Synthesis and Properties of 1,7-Dithiaperylene: a New Peri-condensed Weitz-type Donor

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1,7-Dithiaperylene, a new peri-condensed Weitz-type donor, has been synthesized from anthracene-9,10-dithiolate anion through six steps and characterized; some charge transfer complexes of this new donor show high electrical conductivities.

Multi-stage redox systems are the essential components to explore organic molecular conductors with high electrical conductivities.[1] We have recently reported the synthesis and physical properties of peri-condensed Weitz-type donors, 3,10-dithiaperylene (3,10-DTPR),[2] 1,6-dithiapyrene (1,6-DTPY)[2,3] and their derivatives,[4] which produced some highly conducting charge transfer complexes. In order to search for new organic conductors, it is important to correlate solid state properties of complexes with molecular properties of donor and acceptor. Symmetry of a molecule is an important factor for such correlations, although details are still obscure. We now report the synthesis and some properties of a new isomer of DTPR with C_{2h} molecular symmetry, 1,7-dithiaperylene (1,7-DTPR).

A reasonable starting material for the synthesis† is anthracene-9,10-dithiolate anion whose convenient generation has recently been reported.[5] Reduction of the polysulphide (**1**) with $NaBH_4$ according to the procedure, followed by treatment of the resulting dithiolate with chloroacetic acid gave the diacid (**2**) (89% yield). Chlorination of (**2**) with PCl_5 followed by Friedel–Crafts cyclisation with $AlCl_3$ in CH_2Cl_2 afforded the diketone having the desired skeleton (**3**) (90%). The diketone was reduced to the diol (**4**) with $NaBH_4$ in CH_2Cl_2/EtOH and then methylated with methyl iodide in NaOH/DMSO (DMSO = dimethyl sulphoxide) to give the diether (**5**) (74%). The final conversion of (**5**) into 1,7-DTPR was achieved by treatment with $(Pr^i)_2NLi$ in tetrahydrofuran (THF) (61%), though the direct conversions of (**3**) or (**4**) into 1,7-DTPR were unsuccessful. As dark reddish violet needles, 1,7-DTPR showed m.p. 245 °C (decomp.); ^1H n.m.r. [400 MHz $CS_2/(CD_3)_2CO$] δ 6.52 (2H, d, *J* 10.1 Hz), 6.68 (2H, dd, *J* 10.1, 0.5 Hz), 6.77 (2H, ddd, *J* 6.9, 1.0, 0.5 Hz), 7.14 (2H, dd, *J* 8.9, 6.9, Hz), 7.33 (2H, dd, *J* 8.9, 1.0 Hz); m.s. *m/z*

Table 1. Selected electrical conductivities of 1,7-DTPR complexes.[a]

	$(TCNQ)_{0.5}$[b]	$(DDQ)_1$[c]	$I_{3.5}$[d]	$(NO_3)_x$[e]
σ/S cm^{-1}	7.7×10^{-1} [f]	1.4×10^{-6} [f]	1.4×10^{-6} [f]	1.4×10 [g]
E_a/eV[h]	0.02	0.14	0.09	0.07

[a] CT complexes were obtained at room temperature in 30—50% yields. [b] Slow evaporation of MeCN solution. [c] Mixing CH_2Cl_2 solutions. [d] Mixing CH_2Cl_2 solutions of the donor and I_2. [e] Electrocrystallisation at 4 μA in Cl_2CHCH_2Cl solution of the donor and Bu_4NNO_3. [f] Compressed pellet measurement. [g] Single crystal measurement. [h] E_a = activation energy.

