Crystal Structure of a Soluble Quinacridone-Precursor and its Thermal Regeneration into the Pigment

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Abstract

The title compound is a soluble precursor ("latent pigment": t-BOC QA) of quinacridone pigment (QA) that can be used for electronic and imaging applications. Regeneration of t-BOC QA into QA have been studied in terms of thermogravimetric and X-ray diffraction analyses, as well as IR and diffuse reflectance spectra on powdered substances. Transformation from t-BOC QA to the parent QA begins around 160°C and is completed around 190°C. A variety of colors (yellow via yellowish red to red) appear during the regeneration process, accompanied by evolution of CO_2*. The crystalline phase of thermally regenerated QA is found to be the* β*-form used widely in paint industries.*

Introduction

Unsubstituted quinacridones as characterized by five-ring polycyclic system (QA: Fig. 1) are industrially important red pigments registered as Pigment Violet 19. QA features typically NH$\cdots$O intermolecular hydrogen bonds in the solid state to hold molecules firmly together. There are three crystal modifications, among which the β (reddish violet color) and γ (bluish red shade) forms gain commercial recognition.[1]

The "latent pigment" technology was developed by Zambounis, Hao and Iqbal on pyrrolopyrrole pigments (DPPs) in 1994.[2,3] This technology was then applied to QAs. The precursor of the title compound is a soluble, yellowish compound of QA and is prepared by replacing the H atom of the NH group with a *t*-butoxycarbonyl (*t*-BOC) group: the precursor is hereafter called *t*-BOC QA. The insoluble parent QA can then be regenerated by thermal decomposition of the precursor (Fig. 1). The latent pigments feature both advantageous properties of pigments and dyestuffs. Dyes readily dissolve in the application medium, offering several advantages over a pigment in terms of transparency, saturation and strength of coloration. On the other hand, pigments are insoluble and feature superior heat, light and chemical fastness.

We have previously reported the regeneration process of *t*-BOC DPP.[4-6] The present paper deals with the process of *t*-BOC QA to QA, with special attention to the initial (*t*-BOC QA) and final (QA) phases.

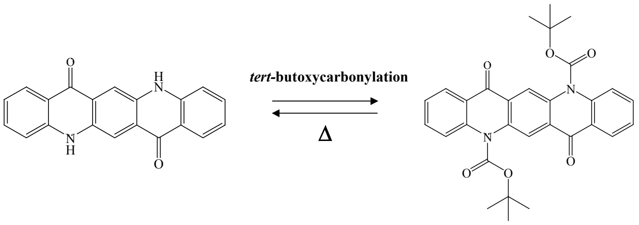

Figure 1. QA and t-BOC QA and the regeneration process.

Experiment

Preparation of Materials

t-BOC QA was prepared according to the method described in the literature, using QA obtained from CIBA Specialty Chemicals Inc. The product was yellow powders. Single crystals were then grown from an acetonitrile solution.

For comparison with regenerated QA, powders of the β-form were also prepared, by dissolving crude QA in toluene, followed by precipitation with water.[1]

Equipment

Diffuse reflectance spectra for powdered pigments were measured on a UV-2400PC spectrophotometer together with an integrating sphere attachment (ISR-240A from Shimadzu). The diffuse reflectance spectra were corrected by the Kubelka-Munk equation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were made on powdered samples at a heating rate of 5°C/min by means of a Rigaku Thermo Plus 8230 and Thermo plus DSC 8232, respectively. Powder X-ray diffraction diagrams were measured on a Rigaku diffractometer (model: Rapid F).

Regeneration Process

The powdered samples were sandwiched between two thin slide glasses (thickness: 100 μm) and then placed on a hot plate. Regeneration from *t*-BOC QA to QA was carried out at a heating rate of about 10°C. The color was found to change from yellow to orange/red at about 150°C and then to red around 160°C. At about 165°C, the powder reacted violently, evolving gases to finally give rise to dull red powders. In view of the present preliminary experiment, the following three samples were used for the study of the regeneration process: *t*-BOC QA at room temperature, orange/red powder heated at 150°C for 75 minutes and dull red sample heated at 200°C for 75 minutes.

Results and Discussion

Crystal Structures of t-BOC QA [8]

Table 1 details the crystallographic parameters for *t*-BOC QA. The molecule belongs to the molecular symmetry of C_i. The *ORTEP* plot is shown in Fig.2. The *t*-BOC groups attached to the N atom of the acridine skeleton are symmetrically twisted in the same direction by 55.57 (8)° (N1/C11/O2/O3 and N1/C1/C2/C7/C8/C10). The condensed ring system is not entirely planar. The dihedral angles between two condensed rings are: 174.56(6)° [N1/C1/C2/C7/C8/C10 and C8-C10/C8^i-C10^i; symmetry code: (i) 1-x, -y, 1-z] and 179.11(8)° (N1/C1/C2/C7/C8/C10 and C2-C7).

Table 1: Crystallographic Parameters for *t* -BOC QA.

