

Color Generation Mechanism of Quinacridone Derivatives as Viewed from the Intermolecular Hydrogen Bond

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Abstract

Quinacridones are industrially important hydrogen-bonded pigments. The shade in the solid state is vivid red while pale yellow in solution, indicating the involvement of intermolecular interactions in the color generation. The electronic structure has therefore been investigated based on the crystal structure with special attention to the intermolecular N–H···O hydrogen bond using four kinds of quinacridone compounds with different H-bond forming characteristics: unsubstituted quinacridone (γ -QA), mono-*N*-methylquinacridone (MMQA), *N,N*-dimethylquinacridone (DMQA) and 2,9-dimethylquinacridone (2,9-DMQA). γ -QA, 2,9-DMQA and MMQA are found to form three-dimensional (“hunter’s fence”), two-dimensional (sheet-like) and one-dimensional (chain-like) hydrogen bond networks, respectively. The present H-bond aligns the transition dipole in a way “head-to-tail”. The bathochromic shift upon crystallization (pale yellow to vivid red) is mostly attributed to resonance interactions between transition dipoles.

Introduction

Quinacridones are industrially important hydrogen-bonded pigments of red color.¹ Among several commercially used derivatives of quinacridones, unsubstituted quinacridone (QA) and 2,9-dimethylquinacridone (2,9-DMQA) enjoy widespread use in the imaging area due to their high tinctorial strength and outstanding light and heat fastness. In these pigments, the shade in the solid state is vivid red while only pale yellow in solution. This clearly indicates that intermolecular interactions are involved in the color generation. The structural and electronic properties have therefore been investigated in the present investigation with major focus on the effect of intermolecular hydrogen bonds on the color generation mechanism. For this purpose, we used the following four quinacridone compounds with different H-bond forming characteristics: unsubstituted quinacridone with two NH groups, mono-*N*-methylquinacridone with one NH group (MMQA), *N,N*-dimethylquinacridone with no NH group (DMQA) and 2,9-

dimethylquinacridone with two NH and methyl groups. The molecular structure of these compounds is shown in Fig. 1.

The crystal structure of the γ phase of QA were determined by Potts et al. using synchrotron radiation ($R_1 = 0.1214$).² We have recently reinvestigated the structure by X-rays at 223 K ($R_1 = 0.073$).³ Both results are basically in good agreement. We have also determined the structure of 2,9-DMQA at 123 K,⁴ although Lincke et al. reported the simulated structure based on the powder X-ray diffraction data.⁵ The structure of MMQA has newly been determined in the present investigation.⁶ On the other hand, the crystal structure of DMQA has variously been reported by Ohmasa et al. ($R_1 = 0.15$ for 726 non-zero reflections),⁷ Zavodnik et al. ($R_1 = 0.047$ for 532 reflections with $I > 3\sigma$)⁸ and also by us ($R_1 = 0.044$ for 1349 reflections with $I > 2\sigma$).⁹

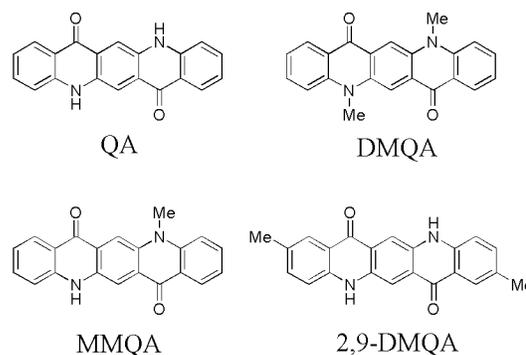


Figure 1. Molecular structure of quinacridone derivatives.

Experimental

QA and 2,9-DMQA were obtained from Ciba Specialty Chemicals. MMQA and DMQA were synthesized according to the method described in the literature.¹⁰ The samples were purified by sublimation, using a two-zone furnace.¹¹ The single crystals of QA and DMQA were grown from solution in dimethylformamide using an autoclave; whereas the single crystals of MMQA and 2,9-DMQA were grown from the vapor phase at about 583 and 703 K, respectively.

X-ray diffraction data on single crystals were collected on a Rigaku R-AXIS RAPID-F diffractometer with CuK α radiation ($\lambda = 1.5419 \text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least squares on F^2 . UV-vis spectra were recorded on a Shimadzu UV-2400PC spectrophotometer. Polarized reflection spectra were measured on single crystals by means of a microscope-spectrophotometer (UMSP 80 from Carl Zeiss).

