First Syntheses of Iodinated 1,6-Dithiapyrene Derivatives

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An improved synthetic method of 1,6-dithiapyrene (DTPY) was found with a practical yield in a reproducible manner. Iodinated DTPY derivatives were prepared as new donor molecules, and the crystal structure of 2,7-diiodoDTPY was clarified by an X-ray structure analysis.

A remarkable development of charge transfer (CT) complexes and CT salts based on tetrathiafulvalene (TTF) type donors is continuing to attract considerable interest in the fields of organic conductors and superconductors.[1] One of the most difficult challenges is the creation of donor molecules which have a new skeleton with relatively low oxidation potentials. We have designed and synthesized 1,6-dithiapyrene (DTPY) and its derivatives for new donor molecules (Chart 1).[2,3] The CT complexes of bis(methylthio)DTPY (MTDTPY) with chloranil or bromanil were the first molecular metals which contained neither TTF- nor TCNQ-type molecules.[3] Unfortunately, the low yield and poor reproduction in the synthesis of DTPY hampered any further study of DTPY. In this paper, we report on an improved synthetic method of DTPY and the first syntheses of its iodinated derivatives, which were beneficial not only as new donors for CT complexes with possible halogen bondings,[4] but also as synthetic intermediates for the further derivatives via coupling reactions by using iodine atom(s) as leaving group(s).

A key synthetic step for DTPY is a cyclization reaction of acetal **1**,[3] whose experimental procedure was improved by the following operations: i) the use of four flasks at the same time, ii) an increase in the amount of P_2O_5 versus **1** and an elongation of the reaction time, iii) the addition of Et_3N to keep weak basic conditions, and iv) the avoidance of complete concentration of the crude reaction solution. This revised method gave 3.7 g (42% yield) (1.26 g and 22% yield in previous method) of DTPY by a single operation in a reproducible manner. New iodinated derivatives, 2-iodoDTPY (IDTPY) and 2,7-diiodoDTPY (DIDTPY), were synthesized by the treatment of DTPY with one or two molar amounts of *n*-BuLi, followed by perfluorohexyl iodide in 28% and 82% yields, respectively (Scheme 1).

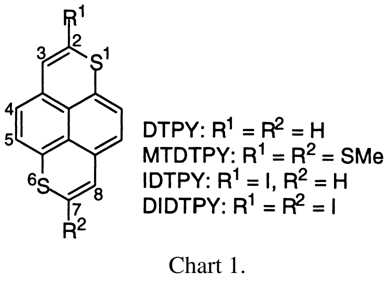
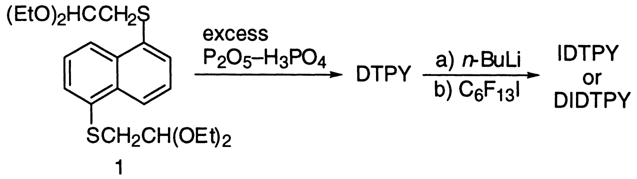


Chart 1.



Scheme 1. Syntheses of IDTPY and DIDTPY.

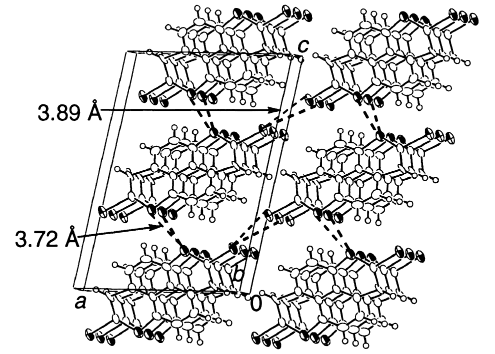


Fig. 1. Crystal packing for DIDTPY viewed down the *b*-axis.

Cyclic voltammograms of IDTPY and DIDTPY in DMF show two-stage one-electron reversible oxidation waves.[5] The donor abilities of the iodinated DTPY derivatives were decreased compared with that of DTPY, which were consistent with the electrochemical behaviors of iodinated TTFs.[6] The ΔE values of IDTPY and DIDTPY were slightly decreased compared with that of DTPY.[5]

A crystal structure of DIDTPY is shown in Fig. 1. DIDTPY is centrosymmetric and the S^1, S^6 atoms and the C^3, C^8 atoms of DIDTPY were disordered by 30% in the crystal. DIDTPY stacks along the *b*-axis, and the interplanar distance is 3.47 Å. There are weak S···S (3.72 Å) and strong I···I (3.89 Å) contacts, judging by the sum of the van der Waals radii (3.70 and 3.98 Å, respectively). Preparations of CT complexes and salts of IDTPY and DIDTPY are in progress and will be reported.

