Polymorph of 2,9-Dichloroquinacridone and Their Electronic Properties

Takatoshi Senju, Naoko Nishimura and Jin Mizuguchi; Graduate School of Engineering, Yokohama National University; 79-5 Tokiwadai, Hodogaya-ku, 240-8501, Yokohama, Japan

Abstract

2,9-Dichloroquinacridone is an industrially important bluish-red pigment which falls in the category of hydrogen-bonded pigments. In addition to red single crystals, we have recently isolated black single crystals from the vapor phase. Structure analysis of both crystals revealed that the red phase is typically characterized by NH···O intermolecular hydrogen bonds and corresponds to the commercial product; whereas, in the black phase, there exist no intermolecular hydrogen bonds, quite contrary to our expectation. Furthermore, the molecule in the black phase is heavily deformed and has a higher heat of formation than that in the red phase. Because of this, the black phase can easily be transformed into the red phase by heating at about 530 K for several minutes. Additionally, molecular distortion upon crystallization is found to largely displace the absorption band toward longer wavelengths, giving rise to a black color in the solid state.

1. Introduction

2,9-Dichloroquinacridone (2,9-DClQA: Fig. 1) is an industrially important red pigment which belongs to the class of hydrogen-bonded pigments [1]. 2,9-DClQA is practically used in painting and imaging industries together with a similar 2,9-dimethyl derivative (i.e. 2,9-DMQA). Both are quite resistant to heat and light irradiation. However, the former is characterized by more bluish and duller shade than the latter, although no significant difference is recognized in molecular spectra of both compounds. For this reason, we have focused our attention, in the present investigation, on the crystal structure of both compounds in order to elucidate the difference in shade between these derivatives.

Previously, we have studied the electronic structure of 2,9-DMQA on the basis of the crystal structure [2]. Structure analysis revealed that there are chains of NH···O intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one and these constitute a two-dimensional hydrogen bond network in the solid state. Furthermore, NH···O hydrogen bond is also found to be responsible for the large spectral displacement on going from solution to the solid state. That is, the NH···O hydrogen bonds align two transition dipoles in a fashion “”heat-to-tail” to induce a large spectral shift upon crystallization.

In the course of the above investigation, we encountered unexpectedly black crystals of 2,9-DClQA [3] as well as red one [4]. The present paper deals with structure analysis of both crystals and discusses their electronic structure with special attention to the interconversion between crystal phases.

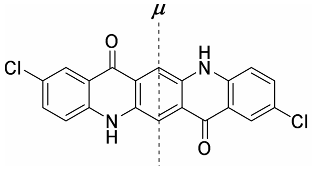

Figure 1. *Molecular structure of 2,9-DClQA. The dashed line denotes the direction of the transition dipole (μ) predicted by MO calculations that corresponds to the optical absorption in the visible region.*

2. Experimental Section

2.1 Materials and crystal growth

2,9-DClQA was obtained from Dainippon Ink and Chemicals, Inc. The samples were purified by sublimation, using a two-zone furnace [5]. Single crystals of 2,9-DClQA were grown from the vapor phase at about 768 K. Tiny red platelet crystals were condensed at a high temperature region around 653 K, whereas a number of black needles were grown in the low temperature region around 423 K.

2.2 Equipment and Measurements

Solution spectrum in dimethyl sulfoxide (DMSO) was recorded on a UV-2400PC spectrophotometer (Shimadzu). Reflection spectra on single crystals were measured by means of a UMSP80 microscope–spectrophotometer (Carl Zeiss). An Epiplan Pol (×8) objective was used together with a Nicol-type polarizer. Reflectivities were corrected relative to the reflection standard of silicon carbide. Differential scanning calorimetry (DSC) analysis was made on single crystals in air by means of a Thermo Plus 2 DSC-8230 from Rigaku at a heating rate of 5 K/min. Scanning electron micrographs of the surface of the single crystals were taken using a VE-8800 from Keyence.

