Synthesis of Soluble Quinacridones

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The synthesis of 4,11-dialkylthioquinacridones and 5,12-dialkyl-4,11-dialkylthioquinacridone from *o*-alkylthioanilines and diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate is described. These compounds are easily soluble in organic solvents in contrast to unsubstituted quinacridone.

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We have investigated the synthesis and applications to the Langmuir-Blodgett films of soluble organic pigments which were phthalocyanine derivatives and carbazole dioxazine derivatives [1-5]. In connection of these investigations we report here the synthesis of soluble quinacridones. Quinacridones (5,7,12,14-tetrahydroquino[2,3-*b*]acridine-7,14-diones, QAs) are reddish organic pigments and possess excellent characteristics in printing ink and as colorants for plastics. Recently, there has been considerable interest in organic pigments in the field of optoelectronics. QAs exhibited photovoltaic and photoconductive properties [6,7]. QAs presented a high resistance to organic solvents probably resulting from strong intermolecular hydrogen bonds shown in Figure 1 [8]. Therefore we introduced alkylthio groups into the 4 and 11 positions of QA to weaken intermolecular hydrogen bonds. Furthermore, *N*-alkylation of QA was examined.

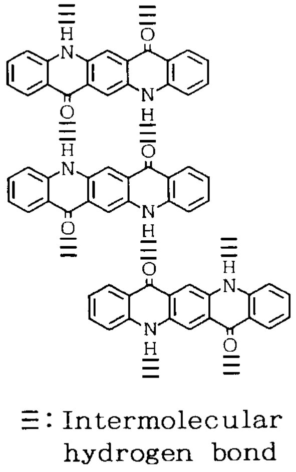
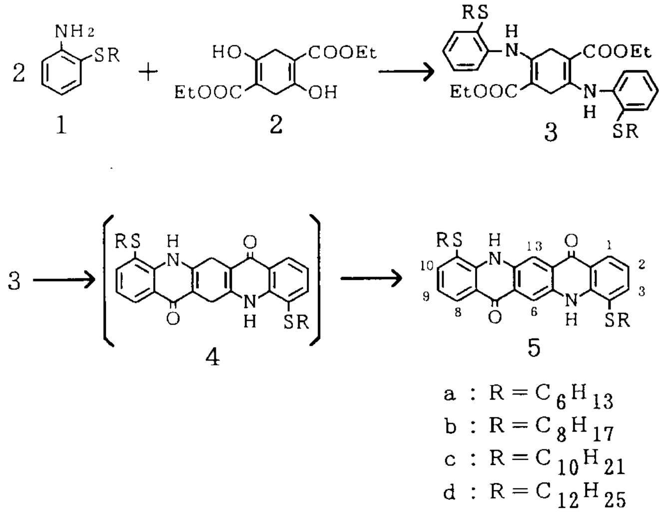


Figure 1. A model of aggregation for quinacridone.

Results and Discussion.

Synthetic routes to QAs are shown in Scheme 1. 4,11-Dialkylthioquinacridones **5a-5d** were synthesized by condensation of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate **2** with *o*-alkylthioanilines **1**, followed by cyclization and oxidation of diethyl 2,5-bis(*o*-alkylthioanilino)-3,6-dihydroterephthalates **3** in a solvent of high boiling temperature. Compound **1** was prepared according to a known procedure [9] from an alkyl bromide with *o*-aminobenzenethiol in the presence of a phase transfer catalyst. Compound **3** was obtained by the reaction of **2** with **1** in moderate yield. In the ^{1}H-nmr spectra, the signal of the methylene protons of **3** appeared as a singlet at δ 3.21-3.31 ppm. In the ir spectra, the absorptions of ester and alkyl groups were observed. The ms and elemental analysis consist of their molecular formula. The thermal behavior of **3b** was investigated in the solid phase by TG-DTA in a nitrogen atmosphere at a heating rate of 10°/minute. After the endothermic curve corresponding to the melting point of **3b** was observed, the weight loss at 195-290° reached 13.5% which approximately agreed with the calculated value of 13.3% for the elimination of two moles of ethanol from **3b**. The cyclization of **3** in dibutyl phthalate as a solvent of high boiling point under a nitrogen atmosphere proceed-