Formula	$C_{30}H_{28}N_2O_6$
Molecular weight	512.56
Crystal system	monoclinic
Space group	$P2_1/n$
Molecular symmetry	C_i
a (Å)	14.020(2)
b (Å)	6.5225(8)
c (Å)	14.153(2)
β (°)	106.704(9)
Z	2
R factor	0.042

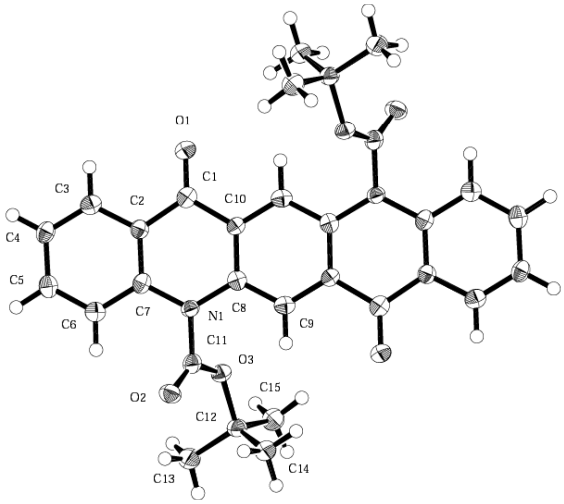

Figure 2. ORTEP plot of t-BOC QA.

TGA Measurements

Figure 3 shows the TGA/DSC curves for the process from *t*-BOC QA to QA. The weight loss begins to occur around 160°C and is completed around 190°C. A weight loss of about 39 % during this process corresponds exactly to the difference in molecular weight between *t*-BOC QA (M_w = 512.6) and QA (M_w = 312.3). This indicates that *t*-BOC groups are completely eliminated and replaced by H atoms to form NH⋯O intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one. It is also to be noted that there observed two pairs of endothermic and exothermic peaks during the weight loss between 160 and 190°C. This suggests that *t*-BOC groups are eliminated, not at one time, but successively in two steps.

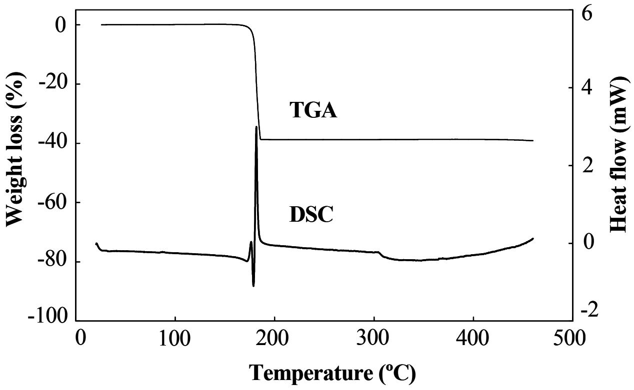

Figure 3. TGA/DSC curves measured on powdered t-BOC QA. The weight loss amounts to about 39 % which corresponds to the difference in weight between t-BOC QA and QA.

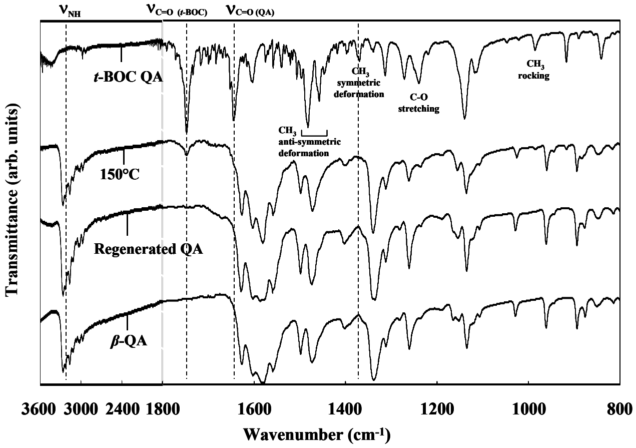

Figure 4. IR spectra for the initial state (t-BOC QA), intermediate state at 150℃ and the final state at 200℃. The IR spectrum of β-QA is also shown for comparison.

IR Spectra

Figure 4 shows the change of the IR spectra of *t*-BOC QA monitored at various temperatures from room temperature via 150 to 200°C during the regeneration process of *t*-BOC QA. At room temperature before the start of regeneration, there are two C=O stretching bands around 1750 and 1650 cm^{-1}, the former of which is due to the C=O stretching of *t*-BOC group and the latter is assigned to the C=O stretching of the QA skeleton. Also observed are the three characteristic absorption bands around 1480, 1460 and 1370 cm^{-1}. The former two bands are attributed to the anti-symmetric deformation vibration while the latter is due to the symmetric one. A rather weak CH_3 rocking mode is also recognized around 980 cm^{-1}. Furthermore, a small band around

1240 cm^{-1} is attributed to C-O stretching of the *t*-BOC group. At 150°C, the C=O stretching of the *t*-BOC group, all the CH_3 characteristic bands as well as the C-O stretching band disappear. Instead, the NH stretching band appears around 3280 cm^{-1}. This band is displaced toward lower wavenumbers due to the formation of the $NH\cdots O$ intermolecular hydrogen bonds, as compared with the free NH stretching band (about 3500 cm^{-1}). Likewise, the C = O stretching of the QA skeleton is also shifted from 1650 to 1630 cm^{-1} due to the hydrogen bond formation. Unassigned is the band around 1360 cm^{-1} whose intensity is greatly enhanced upon heating. This band is also characteristic of regenerated QA and *β*-QA. It is apparent that the IR spectrum of regenerated QA is in good agreement with that of *β*-QA . This indicates that *t*-BOC QA ends up with the *β* phase, as will also be confirmed by diffuse reflectance spectra as well as powder X-ray diffraction diagrams.