The absorption bands were calculated for QA, MMQA, DMQA and 2,9-DMQA on the basis of the INDO/S Hamiltonian using Quantum CAChe Ver.3.2 on a PC workstation.¹²

Results

Crystal Structure of Quinacridone Derivatives

Table 1 details the crystallographic parameters for QA, MMQA, DMQA and 2,9-DMQA. The molecular arrangement is also shown in Fig. 2 for these derivatives.

i) γ -QA.³ The molecule is entirely planar and belongs to the point group of C_1 . As shown in Fig. 2(a), there are chains of intermolecular hydrogen bonds along the c -axis between the NH group of one molecule and the O atom of the neighboring one. One molecule is hydrogen-bonded to four different molecules in a fashion "hunter's fence", leading to the formation of a three-dimensional H-bond network. This kind of molecular arrangement is typical of indigo¹³ and dithioketoquinacridone pigments.¹⁴ The N/O distance and the NH/O angle are 2.756 \AA and 163°, respectively.

ii) MMQA.⁶ The molecule is again entirely planar. A small dipole moment of about 0.44 D appears as a result of C_1 symmetry. Figs. 2(b) and 2(c) show the projection of the crystal structure onto the (a,c) and (b,c) planes, respectively. There are two kinds of stacking columns along the b -axis. The molecules in one column are inclined at about 45° with respect to the molecules in the neighboring column. In each column, the MMQA molecule and its inverted one are stacked pairwise alternately along the b -axis. There is one-dimensional (chain like) intermolecular N-H...O hydrogen bond along the a -axis. One molecule is H-bonded to two neighboring molecules. The N/O distance and the NH/O angle are 2.721 \AA and 166°, respectively.

iii) DMQA.⁹ The molecule is entirely planar. The molecules are stacked along the a -axis with significant overlap in a herringbone fashion as shown in Fig. 2(d).

iv) 2,9-DMQA.⁴ The molecule is entirely planar and belongs to the point group of C_1 . There is a two-dimensional (sheet-like) H-bond network similar to that in diketopyrrolopyrrole pigments.¹⁵ Each molecule is H-bonded to two neighboring molecules: four H-bonds per molecule. As shown in Fig. 2(e), there are steps of about 0.87 \AA between the molecular planes of the H-bonded molecules. The present molecular arrangement is characteristic of modifications I and II of diketopyrrolopyrrole^{16,17} and thiazine-indigo pigments.¹⁸ The N/O distance and NH/O angle are 2.850 \AA and 150°, respectively.

Table 1. Crystallographic parameters.

	γ -QA ³	MMQA ⁶	DMQA ⁹	2,9-DMQA ⁴
Formula	C ₂₀ H ₁₂ N ₂ O ₂	C ₂₁ H ₁₄ N ₂ O ₂	C ₂₂ H ₁₆ N ₂ O ₂	C ₂₂ H ₁₆ N ₂ O ₂
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P-1$
Z	2	8	2	1
Molecular weight	312.32	326.35	340.37	340.37
Molecular symmetry	C_1	C_1	C_1	C_1
a (\AA)	13.70(1)	13.517(2)	4.928(3)	3.865(3)
b (\AA)	3.84(1)	7.340(2)	11.103(3)	6.372(3)
c (\AA)	13.35(2)	29.033(2)	14.462(2)	15.78(2)
α (°)	90	90	90	93.94(6)
β (°)	100.09(9)	90	98.39(2)	91.51(8)
γ (°)	90	90	90	100.00(6)
V (\AA^3)	691.5	2880.5	782.8	381.5
T (K)	223	93	223	123
R_1	0.073	0.072	0.049	0.056
Dipole moment (D) ^a	0	0.44	0	0

^a Determined by MOPAC Ver. 6 using the AM1 Hamiltonian.