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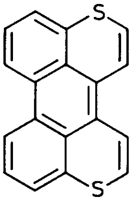
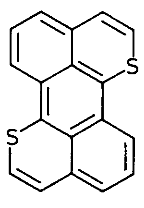
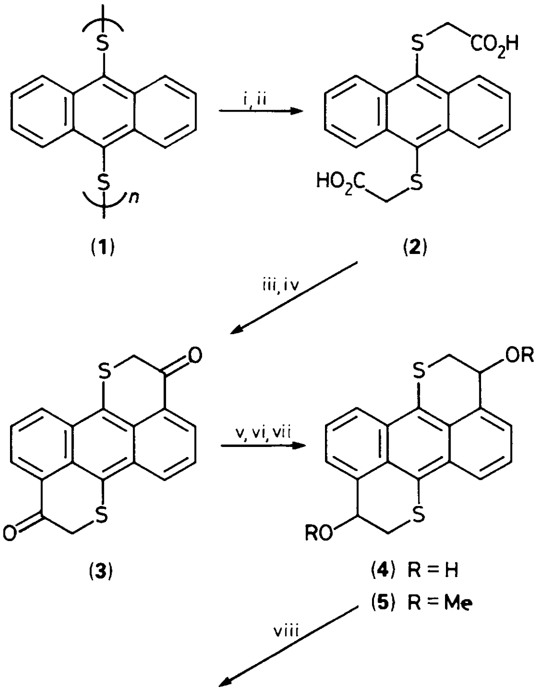
† All new compounds described here gave correct spectroscopic data, and (**2**), (**5**), and 1,7-DTPR gave satisfactory elemental analysis. Selected physical data: (**2**) yellow needles; m.p. 236—237 °C; i.r. ν_{max} 1695 cm^{-1}; m.s. *m/z* 358 (M^+, 54%). (**3**) red crystals; m.p. 180 °C (decomp.); ^1H n.m.r. δ 4.18 (4H, s), 7.91 (2H, dd, *J* 6.5, 8.5 Hz), 8.31 (2H, dd, *J* 6.5, 1.5 Hz), 8.88 (2H, dd, *J* 8.5, 1.5 Hz); i.r. $\nu_{max.}$ 1670 cm^{-1}; m.s. *m/z* 322 (M^+, 100%). (**4**) as a mixture of possible stereo isomers; m.p. 209—213 °C; ^1H n.m.r. δ 3.12—3.54 (4H, m), 4.80—5.10 (2H, br. s), 5.20—5.42 (2H, m), 7.59 (2H, dd, *J* 8.5, 6.5 Hz), 7.84 (2H, dd, *J* 6.5, 2.0 Hz), 8.39 (2H, dd, *J* 8.5, 2.0 Hz); m.s. *m/z* 326 (M^+, 100%). (**5**) orange prisms (m.p. 212—214 °C) and dark orange oil; data for crystals; ^1H n.m.r. δ 3.54 (6H, s), 3.22—3.58 (4H, m), 4.79—4.89 (2H, m), 7.40—7.61 (4H, m), 8.37—8.55 (2H, m); m.s. *m/z* 354 (M^+, 100%).



3,10-DTPR



1,7-DTPR



Scheme 1. *Reagents*: i, $NaBH_4$, THF, room temp., overnight; ii, $ClCH_2CO_2H$, 6 h; iii, PCl_5, CH_2Cl_2, reflux, 45 min; iv, $AlCl_3$, −78 to −15 °C, 6 h; v, $NaBH_4$, CH_2Cl_2, EtOH, room temp., 3 h; vi, KOH, DMSO, room temp., 15 min; vii, MeI, 15 min; viii, $(Pr^i)_2NLi$, THF, −78 °C, 30 min.

(relative intensity) 290 (M^+, 100%); u.v. λ_{max} (CH_2Cl_2) 366sh (log ε 3.67), 382 (3.87), 483 nm (3.83). 1,7-DTPR is stable in the solid state, but decomposes slowly in solution.

Cyclic voltammetry of 1,7-DTPR (in benzonitrile, 0.1 M Et_4NClO_4, Pt working electrode, 100 mV s^{-1}) shows two-stage redox behaviour with relatively low oxidation potentials at +0.39 and +0.82 V [*vs.* standard calomel electrode (S.C.E.)]. The corresponding values for 3,10-DTPR measured under identical conditions are +0.49 and +0.87 V.[3] In accord with the low oxidation potentials of 1,7-DTPR, its dicationic species could be generated simply by dissolving in concentrated D_2SO_4 as a dark blue violet solution; ^1H n.m.r. (500 MHz) 8.56 (2H, t-like, J 8 Hz), 8.72 (2H, d, J 8.5 Hz), 9.00 (2H, d, J 9.2 Hz), 9.27 (2H, d, J 9.2 Hz), 9.35 (2H, d, J 7.8 Hz).

Charge transfer (CT) complexes of 1,7-DTPR with various organic and inorganic acceptors were prepared as preliminary experiments. Some selected electrical conductivity data are summarized in Table 1. 1,7-DTPR produced CT complexes more easily than 3,10-DTPR. In addition, the NO_3 complex is the first example of highly conducting CT complexes of peri-condensed Weitz-type donors with inorganic counter ions except iodine.[2,4] Efforts to grow single crystals suitable for *X*-ray crystal structure analysis and to clarify the characteristics related with molecular symmetry of the new donor are now in progress.

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References

1 J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 519; K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 875.

2 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.*, 1986, **108**, 3460.

3 B. D. Tilak, *Proc. Indian Acad. Sci., Sect. A*, 1951, **33**, 71; K. Bechgaard, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 81.

4 K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto, and J. Tanaka, *J. Am. Chem. Soc.*, 1987, **109**, 6970.

5 M. V. Lakshmikantham, M. Levinson, M. Menachery, and M. P. Cava, *J. Org. Chem.*, 1986, **51**, 411.