2.3 Computational details

Semi-empirical MO calculations were performed using a Quantum CAChe ver. 3.2 program package [6] which includes MOPAC ver. 94.10 and the ZINDO programs [7]. Heat of formation and optical absorption bands of the molecules in the red and black phases were calculated on the basis of the x, y and z X-ray coordinates for non-H atoms while geometry were optimized for H atoms, using the AM1 Hamiltonian [8]. Then, spectroscopic calculations were made by the INDO/S Hamiltonian [9] including 196 configuration interactions composed of 14 occupied and 14 unoccupied molecular orbitals. In parallel, geometry optimization as well as spectroscopic computation was also performed for the 2,9-DClQA molecule. This corresponds to the state in solution.

3. Results and Discussion

3-1. Crystal structure [3,4]

Table 1 lists the crystallographic parameters for the red and black phases of 2,9-DClQA.

The molecule in the black phase (Fig. 2(b)) is deformed relative to the molecule in the red phase (Fig. 2(a)). The two C–N bond lengths around the imide nitrogen atom are antisymmetrical, i.e. r(C5–N1) = 1.39(1) Å and r(C9–N1) = 1.30(1) Å, respectively. As a result, the molecule is not completely flat as indicated by the dihedral angles between the planes of rings A and B (177.9(3)°) and between the planes of rings A and C (176.7(3)°). On the other hand, the molecule in the red phase is entirely planar as the corresponding dihedral angles for the molecule in the red phase are 178.6(1)° and 179.2(1)°, respectively. This structure is in good accord with the optimized structure by semi-empirical MO calculations. In addition, the crystal structure of the red phase is quite similar to that of 2,9-DMQA [2,10].

Hydrogen bonding is usually the most important intermolecular interaction in hydrogen-bonded pigments. On the contrary, in the black phase, there is no intermolecular hydrogen bond since the atomic distance between the H atom of the NH group and the nearest O atom of the carbonyl group is 3.75 Å, which is significantly larger than the sum of the van der Waals radii of H and O atoms (2.72 Å). This is the first example of the crystal structure of hydrogen-bonded pigments without hydrogen bonds in the solid state. On the other hand, the molecules in the red phase are firmly bonded together by NH···O intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one. One molecule is hydrogen bonded to two neighboring molecules with a total of four intermolecular hydrogen bonds. This constitutes a sheet-like two-dimensional hydrogen-bond network. On the other hand, the molecules are arranged in a "hunter's fence" fashion (*viz.* the molecules form a grid-like structure when viewed from the side) along the *a* axis in the black phase.

3-2. MO calculations

The results of MO calculations are summarized in Table 2. It is remarkable to note that the heat of formation for the molecule in the black phase is approximately 80 kJ/mol larger than that in the red phase due to the ring distortion. One should also note that the absorption maximum for the molecule in the black phase is displaced toward longer wavelengths by 42.4 nm (2709 cm^{-1}) relative to that in the red phase. On the other hand, the heat of formation and absorption maximum of the molecule in the red phase is practically the same with those for the optimized structure. These results indicate that the molecular distortion in the black phase has a profound effect on the electronic structure.

3-3. Electronic structure of 2,9-DClQA

3-3-1. Solution spectrum

Fig. 4 shows the solution spectrum for 2,9-DClQA in DMSO. A progression of the absorption bands is observed, which starts from 530 toward shorter wavelengths. The position of the absorption maximum is shifted by 2 nm toward shorter wavelengths relative to that of 2,9-DMQA. Since the longest-wavelength band is quite steep and the absorption bands are equally spaced, the absorption bands are assigned to the 0–0, 0–1, 0–2 and 0–3 transitions as shown in Fig. 4, indicating that one single electronic transition is coupled with vibrational transitions. This is also borne out by the MO calculation which shows one single π–π* electronic transition in the visible region.

Table 1. Crystallographic parameters

	Red phase [4]	Black phase [5]
Molecular formula	$C_{20}H_{10}Cl_2N_2O_2$	
Molecular weight	381.22	
Crystal system	triclinic	monoclinic
Space group	P–1	$P2_1/c$
Z	1	2
a (Å)	3.7919(11)	3.782(1)
b (Å)	5.8314(16)	14.840(4)
c (Å)	16.754(4)	12.942(3)
α (°)	94.956(16)	–
β (°)	95.136(17)	91.93(2)
γ (°)	90.660(18)	–
V (Å^3)	366.56(17)	726.0(3)
D_x (Mg m^{-3})	1.727	1.744
R_1 ($I > 2\sigma(I)$)	5.6	10.0

Table 2. Calculated heat of formation (H_f), absorption maximum (λ_{max}) and oscillator strength (f)