Experimental

^1H NMR spectra were recorded on a JEOL EX-270 spectrometer with $CDCl_3$ as a solvent and Me_4Si as an internal standard. EIMS spectra were recorded at 70 eV on a Shimadzu QP-5000. Cyclic voltammograms were recorded with a 1.6 mm diameter gold working electrode and a Pt wire counter electrode in DMF containing 0.1 M (1 M = 1 mol dm^{-3}) Et_4NClO_4 as the supporting electrolyte at room temperature at a scan rate of 0.1 V/s using an ALS Electrochemical Analyzer Model 612A. The experiments employed an Ag/AgNO$_3$ reference electrode, and the final results were calibrated with a ferrocene/ferrocenium couple. Deactivated alumina (ICN, N-super I) was prepared by mixing with 6% water. Recycle preparative gel permeation chromatography (GPC) was performed using a polystyrene gel column (JAIGEL 1H × 2, Japan Analytical Industry).

1,6-Dithiapyrene (DTPY). Four 200-mL-round-bottomed flasks were arranged, and a mixture of P_2O_5 (98%, 20 g) and H_3PO_4 (85%, 15 mL) was placed in each flask. After the mixtures were heated at 140 °C and stirred at this temperature for 1 h, a powdered acetal **1** (4.0 g, 9.4 mmol) was added over 5 min to each flask. After being stirred at 140 °C for 0.5 h, the reaction mixtures were poured into a mixture of ice–water (ca. 1.3 L) and CH_2Cl_2 (ca. 2.7 L), and neutralized with an aqueous NaOH solution (6 M). After the black precipitates were removed by filtration, the resulting filtrates were extracted with CH_2Cl_2 (100 mL × 3). To the organic extracts Et_3N (3 mL) was added; this mixture was then dried over Na_2SO_4, filtered and concentrated under reduced pressure until the total volume was ~500 mL. The residual solution was subjected to flash alumina column chromatography with CH_2Cl_2 as the eluant, and then reprecipitated from toluene–hexane to give almost pure DTPY as a brownish-orange powder (3.7 g, 42%, $>$ 99% purity by ^{1}H NMR). This powder was used for the next iodination reactions. Further purification of DTPY was accomplished by sublimation at 140 °C under reduced pressure, and then recrystallization from toluene–hexane to give reddish orange needles. mp 220–221 °C; R_f = 0.54 (hexane:CH_2Cl_2 = 4:1); ^{1}H NMR δ 5.55 (2H, d, J = 9.9 Hz), 5.74 (2H, d, J = 9.9 Hz), 6.03 (2H, d, J = 7.6 Hz), 6.22 (2H, d, J = 7.6 Hz); EIMS *m/z* (rel intensity) 240 (M^+; 100); Anal. Calcd for $C_{14}H_8S_2$: C, 69.96; H, 3.35%. Found: C, 69.64; H, 3.19%.

2-Iodo-1,6-dithiapyrene (IDTPY). A solution of DTPY (500 mg, 2.1 mmol) in THF (50 mL) was cooled at −78 °C under an Ar atmosphere. To this solution was added *n*-BuLi (1.5 M hexane solution, 1.4 mL, 2.1 mmol) over 5 min; the reaction mixture was then stirred for 1 h at −78 °C. Perfluorohexyl iodide (0.45 mL, 2.1 mmol) was added, and the mixture was stirred for 0.5 h at −78 °C. After a pH 7 phosphate buffer solution (0.1 M, 6 mL) and a saturated NaCl solution (50 mL) were added, the products were extracted with EtOAc (100 mL). The organic layer was washed with a saturated NaCl solution (30 mL × 2), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residual brown solid was subjected to GPC with $(CH_2Cl)_2$ as the eluant and recrystallized from toluene–hexane to give pure IDTPY as red microcrystals (209 mg, 28%). mp 193–194 °C; R_f = 0.59 (hexane:CH_2Cl_2 = 4:1); ^{1}H NMR δ 5.64 (1H, d, J = 10 Hz), 5.82 (1H, d, J = 10 Hz), 6.04 (1H, d, J = 7.7 Hz), 6.11 (1H, d, J = 7.7 Hz), 6.20 (1H, d, J = 7.7 Hz), 6.28 (1H, d, J = 7.7 Hz), 6.40 (1H, s); EIMS *m/z* (rel intensity) 366 (M^+; 35), 239 ($M^+ - I$; 100); Anal. Calcd for $C_{14}H_7S_2I$: C, 45.91; H, 1.93%. Found: C, 46.14; H, 1.89%.