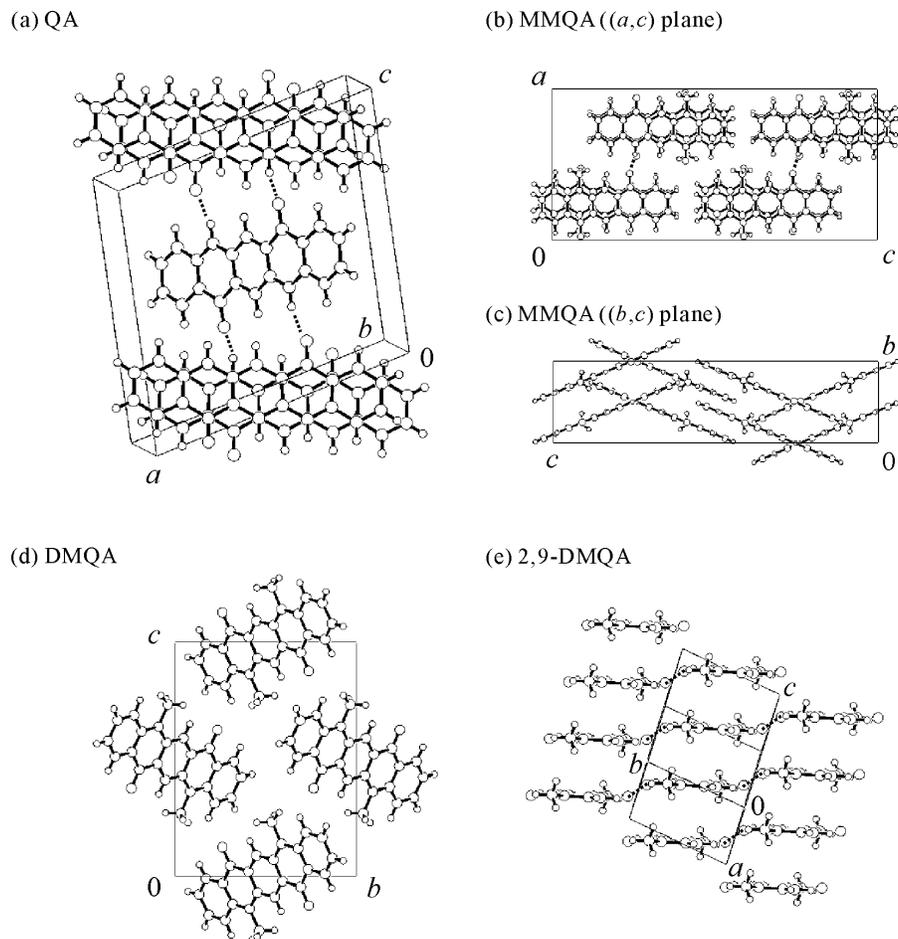


Figure 2. Molecular arrangement. (a) QA, (b) MMQA ((a,c) plane), (c) MMQA ((b,c) plane), (d) DMQA, (e) 2,9-DMQA. The dotted lines designate N-H...O intermolecular hydrogen bonds.

Solution Spectra of QA Derivatives

Figure 3 shows solution spectra in dimethylsulfoxide for QA, MMQA, DMQA and 2,9-DMQA. There observed progressions of the absorption bands starting from 523 nm for QA, MMQA and DMQA and 532 nm for 2,9-DMQA. Since the longest-wavelength band is quite steep and the absorption bands are equally spaced in all compounds, the absorption bands are assigned to the 0-0, 0-1 and 0-2 as shown in Fig. 3, indicating that one single electronic transition is coupled with vibrational transitions. The MO calculation also bears out the present assignment that shows there is one single π - π^* electronic transition in the visible region.

Polarized Reflection Spectra Measured on Single Crystals

Figure 4 shows the polarized reflection spectra measured on the (001) plane of 2,9-DMQA single crystals together with its projection onto the (a,b) plane. A prominent reflection band appears around 572 nm together with two small bands around 480 and 530 nm for

polarization parallel to the direction of the N-H...O intermolecular hydrogen bonds as designated by the dotted line in Fig. 4(b). On the other hand, these bands are completely quenched for polarization perpendicular to this direction. This clearly indicates that all the reflection bands belong to one single electronic transition and that the direction of the transition dipole points along the intermolecular hydrogen bond. The present result is also borne out by the MO calculation which shows that there is only one electronic transition in the visible region and that the direction of the transition dipole appears along the intermolecular H-bond. Then, it follows that the longest-wavelength band (around 572 nm), the second-longest (around 530 nm) and the third-longest band (480 nm) in Fig. 4 correspond to the 0-0, 0-1, 0-2 transitions in solution spectra, respectively. The present one-to-one correspondence between solution and solid-state spectra indicates that there is a large bathochromic shift (540 \rightarrow 580 nm) on going from solution to the solid state in 2,9-DMQA.

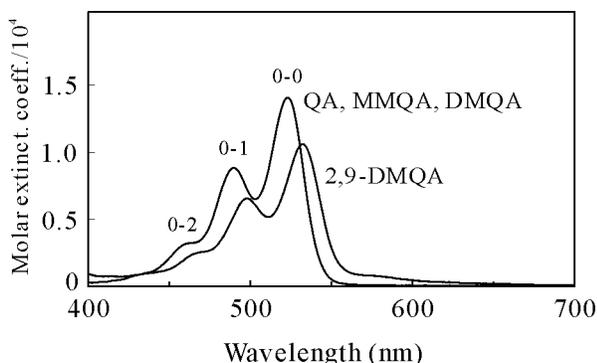


Figure 3. Solution spectra in dimethylsulfoxide for QA, MMQA, DMQA, and 2,9-DMQA.