Scheme 1



ed to give 4,11-dialkylthio-5,7,12,14-tetrahydroquinacridones **4**. Compound **4** was easily oxidized to afford 4,11-dialkylthioquinacridone **5**. The purification of QA was limited because of low solubility in organic solvents. Compound **5** could be purified by column chromatography and recrystallization to yield red plates or a powder. The ir showed the absorptions of the alkyl and carbonyl groups, but the ester groups of **3** disappeared. The ms and elemental analysis consist of their molecular formula. The ^{1}H-nmr spectrum of QA in sulfuric acid-d_2 or dimethyl sulfoxide-d_6/sodium hydroxide-d_1 only was reported [10,11]. As **5** became soluble in organic solvents, the coupling of their aromatic rings was clearly observed. The imino proton signal was observed for the first time at δ 9.46-9.50 ppm. The isolated aromatic proton of the 6 and 13 positions were singlets at δ 8.55-8.60 ppm. Introduction of the long alkylthio groups into QA resulted in solubility in chloroform, toluene and so on. These results explain the alkylthio groups at the 4 and 11 positions of QA weakened the intermolecular hydrogen bonds by their steric hindrance. The solubility of **5** in ethanol at 30° are listed in Table 1. The melting points were lowered in proportion to the length of the alkylthio groups. The visible absorptions of **5b** in dimethylformamide were observed at 482 and 514 nm which were almost constant by comparison with those of unsubstituted QA.

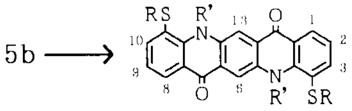
Table 1

Physical Data of Quinacridone Derivatives **5** and **6**

Compound	Substituent R	Substituent R'	Solubility [a] (mol/l)	Mp (°C)
5a	C_6H_{13}	----	4×10^{-5}	294
5b	C_8H_{17}	----	1×10^{-5}	290
5c	$C_{10}H_{21}$	----	4×10^{-5}	283
5d	$C_{12}H_{25}$	----	6×10^{-5}	272
6	C_8H_{17}	C_8H_{17}	2×10^{-3}	99

[a] Measured in ethanol at 30°.

Scheme 2



6

R = C_8H_{17}
R' = C_8H_{17}

Furthermore, *N*-alkylation of **5b** was attempted as shown in Scheme 2. We have already reported the *N*-alkylation of acridone and carbazole using a phase transfer catalyst in good yield [12]. *N*-Octylation of compound **5b** with octyl bromide in the presence of benzyltriethylammonium chloride as the phase transfer catalyst gave **6**. Compound **6** was obtained as orange needles by column chromatography and recrystallization. In the ^{1}H-nmr spectra, the proton signal of the methylene group ($>N-CH_2-$) appeared at δ 4.85 ppm and the imino proton signal of **5b** disappeared. The structure of **6** was confirmed by ms, ir and elemental analysis. Compound **6** was easily soluble in all organic solvents and its solubility in ethanol was 2 x 10^{-3} mole/ℓ which was 200 times that of **5b**. This implies that the intermolecular hydrogen bonds of QA were broken by *N*-alkylation. Compound **6** melted at 99°. The visible absorption of **6** exhibited a maximum at 528 nm, which indicated a bathochromic shift compared with that of **5b**.

EXPERIMENTAL

Melting points of the colored compounds and the thermal behavior were measured by a Rigaku TG-DTA. The ir, mass and electronic absorption spectra were measured with a Perkin-Elmer FTIR-1640, a Shimadzu QP-1000 and a Shimadzu UV-2100 spectrometers, respectively. The ^{1}H-nmr spectra were recorded with a JEOL PMX60Si and a Bruker AM400 with TMS as the internal standard.

Materials.

o-Alkylthioanilines **1** were prepared according to a known procedure [9]. *o*-Hexylthioaniline **1a** was a pale yellow liquid, yield 66%, bp 133°/4 mm Hg; ^{1}H-nmr (carbon tetrachloride): δ 0.65-1.85 (m, 11H, C_5H_{11}), 2.64 (t, 2H, CH_2), 4.14 (br, 2H, NH_2), 6.26-7.28 (m, 4H, aromatic). *o*-Octylthioaniline **1b** was a pale yellow liquid, yield 52%, bp 150°/3 mm Hg; ^{1}H-nmr (carbon tetrachloride): δ 0.63-1.87 (m, 15H, C_7H_{15}), 2.67 (t, 2H, CH_2), 4.12 (s, 2H, NH_2), 6.27-7.30 (m, 4H, aromatic). *o*-Decylthioaniline **1c** was a pale yellow liquid, yield 55%, bp 170°/3 mm Hg; ^{1}H-nmr (carbon tetrachloride): δ 0.65-1.79 (m, 19H, C_9H_{19}), 2.66 (t, 2H, CH_2), 4.25 (s, 2H, NH_2), 6.35-7.35 (m, 4H, aromatic). *o*-Dodecylthioaniline **1d** was a pale yellow liquid, yield 65%, bp 169°/3 mm Hg; ^{1}H-nmr (carbon tetrachloride): δ 0.65-1.92 (m, 23H, $C_{11}H_{23}$), 2.65 (t, 2H, CH_2), 4.19 (br, 2H, NH_2), 6.36-7.35 (m, 4H, aromatic).

Diethyl 2,5-Bis(*o*-octylthioanilino)-3,6-dihydroterephthalate **3b**.

