HETEROCYCLES, Vol. 80, No. 1, 2010, pp. 183 - 186. © The Japan Institute of Heterocyclic Chemistry
Received, 15th July, 2009, Accepted, 4th September, 2009, Published online, 4th September, 2009
DOI: 10.3987/COM-09-S(S)53

PHOTOLYTIC PREPARATION OF TETRABROMOTHIANTHRENE AND ITS TRANSFORMATION TO DINUCLEAR PHTHALOCYANINES

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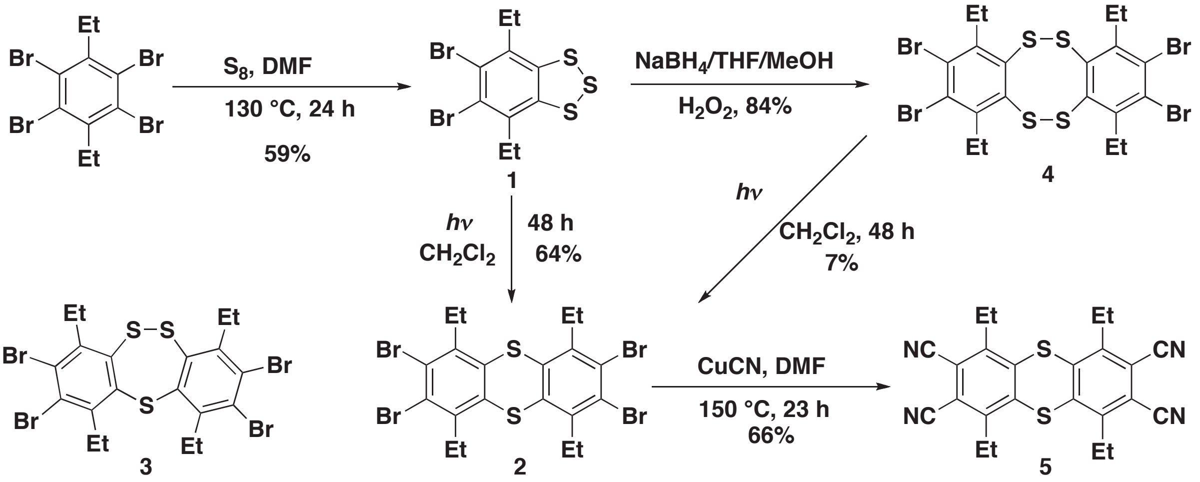
This paper is dedicated to Dr. Akira Suzuki on the occasion of his 80th birthday.

Abstract – Photolysis of dibromobenzotrithiole (**1**) and tetrabromodibenzotetrathiocin (**4**) in CH_2Cl_2 produced tetrabromothianthrene (**2**). Compound (**2**) was treated with CuCN in DMF at 150 °C to give tetracyanothianthrene (**5**). Dinuclear phthalocyanine (**9**) was constructed by treatment of a mixture of **5** and dioctoxyphthalonitrile (**6**) with lithium in *n*-pentanol.

New types of phthalocyanines (Pcs) have been desired to develop advanced functional materials for use with electrochromic displays, field-effect transistors, dye-sensitized solar cells, and so on, which has stimulated the study of the compounds and related functional dyes.[1,2] Dinuclear phthalocyanine (DNPc), consisting of two Pcs connected by one or several benzene rings in a peripheral direction, has an enlarged π-electronic system.[3] The molecules are expected to show redshifts of Q-band absorption and lowering of the oxidation potential compared with mononuclear Pcs. However, it is known that DNPc has low solubility without appropriate substituents because of its planarity and highly aggregative properties. It was reported that DNPc in which two Pcs are linked by two sp^3 carbon atoms has a gable structure and can suppress its aggregation.[4] If a 1,4-dithiin ring is introduced between two Pcs instead of the 1,4-cyclohexadiene ring, DNPc could have a wedged form as the two sulfur atoms of the dithiin ring have an sp^3 structure. While the angle between two benzene rings of thianthrene [dibenzodithiin] was reported to be 132°,[5] its conformation could change to planar form by oxidation.[6] It was reported that thianthrene derivatives were prepared by the photolysis of dibenzotetrathiocins.[7a] We also reported the photolysis of ethylenedithiodiethylbenzotrithiole in CH_2Cl_2 produced bis(ethylenedithio)-

