

Dinaphtho[2',3':5,6][1,4]dithiino[2,3-*b*:2,3-*e*]pyridine, its 16-butyl derivative and dinaphtho[2',3':5,6][1,4]dioxo[2,3-*b*:2,3-*e*]pyridine: novel heterocycles as electron donor compounds

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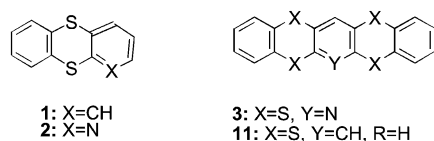
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Dinaphtho[2',3':5,6][1,4]dithiino[2,3-*b*:2,3-*e*]pyridine (**4a**), its 16-butyl derivative (**4b**), and dinaphtho[2',3':5,6][1,4]dioxo[2,3-*b*:2,3-*e*]pyridine (**5**) have been prepared and fully characterized. The electrochemical properties of **4a**, **4b** and **5** have been studied by cyclic voltammetry in CH₂Cl₂:trifluoroacetic acid (1:1); in agreement with their donor character, they exhibit a first reversible oxidation wave to their radical cations with very similar potential peak values and a second irreversible wave to their dications, the lowest potential peak value of this second oxidation corresponding to **5**. Their radical cations, generated by oxidation of the parent compounds, are relatively stable and have been analyzed in liquid solution by electron paramagnetic resonance (EPR). Spin density distributions in the SOMO have been calculated by the semiempirical MNDO method. Electronic spectra of **4a** and **4b** in trifluoroacetic acid show peaks at 417 and 401 nm, respectively, and in the presence of thallium(III) trifluoroacetate two characteristic peaks at λ_{\max} 411 and 868 nm for **4a**^{•+}, and at 411 and 872 nm for **4b**^{•+}. X-Ray analysis of **4b** shows a molecular structure with a stable chair-shaped conformation with interplanar angles between naphthalenes and the pyridine ring of 139.0(1) and 146.4(1)°.

Thianthrene (**1**) (Scheme 1) and substituted thianthrenes give strongly coloured solutions when dissolved in concentrated sulfuric acid¹ or in other oxidant systems² due to the formation of persistent radical cations which have been detected by electron paramagnetic resonance (EPR) spectroscopy. Under aprotic conditions **1**^{•+} has been isolated as a radical cation salt with AlCl₄[−] as a counter ion and its crystal structure analyzed by X-ray diffraction.^{2d} The bent molecular structure of **1**³ is considerably flattened upon oxidation to **1**^{•+}.^{2d} As a consequence of these properties, thianthrenes have gained new interest as electron donor components in charge transfer complexes.^{2d,4} Oxidation of 1-azathianthrene (**2**) showed simi-

lar behaviour in EPR, the splittings in the spectrum of its radical cation are practically equal to those found in **1**^{•+} suggesting that the SOMO does not show any estimable perturbation in spite of the asymmetry of the molecule.⁵ The stability of these charged species is due to delocalization of the unpaired electron over the whole system. Expanding the π system to multi-ring molecules, we have also reported the new heterocycle di[1,4]benzodithiino[2,3-*b*:2,3-*e*]pyridine (**3**) (Scheme 1),^{5,6} a stable chair-shaped conformation with interplanar angles between phenyls and pyridine rings (when R = H in **3**) of 135°. In the EPR spectrum of **3**^{•+}, the splitting of the electron spin with hydrogens was rationalized by complete planarization of the molecule as a consequence of the removal of one electron.

Searching for new π -electron systems with electron donating properties, now we report the synthesis and electrochemical behaviour of three novel heptacenes, two tetrathioheptacenes, dinaphtho[2',3':5,6][1,4]dithiino[2,3-*b*:2,3-*e*]pyridine (**4a**) and its 16-butyl derivative (**4b**), and one tetraoxoheptacene, dinaphtho[2',3':5,6][1,4]dioxo[2,3-*b*:2,3-*e*]pyridine (**5**). The EPR spectra of their radical cations have been recorded. In addition, we also report the molecular structure of **4b** and compare it with that of a new tetraoxopentacene,



Scheme 1

di[1,4]benzodioxino[2,3-*b*:2,3-*e*]pyridine (**6**), due to the difficulties of obtaining good crystals for X-ray analysis from **5**.

Results and discussion

The heptacenes **4a**, **4b** and **5**, and pentacene **6** were prepared as shown in Scheme 2, starting from 2,3,5,6-tetrachloropyridine and using the same methodology reported for **3**.^{5–7} In the synthesis of intermediates 2,3-dichloronaphtho[2',3':5,6]-[1,4]dithiino[2,3-*b*]pyridines (**7a**) and (**7b**), and 2,3-dichloro-[1,4]benzodioxino[2,3-*b*]pyridine (**8**), small quantities of by-products **9a**, **9b**, and **10** were also obtained.