A mixture of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate **2** (1.5 g, 6.0 mmoles), 50% hydrochloric acid (0.6 ml) and ethanol (60 ml) was heated under a nitrogen atmosphere. After **2** dissolved, **1b** (4.3 g, 18 mmoles) was added to the solution. It was refluxed for 3 hours. The precipitate was collected by filtration, washed with ethanol and water. It was recrystallized from ethanol to give a pale orange powder (2.4 g, 59%), mp 45-47°; ir (potassium bromide): 2923, 2852 (CH_2), 1673, 1240 (ester) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 0.67-1.78 (m, 36H, CH_3 and C_7H_{15}), 2.77 (t, 4H, CH_2), 3.21 (s, 4H, CH_2), 4.15 (q, 4H, CH_2), 6.82-7.42 (m, 8H, aromatic), 10.32 (s, 2H, NH); ms: m/z 694 (M^+).

Anal. Calcd. for $C_{40}H_{58}N_2O_4S_2$: C, 69.12; H, 8.41; N, 4.03. Found: C, 69.05; H, 8.40; N, 3.79.

Diethyl 2,5-Bis(*o*-hexylthioanilino)-3,6-dihydroterephthalate **3a**.

The same procedure gave **3a** as a pale orange powder, yield 78%, mp 67-68°; ir (potassium bromide): 2930, 2855 (CH_2), 1658, 1229 (ester) cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 0.67-1.83 (m, 28H, CH_3 and C_5H_{11}), 2.79 (t, 4H, CH_2), 3.25 (s, 4H, CH_2), 4.05 (q, 4H, CH_2), 6.67-7.33 (m, 8H, aromatic), 10.17 (s, 2H, NH); ms: m/z 638 (M^+).

Anal. Calcd. for $C_{36}H_{50}N_2O_4S_2$: C, 67.67; H, 7.89; N, 4.39. Found: C, 67.39; H, 7.69; N, 4.17.

Diethyl 2,5-Bis(*o*-decylthioanilino)-3,6-dihydroterephthalate **3c**.

The same procedure gave **3c** as a pale orange powder, yield 81%, mp 50-51°; ir (potassium bromide): 2922, 2852 (CH_2), 1659, 1238 (ester) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.60-1.93 (m, 44H, CH_3 and C_9H_{19}), 2.78 (t, 4H, CH_2), 3.23 (s, 4H, CH_2), 4.07 (q, 4H, CH_2), 6.87-7.43 (m, 8H, aromatic), 10.36 (s, 2H, NH); ms: m/z 750 (M^+).

Anal. Calcd. for $C_{44}H_{66}N_2O_4S_2$: C, 70.35; H, 8.86; N, 3.73. Found: C, 70.43; H, 8.75; N, 3.49.

Diethyl 2,5-Bis(*o*-dodecylthioanilino)-3,6-dihydroterephthalate **3d**.

The same procedure gave **3d** as a pale orange powder, yield 70%, mp 51-52°; ir (potassium bromide): 2918, 2851 (CH_2), 1662, 1238 (ester) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.72-1.78 (m, 52H, CH_3 and $C_{11}H_{23}$), 2.84 (t, 4H, CH_2), 3.31 (s, 4H, CH_2), 4.12 (q, 4H, CH_2), 6.95-7.45 (m, 8H, aromatic), 10.34 (s, 2H, NH); ms: m/z 806 (M^+).

Anal. Calcd. for $C_{48}H_{74}N_2O_4S_2$: C, 71.42; H, 9.24; N, 3.47. Found: C, 71.08; H, 9.02; N, 3.08.

4,11-Dioctylthioquinacridone **5b**.

A mixture of **3b** (0.5 g, 0.72 mmole) and dibutyl phthalate (8 ml) was refluxed for 10 minutes under a nitrogen atmosphere and next refluxed for 10 minutes in air. The precipitate was collected by filtration and washed with ethanol. It was purified by column chromatography on silica gel using chloroform as the eluent and recrystallized from ethanol to give red plates (0.13 g, 30%), mp 290°; ir (potassium bromide): 2925, 2854 (CH_2), 1600 (C=O) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.84 (t, 6H, CH_3), 0.99-1.83 (m, 24H, C_6H_{12}), 2.86 (t, 4H, S-CH_2), 7.19 (dd, 2H, CH-2 and 9), 7.92 (d, 2H, CH-3 and 10, J = 7.7 Hz), 8.45 (d, 2H, CH-1 and 8, J = 7.7 Hz), 8.56 (s, 2H, CH-6 and 13), 9.50 (s, 2H, NH); uv-vis (chloroform): λ max 290 (log ϵ 4.8), 482 (3.8), 513 (4.0); ms: m/z 600 (M^+).

