Synthesis and Properties of 3,9-Dithiaperylene: A Third Isomer of Peri-Condensed Weitz-Type Donors based on the Perylene Skeleton

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3,9-Dithiaperylene (3,9-DTPR), a third isomer of peri-condensed Weitz-type donors based on the perylene skeleton, has been synthesized from 1,5-dichloroanthracene in four steps using titanium-induced dicarbonyl cyclization as a key step, and its physical properties have been compared with those of 1,7- and 3,10-DTPRs.

Peri-condensed Weitz-type donors, dithiaperylene (DTPR) and dithiapyrene (DTPY) have produced a variety of organic conductors ranging from semiconductors to molecular metals.[1–3] DTPR has four reasonably stable isomers, two with C_{2h} symmetry and two with C_{2v} symmetry. We have already reported the synthesis of the 3,10-(C_{2v})[1] and 1,7-isomers (C_{2h}).[4] In order to investigate the influence of the positions of the sulphur atoms on the electronic properties, we prepared the third isomer 3,9-DTPR, with C_{2h} symmetry, and compared the oxidation potentials and the lowest electronic transition energies of the three isomers.

Titanium-induced cyclisation of quinone-aldehyde (**4**) was employed as a key step in constructing the basic skeleton of 3,9-DTPR, the dihydro-DTPR (**5**).[†] Reduction of thiocyanatoacetaldehyde diethyl acetal (**1**) with $NaBH_4$ generated an ethanol solution of sulphidoacetaldehyde diethyl acetal *in situ*. To this solution was added 1,5-dichloroanthraquinone (**2**) to give the dithio-acetal (**3**) as orange needles (88% yield). Hydrolysis of (**3**) with concentrated HCl in a mixture of acetone and dichloromethane gave the dicarbothioaldehyde (**4**) as yellow needles (96%). Intramolecular dicarbonyl-coupling of (**4**) with $TiCl_4$–Zn[5] in tetrahydofuran (THF) at room temperature afforded the dihydro-DTPR (**5**) as colourless plates (11%). This reaction step had to be improved to overcome the sparing solubility of (**4**) and the poor reproducibility in large scale reactions. Treatment of (**5**) with *N*-chlorosuccininide (NCS) provided the target 3,9-DTPR as dark violet needles (28%): m.p. 255 °C in a sealed tube; ^1H NMR (400 MHz, CS_2/CD_2Cl_2 with trace of NEt_3),δ 6.36 (2H, d, *J* 10.4 Hz), 6.88 (2H, d, *J* 7.2 Hz), 7.00 (2H, dd, *J* 7.2, 8.8 Hz),

Table 1. Selected properties for 3,9-, 1,7-, and 3,10-DTPR.

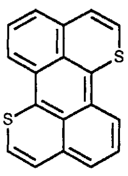
DTPR	E_1^{ox} [a] /V	$\lambda_{max}(D)$ [b] /10^3 cm^{-1}	$\lambda_{max}(D^{2+})$ [c] /10^3 cm^{-1}	$\varepsilon(D)$ [d] /eV	$\varepsilon(D^{2+})$ [e] /eV
3,9-	0.30	16.9	18.7	−7.61	−15.85
1,7-	0.39	18.0	16.7	−7.62	−15.71
3,10-	0.49	24.0	14.9	−7.87	−15.67
1,12-				−7.88	−15.58

[a] First oxidation potentials (*vs.* standard calomel electrode). [b] Transition energies of neutral species. [c] Transition energies of dicationic species. [d] Calculated (MNDO) HOMO energies of neutral species. [e] Calculated (MNDO) HOMO energies of dicationic species.

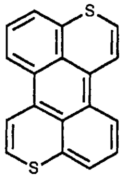
[†] All new compounds described gave satisfactory elemental analyses and spectroscopic data. *Selected physical data* for (**3**): orange needles; m.p. 215 °C; ^1H NMR, δ 1.22 (12H, t, *J* 7.0 Hz), 3.26 (4H, d, *J* 5.2 Hz), 3.44—3.94 (8H, m), 4.83 (2H, t, *J* 5.2 Hz), 7.56—7.86 (4H, m), 8.16 (2H, dd, *J* 6.5, 2.2 Hz); IR, ν_{max} 1650 cm^{-1}; MS, *m/z* 504 (M^+, 20%).

(**4**): yellow needles; m.p. 247 °C; ^1H NMR, δ 4.15 (4H, d, *J* 2.0 Hz), 7.64—8.14 (6H, m), 9.64 (2H, t, *J* 2.0 Hz); IR, ν_{max} 1715, 1650 cm^{-1}; MS, *m/z* 356 (M^+, 73%).