	H_f (kJ/mol)	λ_{max} (nm)	f
Black phase	152.34	417.4	0.32
Red phase	72.80	375.0	0.30
Optimized geom.	49.20	374.8	0.30

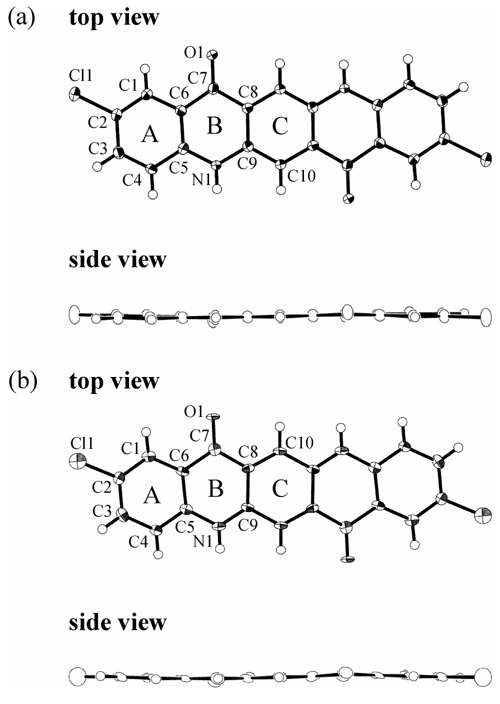

Figure 2. Molecular conformation in the (a) red and (b) black phases. Three six-membered rings are designated as A, B and C as shown in the figure.

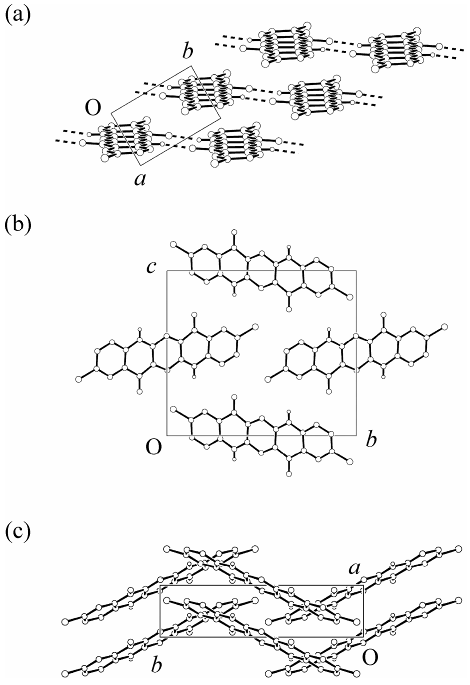

Figure 3. *(a) Molecular arrangement of the red phase. The dashed line designates the intermolecular hydrogen bond. (b) The projection of the crystal structure of the black phase onto the (100) plane. (c) The projection of the crystal structure of the black phase onto the (001) plane. Hydrogen atoms except for the one in the NH group are omitted for clarity.*

3-3-2. Solid-state spectra

Fig. 5 shows the reflection spectra in the visible region for the red and black phases of 2,9-DClQA measured on single crystals. The longest-wavelength band appears around 586 nm in the red phase while around 684 nm in the black phase: the difference of the reflection peaks amounts to 98 nm (2445 cm–1). It is also important to note that the spectral shapes of the both spectra are quite similar to each other and are in fairly good accord with that of the solution spectrum shown in Fig. 4. This indicates that the red and black colors appear in the solid state as a result of a large bathochromic shift on going from solution to the solid state. It is also to be noted that the absorption maximum in the red phase is red-shifted by approximately 14 nm relative to that of 2,9-DMQA. This accounts for the more bluish shade of 2,9-DClQA than 2,9-DMQA.

