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NEW COMPOUNDS

Benzoxanthene-3,4-dicarboximides and Benzimidazoxanthenoisoquinolinones

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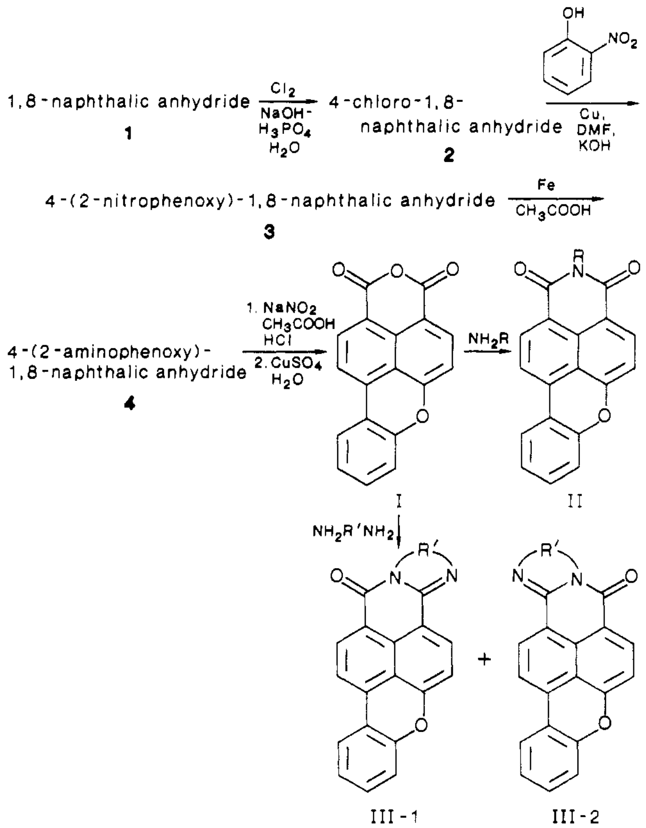
Some benzoxanthene-3,4-dicarboximides and benzimidazoxanthenoisoquinolinones are synthesized, and their physical properties and spectral data are determined.

Benzoxanthene derivatives can be used as organic pigments, laser dyes, textile dyes, and fluorescent whitening agents (*1*). We report here the synthesis and properties of benzoxanthene-3,4-dicarboximides and benzimidazoxanthenoisoquinolinones derived from benzoxanthene-3,4-dicarboxylic anhydride.

The syntheses of benzoxanthene-3,4-dicarboximides and benzimidazoxanthenoisoquinolinones are similar to that of benzothioxanthene-3,4-dicarboximides and benzimidazothioxanthenoisoquinolinones (*2*, *3*), which may be synthesized through chlorination, condensation, reduction, cyclization, and imidation with 1,8-naphthalic anhydride as raw materials. The route of the syntheses is as in Scheme I.

Scheme I[a]



[a] In compound II, R = CH_3, IIa, R = C_6H_{11}, IIb; R = C_6H_5, IIc; R = $C_6H_4NH_2$-*m*, IId; R = C_6H_4Cl-*p*, IIe; R = $C_6H_4CH_3$-*p*, IIf. In compound III, R′ = $-CH_2-CH_2-$, IIIa; R′ = $-C_6H_4-$, IIIb.

Experiment

1,8-Naphthalic anhydride (50 g, 95%) and phosphoric acid (4 mL, 85%) are dissolved in a solution containing NaOH (75 g) and water (1800 mL). At the room temperature, the chlorine is allowed to pass through the solution for 3 h to ensure complete chlorination. The solution is salted and acidified to give compound **2** in 82% yield. Recrystallization from ethanol gave white needles, mp 216-217 °C (*1*).

Compound **2** (10.2 g), KOH (4.8 g), copper powder (0.4 g), and 2-nitrophenol (13.2 g) are refluxed in DMF (220 mL) for 1 h. The liquor is added to 20% hydrochloric acid to give compound **3** in 71% yield. Recrystallization from acetic acid gave orange needles, mp 277-278 °C.

Iron powder (4.8 g) and compound **3** (10 g) were dropped in glacial acetic acid (320 mL) and then refluxed for 1 h. The liquor was poured into water to give compound **4** in 90% yield.

Hydrochloric acid (16 mL) was added to acetic acid (200 mL) in which compound **4** (8 g) had been added. The mixture was cooled and then diazotized by adding an aqueous solution of sodium nitrite. The resulting diazonium liquor was added gradually (1 h) to a boiling solution of hydrated copper sulfate to give compound I in 98% yield. Recrystallization from DMF gave yellow needles, sublimation point 305-307 °C. Anal Calcd for $C_{18}H_8O_4$: C, 75.00%; H, 2.80%. Found: C, 74.82%; H 2.70%.

