.78(4H, td, J=7.3, 0.7 Hz), 7.81(2H, br t, J=0.7 Hz), 7.8-7.9(2H, m), 8.2-8.3(2H, m), and 9.18(2H, s); ^{13}C NMR ($CDCl_3$) 14.0(2C), 22.7 (2C), 38.1(2C), 129.3(2C), 130.1(2C), 132.1(2C), 136.6(2C), 140.0(2C), 142.3 (2C), 145.6(2C), 149.7(2C), 150.2(2C), and 188.4.

3: Yellow needles, mp 294-296 °C (decomp); ^{1}H NMR ($CDCl_3$) 6.99(2H, dm, J=12.8 Hz), 7.35-7.5(6H, m), 7.6-7.65(4H, m), 7.86(2H, dm, J=12.8 Hz), and 9.00(2H, s); ^{13}C NMR ($CDCl_3$) 128.4(4C), 129.3(2C), 129.9(2C), 130.0(4C), 136.8(2C), 138.4(2C), 140.5(2C), 140.9(2C), 141.2(2C), 149.7(2C), 156.3(2C), and 187.3.

4) H. I. X. Mager and W. Berends, Rec. Trav. Chim., 76, 28 (1957); Chem. Abstr., 51, 12104e (1957).

5) The compound **7** was conveniently prepared from **5** and benzil.

6) It is expectable since protonated tropones are isoelectronic with benzene ring.

7) In the fluorescence spectrum of **9**, there is only a weak emission band at 694 nm.

8) Since protonated tropone, hydroxycycloheptatrienium, is isoelectronic to benzene, it will be desirable to compare chemical properties of the pentacyclic tropone derivatives with the corresponding benzo derivatives.

9) G. M. Badger and R. Pettit, J. Chem. Soc., 1952, 3211.

10) M. A. Fox and T. A. Voynick, J. Org. Chem., 46, 1235 (1981).

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