The excitonic interaction between transition dipoles plays a decisive role in determining the electronic structure of organic pigments [11]. In the special case where two transition dipoles are arranged in parallel, the excited state energy level is shifted due to the interactions between those transition dipoles and the amount of the energy shift is approximated by the following dipole–dipole equation: $\Delta E_{\text{exciton}} = |\mu|^2(1 - 3\cos^2\theta)/r^3$, where μ is the transition dipole, r is the distance between the centers of the two dipoles, and θ represents the angle between the one dipole and the vector connecting each center of the two dipoles. Since $|\mu|^2$ is proportional to the absorption coefficient, this interaction plays an important role in pigment systems where the absorption coefficient is generally very large. Especially, when the two dipoles are arranged in a "head-to-tail" fashion (i.e. $\theta \approx 0$), the excited state is stabilized relative to the monomer state, leading to a bathochromic shift. The transition dipoles both in the red and black phases are arranged nearly in a "head-to-tail" fashion, which gives rise to a bathochromic shift on going from solution to the solid state in the both phases. In the black phase, however, the additional spectral shift due to the molecular distortion as discussed in section 3.1 is also operative. Due to this additional shift, the spectrum for the black phase almost covers the whole visible region. This is assumed to be the main reason for the appearance of the black color.

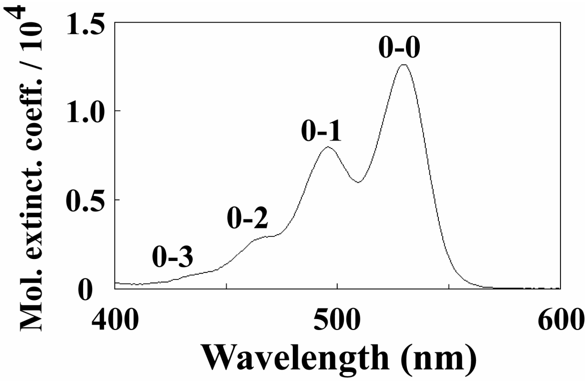

Figure 4. Solution spectrum of 2,9-DClQA in DMSO.

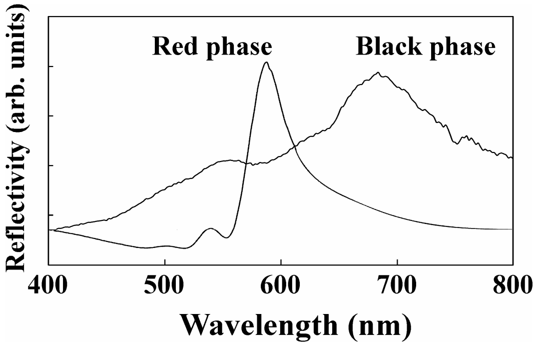

Figure 5. *Reflection spectra in the visible region for the red and black phases of 2,9-DClQA measured on single crystals.*

3-4. Thermal phase transition from the black phase into the red phase

As judged from the heat of formation of the 2,9-DClQA molecule (Table 2), the molecule of the red phase is, by far, more stable than that of the black phase. It is most likely that the black phase can be transformed into the red phase by heat treatment. In fact, the color changed from black via brownish red to vivid red upon heating at 573 K for about 20 min. During the transition process, the overall shape of the crystals was almost intact, while the surface morphology of the crystal changed noticeably as shown by the scanning electron micrographs in Fig. 6.

Fig. 7 shows the DSC curves of the red and black crystals measured in air in the temperature range between 100 and 700 K. No noticeable heat flow was recognized in the red phase, indicating that red phase is quite stable. On the other hand, a prominent exothermic peak was observed in the black phase in the temperature region from about 473 to 613 K, peaking at about 524 K and 549 K. The total exothermic energy amounts to about 237.8 J/g. The present exothermic energy supports directly that the phase has changed from the black to the red phase. The red phase has also been confirmed to be in accord with the result of the structure analysis.

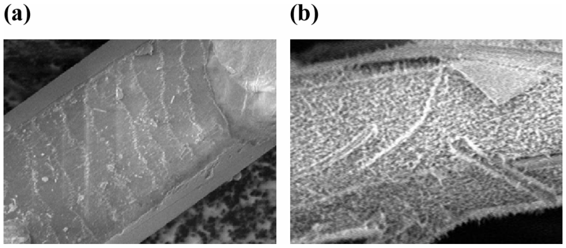

Figure 6. *Scanning electron micrographs of the black needles (a) before and (b) after heat treatment at 300 °C.*