A mixture of compound I and the appropriate amine or diamine was refluxed for 3 h and then added to water to give compound IIa, IIb, and IIIa in 98%, 68%, and 58% yield, respectively.

Compound I and the appropriate amine or diamine were refluxed in acetic acid for 3 h and then added to water to give compounds IIc, IId, IIe, IIf, and IIIb in 76%, 83%, 99%, 98%, and 87% yields, respectively.

Compound III is a mixture of isomer III-1 and isomer III-2 (*3*).

Compound I. Yellow needles (from DMF), IR: 1775 and 1725 cm^{-1} (C=O), 1160 cm^{-1} (C-O-C). MS: *m/e* (TI%), 288 ($M^{\bullet+}$, 100), 244 (15.41), 216 (11.73), 187 (9.78), 108 (4.66), and 94 (3.24). UV: max (nm) (log ε), 425 (4.32) in DMF. Fl: max, 474.5 nm in DMF.

Compound IIa. Deep yellow needles (from DMF), mp 320 °C. IR: 1685 and 1650 cm^{-1} (C=O), 1165 cm^{-1} (C-O-C). MS: *m/e* (TI%), 301 ($M^{\bullet+}$, 100), 273 (5.05), 256 (8.50), and 187 (4.66). UV: max (nm) (log ε), 424 (4.42) in DMF. Fl: max, 470 nm in DMF.

Compound IIb. Yellow needles (from methylbenzene), mp 306-307 °C. IR: 1690 and 1650 cm^{-1} (C=O), 1240 cm^{-1}

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(C-O-C), 1330 $\mathrm{cm^{-1}}$ (C-N). UV: max, nm (log ϵ), 425 (4.43) in DMF. Fl: max, 472.2 nm in DMF.

Compound IIc. Greenish yellow needles (from methylbenzene), mp 311-312 °C. IR: 1690 and 1655 $\mathrm{cm^{-1}}$ (C=O), 1254 $\mathrm{cm^{-1}}$ (C-O-C), 1350 $\mathrm{cm^{-1}}$ (C-N). MS: *m/e* (TI%), 363 ($M^{\bullet+}$, 100), 319 (4.26), 270 (4.01), and 187 (3.84). UV: max (nm) (log ϵ), 423 (4.39) in DMF. Fl: max 472 nm in DMF.

Compound IId. Deep greenish yellow needles (from methylbenzene), mp 213-214 °C. IR: 3300 $\mathrm{cm^{-1}}$ ($-NH_2$), 1660 and 1590 $\mathrm{cm^{-1}}$ (C=O), 1335 $\mathrm{cm^{-1}}$ (C-O-C). UV: max (nm) (log ϵ), 428 (4.44) in DMF. Fl: max 474.6 nm in DMF.

Compound IIe. Greenish yellow needles (from DMF), mp 302-303 °C. IR: 1760 and 1720 $\mathrm{cm^{-1}}$ (C=O), 1230 $\mathrm{cm^{-1}}$ (C-O-C), 1295 $\mathrm{cm^{-1}}$ (C-N). UV: max nm (log ϵ), 425 (4.58) in DMF. Fl: max 474.6 nm in DMF.

Compound IIf. Greenish yellow needles (from methylbenzene), mp 294-296 °C. IR: 1760 and 1720 $\mathrm{cm^{-1}}$ (C=O), 1230 $\mathrm{cm^{-1}}$ (C-O-C), 1295 $\mathrm{cm^{-1}}$ (C-N). MS: *m/e* 377. UV: max (nm) (log ϵ), 424 (3.98) in DMF. Fl: max 473.6 nm in DMF.

Compound IIIa (IIIa-1 and IIIa-2). Orange-yellow needles (from methylbenzene), mp 235-236 °C, IR: 1660 $\mathrm{cm^{-1}}$ (C=O), 1620 $\mathrm{cm^{-1}}$ (C=N), 1450 $\mathrm{cm^{-1}}$ ($>CH_2$), 1240 $\mathrm{cm^{-1}}$ (C-O-C). UV: max (nm) (log ϵ), 426 (3.97) in DMF. Fl: max 474.7 nm in DMF.

Compound IIIb (IIIb-1 and IIIb-2). Orange-red needles (from DMF), mp 320 °C. IR: 1680 $\mathrm{cm^{-1}}$ (C=O), 1630 $\mathrm{cm^{-1}}$ (C=N), 1240 $\mathrm{cm^{-1}}$ (C-O-C). MS: *m/e* (TI%), 360 ($M^{\bullet+}$, 100), 180 (3.67), 44 (6.94), 32 (3.55), 28 (10.54), 18 (8.72). UV: max (nm) (log ϵ), isomer IIIb-1 479 (4.47) and isomer IIIb-2 453 (4.45) in DMF. Fl: max (nm), isomer IIIb-1 531.5 and isomer IIIb-2 499 in DMF.