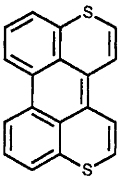
(**5**): colourless plates; m.p. 189—191 °C; ^1H NMR, δ 3.50 (4H, d, *J* 5.8 Hz), 6.56 (2H, t, *J* 5.8 Hz), 7.12—7.64 (6H, m); MS, *m/z* 292 (M^+, 100%).



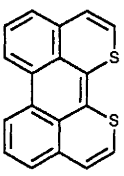
1, 7 - DTPR



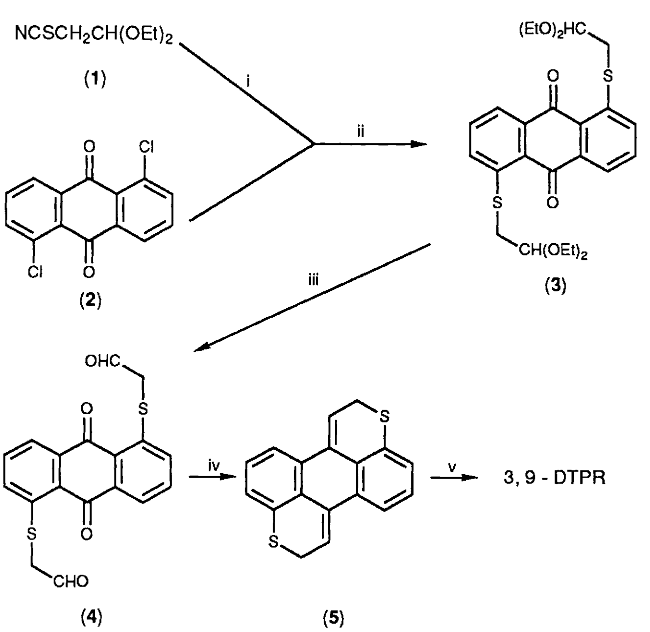
3, 9 - DTPR



3, 10 - DTPR



1, 12 - DTPR



Scheme 1. *Reagents and conditions*: i, $NaBH_4$, EtOH, room temp., 3 h; ii, reflux, 17 h; iii, conc. HCl, CH_2Cl_2, Me_2CO, room temp., 1 h; iv, $TiCl_4$, Zn, THF, room temp., 2 h, 10% aqueous Na_2CO_3, 1 h; v, NCS, CH_2Cl_2, room temp., 15 min.

7.07 (2H, d, *J* 10.4 Hz), 7.44 (2H, d, *J* 8.8 Hz); MS, *m/z* (relative intensity) 290 (M^+, 100%); UV, λ_{max} (CH_2Cl_2) 386sh (log ε 3.68), 409 (3.88), 553 (4.06), 593 nm (4.07).

Comparison of the physical properties of the three isomers of DTPRs provides good correlation between their electronic and structural characteristics (Table 1). The oxidation potentials (E_1^{ox}) and the lowest electronic transition energies [λ_{max}(D)] of the neutral species increase in the order 3,9- < 1,7- < 3,10-DTPR. The E_1^{ox} data indicate that the HOMO energy levels of the three donors decrease in that order. Such behaviour of the HOMOs is consistent with the energy change in λ_{max}(D), if the HOMO energy levels predominantly affect the transition energies. Thus, the donor with a lower HOMO (a lower oxidation potential) shows the higher transition energy in the neutral state. Interestingly, the lowest electronic transition energies [$\lambda_{max}(D^{2+})$] of the dicationic species decrease in the order above. MNDO calculations for the HOMO energies of both species [ε(D) and ε(D^{2+}) in Table 1] are consistent with the behaviour of the experimental data in Table 1, though there are some discrepancies between E_1^{ox} and ε(D) of 3,9- and 1,7-DTPR. This can be attributed partly to a solvent effect which stabilizes the oxidized form of the 3,9- to a larger extent than the 1,7-isomer and therefore lowers its oxidation potential. 3,9- and 1,7-DTPR possess higher HOMOs than 3,10-DTPR. This feature coincides with the structural contribution of the anthracene moiety in the C_{2h} isomers, which raises their HOMOs to a larger extent than does the phenanthrene moiety in the C_{2v} isomer. Therefore, the electronic properties of unknown C_{2v} isomer, 1,12-DTPR, can be predicted to bear a close resemblance to those of the 3,10-isomer. Although preliminary studies for charge transfer complexes of 3,9-DTPR are in progress, it should be noted that a single crystal of the iodine complex showed a relatively high conductivity (7 S cm^{-1}).

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