Anal. Calcd. for $C_{36}H_{44}N_2O_2S_2$: C, 71.96; H, 7.38; N, 4.66. Found: C, 71.88; H, 7.31; N, 4.58.

4,11-Dihexylthioquinacridone **5a**.

The same procedure gave **5a** as a red powder, yield 56%, mp 294°; ir (potassium bromide): 2925, 2854 (CH_2), 1605 (C=O) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.86 (t, 6H, CH_3), 1.19-1.70 (m, 16H, C_4H_8), 2.87 (t, 4H, S-CH_2), 7.20 (dd, 2H, CH-2 and 9), 7.92 (d, 2H, CH-3 and 10, J = 7.3 Hz), 8.45 (d, 2H, CH-1 and 8, J = 8.0 Hz), 8.55 (s, 2H, CH-6 and 13), 9.46 (s, 2H, NH); uv-vis (chloroform): λ max 290 (log ϵ 4.9), 481 (3.9), 513 (4.1); ms: m/z 544 (M^+).

Anal. Calcd. for $C_{32}H_{36}N_2O_2S_2$: C, 70.55; H, 6.66; N, 5.14. Found: C, 70.32; H, 6.80; N, 4.83.

4,11-Didecylthioquinacridone **5c**.

The same procedure gave **5c** as a red powder, yield 19%, mp 283°; ir (potassium bromide): 2923, 2852 (CH_2), 1600 (C=O) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.85 (t, 6H, CH_3), 1.14-1.68 (m, 32H, C_8H_{16}), 2.86 (t, 4H, S-CH_2), 7.21 (dd, 2H, CH-2 and 9), 7.93 (d, 2H, CH-3 and 10, J = 7.1 Hz), 8.46 (d, 2H, CH-1 and 8, J = 7.8 Hz), 8.56 (s, 2H, CH-6 and 13), 9.48 (s, 2H, NH); uv-vis (chloroform): λ max 290 (log ϵ 4.9), 481 (3.9), 513 (4.1); ms: m/z 656 (M^+).

Anal. Calcd. for $C_{40}H_{52}N_2O_2S_2$: C, 73.13; H, 7.98; N, 4.27. Found: C, 73.33; H, 8.10; N, 3.97.

4,11-Didodecylthioquinacridone **5d**.

The same procedure gave **5d** as a red powder, yield 17%, mp 272°; ir (potassium bromide): 2922, 2852 (CH_2), 1601 (C=O) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.86 (t, 6H, CH_3), 1.04-1.83 (m, 40H, $C_{10}H_{20}$), 2.87 (t, 4H, S-CH_2), 7.23 (dd, 2H, CH-2 and 9), 7.94 (d, 2H, CH-3 and 10, J = 7.5 Hz), 8.47 (d, 2H, CH-1 and 8, J = 8.0 Hz), 8.60 (s, 2H, CH-6 and 13), 9.48 (s, 2H, NH); uv-vis (chloroform): 290 (log ϵ 4.9), 481 (3.9), 513 (4.1); ms: m/z 712 (M^+).

Anal. Calcd. for $C_{44}H_{60}N_2O_2S_2$: C, 74.11; H, 8.48; N, 3.93. Found: C, 73.95; H, 8.34; N, 3.92.

5,12-Dioctyl-4,11-Dioctylthioquinacridone **6**.

A mixture of **5b** (0.1 g, 0.17 mmole), benzyltriethylammonium chloride (0.039 g, 0.17 mmole), 50% aqueous sodium hydroxide (16 ml) and *o*-dichlorobenzene (16 ml) was heated while being stirred vigorously. Octyl iodide (2.5 g, 10 mmoles) was added to the solution and it was refluxed for 8 hours. The resulting solution was extracted with chloroform and washed with water until the organic layer became neutralization and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel eluting with toluene and recrystallized from methanol to give orange needles (12 mg, 9%), mp 99°; ir (potassium bromide): 2924, 2853 (CH_2), 1640 (C=O) cm^{-1}; ^1H-nmr (deuteriochloroform): δ 0.73-1.53 (m, 60H, CH_3 and C_6H_{12}), 2.87 (t, 4H, S-CH_2), 4.85 (t, 4H, N-CH_2), 7.26 (dd, 2H, CH-2 and 9), 7.80 (dd, 2H, CH-3 and 10, J = 7.5, 1.6 Hz), 8.35 (dd, 2H, CH-1 and 8, J = 8.0, 1.6 Hz), 8.60 (s, 2H, CH-6 and 13); uv-vis (chloroform): 297 (log ϵ 4.9), 527 (4.0); ms: m/z 824 (M^+).

Anal. Calcd. for $C_{52}H_{76}N_2O_2S_2$: C, 75.67; H, 9.28; N, 3.40. Found: C, 75.44; H, 9.25; N, 3.21.

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