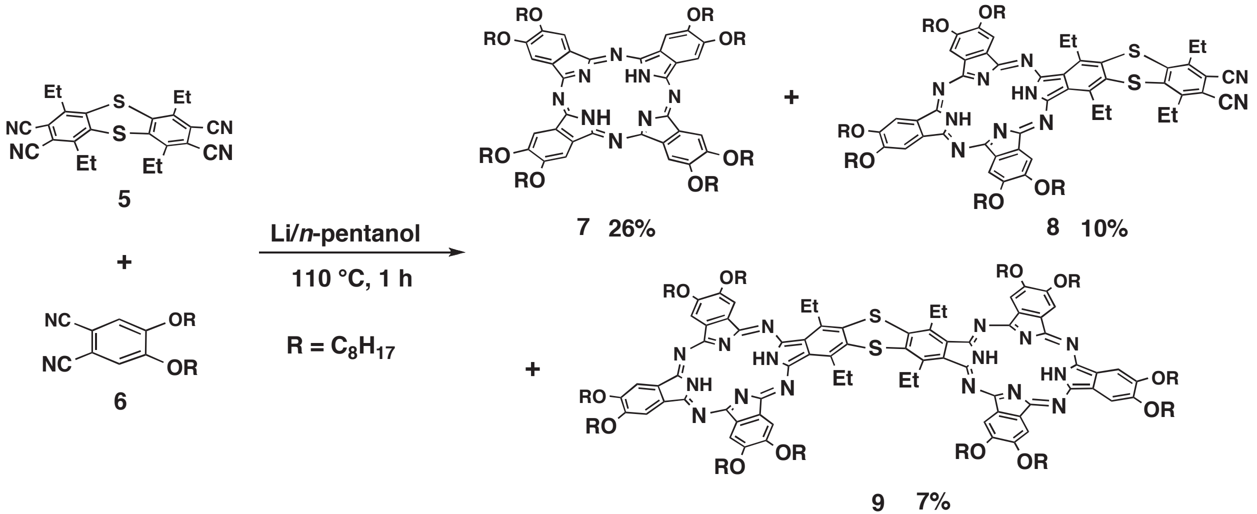
tetraethylthianthrene.[7b,c] This paper describes the preparation of 2,3,7,8-tetracyano-1,4,6,9-tetraethylthianthrene (**5**) from 5,6-dibromo-4,7-diethylbenzo[1,2,3]trithiole (**1**) and the construction of DNPc connected with the dithiin ring on treatment of a mixture of **5** and 4,5-dioctoxyphthalonitrile (**6**) with lithium in *n*-pentanol.



Scheme 1

As a key compound for synthesizing tetracyanothianthrene (**5**), **1** was prepared from tetrabromo-*p*-diethylbenzene by the procedure as described previously.[8] When **1** was photolyzed with a 100 W high-pressure mercury lamp in CH_2Cl_2 for 48 h, 2,3,7,8-tetrabromo-1,4,6,9-tetraethylthianthrene (**2**) was produced in 64% yield as colorless crystals *via* the dimerization and ring contraction reactions of **1** (Scheme 1).[9] If the irradiation was insufficient, tetrabromodibenzotrithiepin (**3**), bearing a seven-membered trithiepin ring between the two benzene rings, was produced together with **2**. The mixture of **2** and **3** is difficult to separate without repeated recrystallization. Meanwhile, since dibenzotetrathiocin is a good precursor for the preparation of thianthrene, 2,3,8,9-tetrabromo-1,4,7,10-tetraethyldibenzotetrathiocin (**4**) was prepared in 84% yield upon treatment of **1** with $NaBH_4$ and then H_2O_2 in THF/MeOH. However, the photolysis of **4**, suspended in CH_2Cl_2, for 48 h gave **2** in only 7% yield because of its poor solubility. Four bromine atoms of **2** were then substituted with nitrile groups by the reaction with CuCN in DMF at 150 °C under Ar for 23 h to produce 2,3,7,8-tetracyano-1,4,6,9-tetraethylthianthrene (**5**) in 66% yield as pale yellow crystals.