2,7-Diiodo-1,6-dithiapyrene (DIDTPY). A solution of DTPY (300 mg, 1.25 mmol) in THF (30 mL) was cooled at −78 °C under an Ar atmosphere. To this solution was the added *n*-BuLi (1.5 M hexane solution, 1.7 mL, 2.5 mmol) over 5 min; the reaction mixture was then warmed up to −20 °C over 2 h. After being cooled at −78 °C, perfluorohexyl iodide (0.55 mL, 2.5 mmol) was added, and then the reaction mixture was warmed up to −15 °C over 2 h. A pH 7 phosphate buffer solution (0.1 M, 10 mL) was added, and the generated pure DIDTPY (316 mg, 52%) was obtained by filtration of the reaction mixture. To the filtrate was added a saturated NaCl solution (20 mL); the products were then extracted with EtOAc (60 mL). The organic layer was washed with a saturated NaCl solution and water, successively, and then dried over Na_2SO_4, filtered and concentrated under reduced pressure. A residual brownish-orange solid was reprecipitated from EtOAc–hexane to give DIDTPY as a brownish-orange powder (180 mg, 30%). mp 218–221 °C (decomp); R_f = 0.61 (hexane:CH_2Cl_2 = 4:1); ^{1}H NMR δ 6.11 (2H, d, J = 7.8 Hz), 6.24 (2H, d, J = 7.8 Hz), 6.47 (2H, s); EIMS *m/z* (rel intensity) 492 (M^+; 100); Anal. Calcd for $C_{14}H_6S_2I_2$: C, 34.17; H, 1.23%. Found: C, 34.47; H, 1.53%.

X-ray Analysis of DIDTPY. Crystal data: Formula $C_{14}H_6S_2I_2$, monoclinic, a = 10.6213(7), b = 4.1993(4), c = 15.3026(16) Å, β = 101.633(5)°, V = 668.51(10) Å^3, space group $P2_1/c$, Z = 2, D_{calcd} = 2.445 g cm^{-3}, μ = 49.93 cm^{-1}. An orange plate crystal (0.50 × 0.20 × 0.01 mm) of DIDTPY for X-ray analysis was obtained by slow evaporation of its $(CH_2Cl)_2$–benzene solution. A crystallographic measurement was made on a Rigaku RAXIS-RAPID Imaging Plate with graphite monochromated Mo Kα (λ = 0.71069 Å) radiation at −73 °C. The structures were determined by a direct method using SHELXS-86. The extent of disorder was determined by refining the site occupancies; the S^1 and C^3 sites were at averaged positions with 13 electrons at S^1 and 9 electrons at C^3. The final R factor was 0.044 (R_w = 0.132) for 1181 observed reflections with $I > 2\sigma(I)$. Crystallographic data have been deposited at the CCDC (190601), 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation.

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References

1 "Organic Superconductors" 2nd ed by T. Ishiguro, K. Yamaji, and G. Saito, Springer-Velrag, Berlin, Tokyo (1998).

2 a) N. Thorup, G. Rindorf, C. S. Jacobsen, K. Bechgaard, I. Johannsen, and K. Mortensen, *Mol. Cryst. Liq. Cryst.*, **120**, 349 (1985). b) B. D. Tilak, *Proc. Indian Acad. Sci., Sect. A*, **33**, 71 (1951).

3 a) K. Nakasuji, H. Kubota, T. Kotani, I. Murata, G. Saito, T. Enoki, K. Imaeda, H. Inokuchi, M. Honda, C. Katayama, and J. Tanaka, *J. Am. Chem. Soc.*, **108**, 3460 (1986). b) K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto, and J. Tanaka, *J. Am. Chem. Soc.*, **109**, 6970 (1987).

4 a) H. M. Yamamoto, R. Maeda, J. Yamaura, and R. Kato, *J. Mater. Chem.*, **11**, 1034 (2001). b) T. Imakubo, N. Tajima, M. Tamura, R. Kato, Y. Nishio, and K. Kajita, *J. Mater. Chem.*, **12**, 159 (2002).

5 The oxidation potentials and ΔE of IDTPY, DIDTPY, DTPY and TTF were as follows: E^{ox1}, +0.049, +0.130, −0.036, −0.104; E^{ox2}, +0.347, +0.419, +0.276, +0.149; ΔE, 0.298, 0.289, 0.310, 0.253; conditions, see Experimental.

6 C. Wang, A. Ellern, V. Khodorkovsky, J. Bernstein, and J. Y. Becker, *J. Chem. Soc., Chem. Commun.*, **1994**, 983.