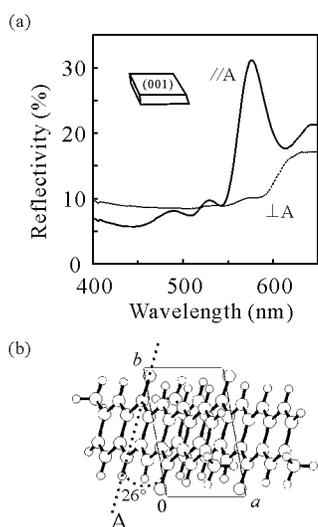


Figure 4. (a) Polarized reflection spectra measured on the (001) plane for 2,9-DMQA and (b) the projection of the crystal structure onto the (a,b) plane. The dotted line in (b) designates the direction of the intermolecular N-H...O hydrogen bond.

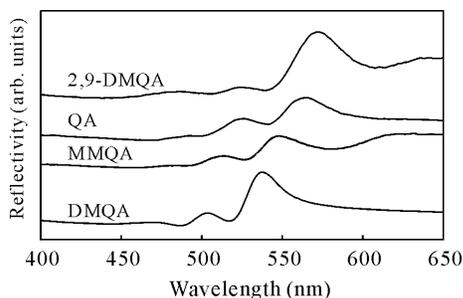


Figure 5. Comparison of the polarized reflection spectra for QA, MMQA, DMQA and 2,9-DMQA. Only the reflection bands corresponding to the direction of the transition dipoles are plotted.

The similar behavior described above is also observed for QA, MMQA and DMQA and their result is summarized in Fig. 5. The longest-wavelength band of QA, MMQA and 2,9-DMQA is displaced toward longer wavelengths, as compared with that of DMQA, in the sequence of MMQA, QA and 2,9-DMQA. This is the sequence of increasing number of intermolecular hydrogen bonds: no H-bond in DMQA, two H-bond in MMQA and four in QA and 2,9-DMQA. This result clearly suggests that the N-H...O hydrogen bond is responsible for the bathochromic shift upon crystallization.

Discussion

Bathochromic Shift Upon Crystallization – Effect of H-Bond On The Spectral Shift

As pointed out in our previous investigations,^{19,20} the excitonic interaction between transition dipoles is of crucial importance in pigment systems where the absorption coefficient of the component molecule is quite large and the molecules are periodically ordered. The resonance interaction (ΔE) is described by the following equation²¹: $\Delta E = |\mu|^2(1-3\cos^2\theta)/r^3$ where μ denotes the transition dipole, r and θ are the distance and angle between two transition dipoles, respectively. The term $|\mu|^2$ determines the strength of the interneighbor coupling while the geometrical term $(1-3\cos^2\theta)/r^3$ the downward or upward shift of the excited state energy level, leading to the bathochromic or hypsochromic displacement of the absorption band. The critical angle is 54.7° below which the bathochromic shift will occur and above which the hypsochromic shift will result. The maximum bathochromic shift appears when the transition dipoles are arranged in a fashion “head-to-tail” ($\theta = 0^\circ$).

Strength of the Hydrogen Bonds

The geometrical consideration of the N/O distance and the NH/O angle gives a measure for the strength of the N-H...O hydrogen bond. If the distance is short and the angle is near to 180° , this is a sign for a strong hydrogen bond. As judged from the result of the structure analysis, the H-bond is the strongest in QA and becomes weaker in the order of MMQA and 2,9-DMQA.

Conclusions

The QA derivatives with different H-bond forming characteristics yield a variety of crystal structures. γ -QA, 2,9-DMQA and MMQA are found to form three-dimensional (“hunter’s fence”), two-dimensional (sheet-like) and one-dimensional (chain-like) hydrogen bond networks, respectively. As judged from the crystal structure, the hydrogen bond is the strongest in QA and becomes weaker in the order of MMQA and 2,9-DMQA. The extent of the bathochromic shift in QA derivatives increases with the number of intermolecular hydrogen bonds and can mostly be interpreted as being due to resonance interactions between transition dipoles aligned in a fashion “head-to-tail” in all QA derivatives.

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Biography

Takatoshi Senju received his B.S. and Ph.D. degrees in Chemistry from the University of Tokyo in 1992 and 1997, respectively. Since then he worked in the Development and Engineering Research Center at Mitsubishi Chemical Co. in Okayama, Japan and then moved to Yokohama National University as Assistant Professor in 1999. His research interest includes synthetic and computational organic chemistry and electronic characterization of organic pigment. He is a member of the Chemical Society of Japan and the American Chemical Society. E-mail: tsenju@ynu.ac.jp