To construct DNPc linked with the dithiin ring, phthalonitriles (**5**) and (**6**) were mixed in a 1:6 ratio (**5**: 44.4 mg, 0.104 mmol; **6**: 239.6 mg, 0.623 mmol). The mixture was treated with lithium (34.3 mg, 4.94 mmol) in *n*-pentanol (3 ml) at 110 °C for 1 h, after preparation of lithium *n*-pentoxide (Scheme 2).[10] The solution was acidified by aqueous HCl and a blue-green precipitate was filtered. The residue was purified by column chromatography using silica gel (Wakogel C-300, $CHCl_3$) followed by Bio-beads (Bio-Rad, SX-1, $CHCl_3$) to produce octaoctoxyphthalocyanine (**7**), dicyanobenzodithiinophthalocyanine (**8**), and DNPc (**9**) in 26%, 10%, and 7% yields, respectively. When 4,5-dibutoxyphthalonitrile was used as a reactant instead of **6**, the products showed lower solubility than that of the octyl derivatives. In the ^{1}H NMR spectra of **8** and **9**, the signals were observed as broadening peaks compared with that of **7**, suggesting that although **8** and **9** have octoxy groups as substituents at the peripheral position, they are more aggregative than that of **7**. The structures of **8** and **9** could be determined by MALDI-TOF-MS and their molecular ion peaks were observed at 1482.234 [M$^-$] for **8** and 2738.185 [M$^+$] for **9**.



Scheme 2

In the UV-vis spectra measured in $CHCl_3$, the Q-band absorptions of **8** and **9** were observed at λ_{max} = 618 (sh), 650 (sh), 683, 704 and 721 (sh) nm for **8** and λ_{max} = 622 (sh), 657 (sh), 686, 702, and 721 (sh) nm for **9**: while the shoulder peak of **9** at 721 nm is clear absorption, that of **8** is faint. These absorptions are at a similar energy level to that of **7** [λ_{max} = 605, 649 (sh), 667, and 704 nm] except for the shoulder peaks at 721 nm, suggesting that the π-electron of the Pc ring weakly interacts with the dithiin ring. In contrast, **9** showed Q-band absorption at λ_{max} = 716, 748, and 810 (sh) nm as broadened peaks when the UV-vis spectrum was measured in $CHCl_3$ containing trifluoroacetic acid (10 vol%). Under the similar condition, Q-band absorption of **7** was observed as two widened peaks at λ_{max} = 716 and 779 nm. It appears that the cationic species of **7** and **9** are generated by protonation of the nitrogen atoms and the π-electronic system of **9** is more strongly affected by the positive charge than that of **7**. These results should be related to the π-electronic interaction of the Pc rings of **9** with the central dithiin ring. The electrochemical property of **9** was determined by cyclic voltammetry using $Ag/AgNO_3$ as a reference electrode (solvent: CH_2Cl_2; scan rate: 200 mV/s). Compound (**9**) shows one reversible and one irreversible oxidation couple ($E_{1/2}$ = 0.34 V, Ep = 0.88 V) and two reversible reduction potentials ($E_{1/2}$ = –1.52, –1.10 V). It appears that the oxidation potential and the two reduction potentials of **9** are positively shifted in comparison with those of **7**, respectively (oxidation potential: $E_{1/2}$ = 0.29 V; reduction potentials: $E_{1/2}$ = –1.65, –1.13 V).

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9. **2**: colorless crystals; mp 242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.25$ (t, $J = 7.5$ Hz, 12H), 3.30 (q, $J = 7.5$ Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) $\delta = 13.5, 31.3, 127.8, 136.5, 142.6$; HRMS (EI) Calcd for $C_{20}H_{20}{}^{79}Br_4S_2$: 639.7740. Found: 639.7744 (M^+); **4**: pale-yellow ccrystals; mp 281-283°C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.24$ (t, $J = 7.5$ Hz, 12H), 3.37 (dq, $J = 13.0, 7.5$ Hz, 4H), 3.44 (dq, $J = 13.0, 7.5$ Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) $\delta = 14.4, 33.20, 131.6, 142.4, 149.1$; HRMS (EI) Calcd for $C_{20}H_{20}Br_4S_4$: 703.7181. Found: 703.7181 (M^+); **5**: pale-yellow crystals; mp 280-283 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.37$ (t, $J = 7.6$ Hz, 12H), 3.24 (q, $J = 7.6$ Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 14.6, 27.6, 114.2, 115.9, 140.9, 146{,}6$; IR (KBr) 2225 cm^{-1}(CN); HRMS (EI) Calcd for $C_{24}H_{20}N_4S_2$: 428.1129. Found: 428.1133 (M^+).
10. **8**: green powder; mp 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.82$-1.04 (m, 18H), 1.21-1.66 (m, 48H), 1.70-2.25 (m, 24H), 3.96-4.66 (m, 20H), 8.10-8.80 (m, 6H); MALDI-TOF-MS (dithranol) *m/z* 1482.234 (M^-); **9**: green powder; mp 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.78$-1.09 (m, 36H), 1.18-2.40 (m, 156H), 3.95-4.70 (m, 32H), 8.20-9.00 (m, 12H); MALDI-TOF-MS (dithranol) *m/z* 2738.185 (M^+).