The elemental analyses of the above compounds are in fair agreement with the calculated values.

The instruments used for analysis are as follows: Mp-Xh (Beijing) for the melting point determination; Shimadzu UV-365 for the recording of the visible spectra; Shimadzu IR-450 for the infrared spectra; Hitachi M-850 for the fluorescence; Hitachi M-80 for mass spectra; elemental analyses were performed by ECICT Analytic Center.

Registry No. 1, 81-84-5; 2, 4053-08-1; 3, 111669-59-1; 4, 111669-60-4; I, 36310-05-1; IIa, 35340-39-7; IIb, 111669-61-5; IIc, 111669-62-6; IId, 111669-63-7; IIe, 111669-64-8; IIf, 111669-65-9; III-1a, 111669-66-0; III-1b, 55231-31-7; III-2a, 111669-67-1; III-2b, 55231-32-8; $MeNH_2$, 74-89-5; $PhNH_2$, 62-53-3; *m*-$NH_2C_6H_4NH_2$, 108-45-2; *p*-$ClC_6H_4NH_2$, 106-47-8; *p*-$MeC_6H_4NH_2$, 106-49-0; $H_2N(CH_2)_2NH_2$, 107-15-3; *o*-$H_2NC_6H_4NH_2$, 95-54-5; *o*-nitrophenol, 88-75-5; cyclohexylamine, 108-91-8.

Literature Cited

(1) Qian Xuhong; Ren Shengwu, *J. East China Inst. Chem. Technol.* **1987**, *13*, 11.
(2) Peters, A. T. et al. *J. Heterocycl. Chem.* **1974**, *11*, 33.
(3) Peters, A. T. et al. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 121.

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Synthesis of Some Metal Phthalocyaninetetrakis(*N*-cyclopropylsulfonamides)

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The synthesis and characterization of 10 new metal phthalocyaninetetrakis(*N*-cyclopropylsulfonamides) are reported. Bivalent Zn, Cu, Co, Ni, and Fe were used as 4-coordinated central metals. ^{1}H NMR, IR, and thermogravimetric measurements studies of both series of compounds are reported.

In continuation of our efforts directed toward further preparations and applications of metal and metal-free phthalocyaninetetrakis(carboxamides) and -(sulfonamides) (*1-4*), we have undertaken the synthesis of 10 novel metal phthalocyaninetetrakis(cyclopropylsulfonamides) (**3a-e**) and (**4a-e**) which were obtained by the reactions of metal phthalocyaninetetrakis(sulfonyl chlorides), (**1a-e**) and (**2a-e**), with cyclopropylamine. Zn, Cu, Co, Ni, and Fe were used as bivalent 4-coordinated central metals. The thermal stabilities of cyclopropane in compounds **3a-e** and **4a-e** was examined.

Experimental Section

The IR spectra were obtained on a Pye Unicam SP-300 infrared spectrophotometer using KBr disk.

^{1}H NMR spectra were obtained on a 80-MHz NMR spectrometer in hexadeuteriated dimethyl sulfoxide using tetramethylsilane as internal reference standard.

Satisfactory elemental analysis, molecular weight measurements, and TLC were obtained for all new compounds.

Elemental analyses were performed on Hereaus C,H,N-rapid computer HP 85 by Samara Laboratory, Samara, Iraq, and submitted for review.

Differential thermal analyses (DTA) of all new compounds were carried out by Hereaus thermal analyzer TA 500; α-Al_2O_3 at 1300 °C was used as reference material. Heating in the range 25-500 °C was programmed at a rate of 10 °C/min under inert nitrogen atmosphere.

Metal phthalocyanine-3,3′,3″,3‴-tetrakis(sulfonyl chlorides) (**1a-e**) were prepared as follows: **1a** was synthesized according to Clark's method (*5*); compounds **1b-d** were prepared by the method given in the literature (*6*); **1e** was obtained according to the procedure of Mayhew (*7*). Metal phthalocyanine-4,4′,4″,4‴-tetrakis(sulfonyl chlorides) (**2a-e**) were prepared as reported (*5*) (Scheme I).

Metal Phthalocyanine-3,3′,3″,3‴-tetrakis(N-cyclopropylsulfonamides) (3a-e). In each treatment (30 g, 29 mmol) of the corresponding compounds (**1a-e**) were added over a period of 30 min at 0 °C to a stirred solution of 8.5% cyclopropylamine and water (100 mL). The mixture was then

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