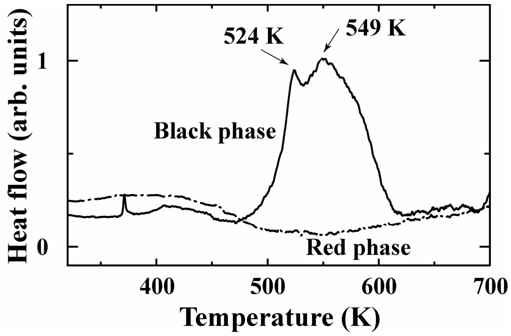

Figure 7. *DSC curves measured on single crystals of the red (dashed line) and black phases (solid line).*

4. Conclusions

Electronic characterization has been made on the red phase (precipitated in the higher temperature region), as well as the black phase (isolated in the lower temperature region). The conclusions drawn from the present investigation can be summarized as follows:

1. The red phase is the phase of the commercial product and is typically characterized by NH···O intermolecular hydrogen bonds. The hydrogen bonds assure heat and light stability and also displace the absorption band toward longer-wavelengths upon crystallization due to interactions between transition dipoles.
2. It is true that 2,9-DClQA is more bluish and duller in commercial products than 2,9-DMQA. No noticeable difference in structure is, however, recognized in the present investigation.
3. The black phase is composed of heavily-deformed molecules and is lack of NH···O intermolecular hydrogen bonds. This indicates that the stability of the black phase is much lower than that of the red one. Because of this, the black phase can easily be transformed into the red phase by heat treatment.

References and Notes

[1] W. Herbst and K. Hunger, Industrial Organic Pigments, 2nd ed. (VCH, Weinheim, 1997) pg. 454.

[2] J. Mizuguchi, T. Senju and M. Sakai, "Crystal structure of 5,12-dihydro-2,9-dimethylquino[2,3-*b*]acridine-7,14-dione, $C_{22}H_{16}N_2O_2$, at 123 K", *Z. Kristallogr. - New Cryst. Struct.*, 217, 525 (2002).

[3] T. Senju, T. Hoki and J. Mizuguchi, "2,9-Dichloro-5,12-dihydroquino[2,3-*b*]acridine-7,14-dione", *Acta Cryst.*, E61, o1061 (2005).

[4] T. Senju, N. Nishimura, T. Hoki and J. Mizuguchi, "2,9-Dichloro-5,12-dihydroquino[2,3-*b*]acridine-7,14-dione (red phase)", *Acta Cryst.*, E61, o2596 (2005).

[5] J. Mizuguchi, "An improved method for purification of β-copperphthalocyanine", *Cryst. Res. Technol.*, 16, 695 (1981).

[6] Quantum CAChe, version 3.2, Fujitsu, Ltd. (Kanagawa, Japan).

[7] J. Ridley and M. C. Zerner, "Intermediate neglect of differential overlap (INDO) technique for spectroscopy. Pyrrole and the azines", *Theor. Chim. Acta*, 32, 111 (1973).

[8] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, "Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model", *J. Am. Chem. Soc.*, 107, 3902 (1985).

[9] M. Kotzian, N. Rosch and M. C. Zerner, "Intermediate neglect of differential overlap spectroscopic studies on lanthanide complexes. I. Spectroscopic parametrization and application to diatomic lanthanide oxides LnO (Ln = lanthanum, cerium, gadolinium, and lutetium)", *Theor. Chim. Acta*, 81, 201 (1992).

[10] Crystallographic data for 2,9-DMQA. $C_{22}H_{16}N_2O_2$, $M_r = 340.37$, $0.23 \times 0.12 \times 0.07$ mm, triclinic, space group $P{-}1$ (No. 2), $a = 3{,}865(3)$ Å, $b = 6.372(3)$ Å, $c = 15.78(2)$ Å, $\alpha = 93.94(6)$ °, $\beta = 91.51(8)$ °, $\gamma = 100.00(6)$ °, $V = 381.5$ Å^3, $Z = 1$, $D_x = 1.481$, $R_1 = 0.056$, $wR(F^2) = 0.167$, $S = 1.483$.

[11] M. Kasha, "Molecular Excitons in Small Aggregates", NATO Advanced Study Institute Series, Series B, Vol. 12, B. D. Bartolo, Ed. (Plenum Press, New York, 1976) pg 337.

Author Biography

Naoko Nishimura received her Bachelor of Engineering from Yokohama National University in 2006. She is currently in the graduate course of the Department of Applied Physics at Yokohama National University. Her research interest includes crystal and electronic structure of organic pigments together with their applications.