Diffuse Reflectance Spectra

Figure 5(a) shows the diffuse reflectance spectra of *t*-BOC QA, intermediate state at 150°C and the final state at 200°C. The absorption spectrum for the sample heated at 150°C illustrates a typical intermediate state between *t*-BOC QA and QA. Fig. 5(b) shows the spectra of regenerated QA and *β*-QA. These spectra are in fairly good agreement, although there is still a slight difference at longer and shorter wavelengths.

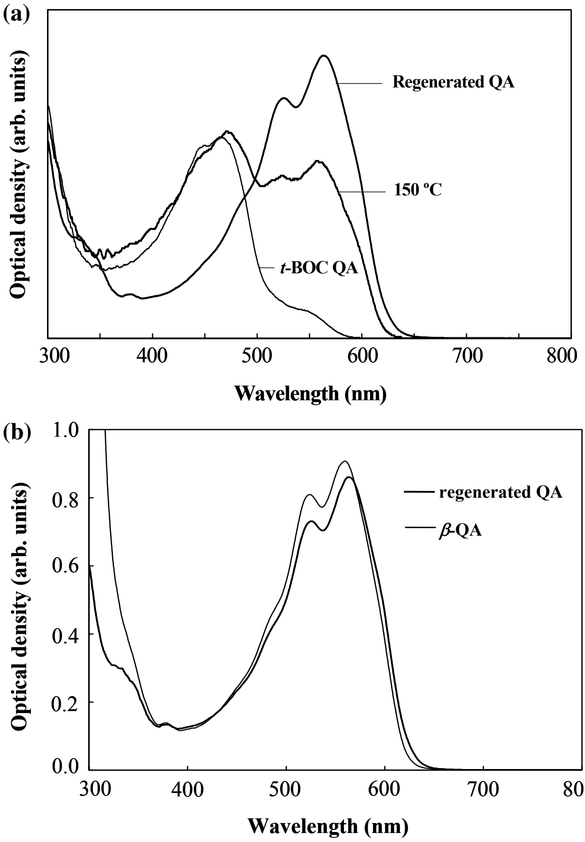

Figure 5. (a) Diffuse reflectance spectra for the initial state (t-BOC QA), intermediate state at 150℃ and final state at 200℃. and (b) spectra for regenerated QA and β-QA.

X-ray Diffraction Diagrams

Figure 6 shows the X-ray diffraction diagrams of *t*-BOC QA, intermediate state at 150°C and the final state at 200°C, together with that of the *β* form. The diffractions peaks of *t*-BOC QA are assigned on the basis of the structure analysis.[7] Here again, the diagram at 150°C reflects well an intermediate state between *t*-BOC QA and the *β* QA. The final phase at 200°C is in good accord with the *β* form.

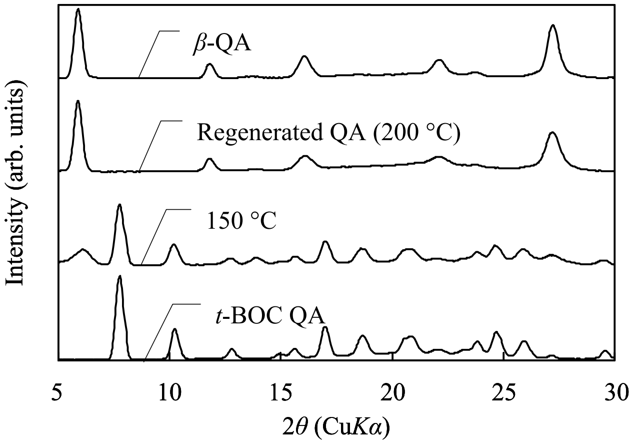

Figure 6. X-ray diffraction diagrams for the initial state (t-BOC QA), intermediate state at 150°C and final state at 200°C. The diagram of the β-QA is also shown for comparison.

Conclusions

Structure of *t*-BOC QA as well as its regeneration process have been studied in the present investigation. The conclusions are summarized as follows:

1. *t*-BOC QA is found to crystallize in space group $P2_1/n$.
2. Transformation from *t*-BOC QA to QA begins around 160 °C and is completed around 190 °C. Elimination of two *t*-BOC groups proceeds, not at one time, but in two steps (*i.e.* one by one).
3. The final phase of regenerated *t*-BOC QA is the *β* phase (reddish violet color) used widely in paint industries together with the γ phase (bluish red shade).

References

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Author 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 at the Development and Engineering Research Center, Mitsubishi Chemical Co. in Okayama, Japan and then moved to Yokohama National University as Assistant Professor. His research interest includes synthetic and computational organic chemistry and electronic characterization of organic pigment.