Due to the poor solubility of **4a** in organic solvents, only good crystals for X-ray analysis were obtained from azatetrathiaheptacene **4b**. Its molecular structure shows a general chair-shaped conformation with interplanar angles between naphthalenes and pyridine of 139.0(1)° and 146.4(1)°, slightly larger than the angles between benzenes and pyridine in azatetrathiapentacene **3** (135°)⁵ and between peripheral and central benzenes in tetrathiapentacene **11** (131.5°)⁸ (Scheme 1). Also due to difficulties with carrying out an X-ray analysis of azatetraoxoheptacene **5**, we have studied the molecular structure of the azatetraoxopentacene **6** and compared it with that of **4b** as shown in Fig. 1 (the butyl substituent has been omitted from the structure of **4b** for clarity). The structure of **6** confirms the planar geometry of the stable conformation (Fig. 1b) with dihedral angles between benzenes and pyridine of 179.17(1)° and 173.84(1)°. This result suggests that the structure of **5** should also be planar.

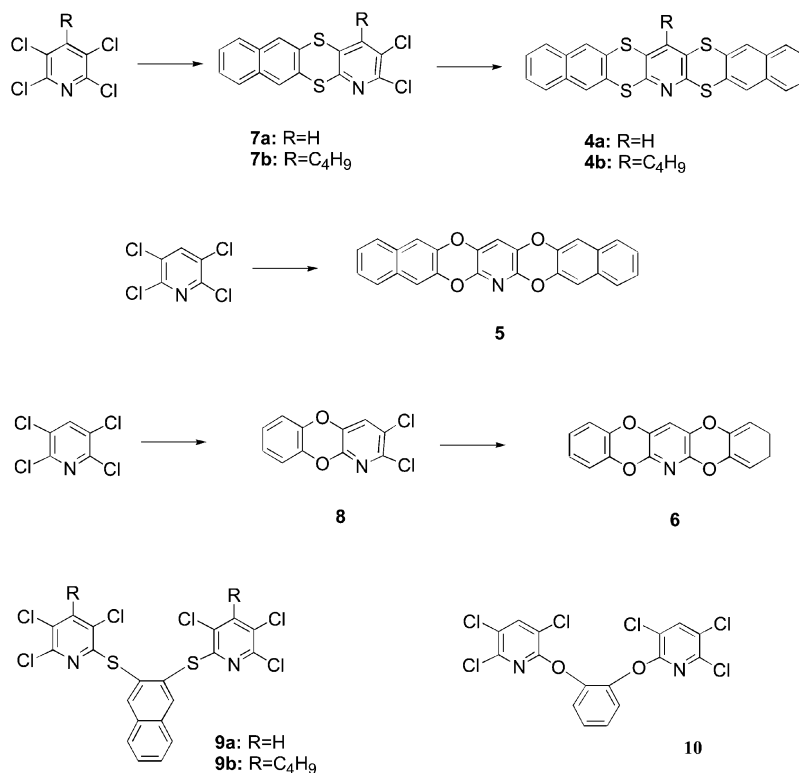
Quantum mechanical calculations (MNDO method)⁹ for **4a** and **5** were performed to investigate the influence of the heteroatoms on the intrinsic conformational preferences of these compounds. For **4a**, the chair-shaped and the boat-shaped conformations were isoenergetic, the planar arrangement being only 1.25 kJ mol^{–1} higher in energy. These results indicate that the two folded conformations are equally preferred, the barrier between them being almost negligible. According

to these results, the chair-shaped conformation observed for **4b** seems to be favored by packing interactions.

A completely different situation was found for **5**. In this case, the lowest energy conformation corresponds to the planar arrangement, the chair-shaped and boat-shaped conformations being less favored by 2.93 and 0.84 kJ mol^{–1}, respectively. These theoretical results for **5** and the observed results for the structure of **6** indicate that in the tetraoxo species the planar arrangement is an intrinsic conformational property and not an effect of the packing interactions.

When degassed solutions of **4a** (10^{–3} M) in benzene containing trifluoroacetic acid (TFA) (10% v/v) were treated at room temperature with thallium(III) trifluoroacetate (TTA) an EPR spectrum with a multiplet of peaks was obtained. Fig. 2a shows the spectrum of **4a**^{•+} and its simulation¹² using the hyperfine splitting (hfs) values showed in Table 1. Under conditions of over-modulation and high amplification the hfs due to the coupling of the electron with naturally abundant ³³S (0.76%) were observed as two multiplet satellite lines ($a = 4.7$ G) which corresponds to the $M_S = \pm 3/2$ groups of the quartet [$I(^{33}\text{S}) = 3/2$], the two $M_S = \pm 1/2$ groups being lost into the very intense central multiplet. Likewise, the spectrum of **4b**^{•+} appeared as a multiplet when degassed solutions of **4b** in CH₂Cl₂–TFA (1:1) were irradiated with a UV lamp at low temperature (–10 °C). The coupling values in **4b**^{•+} (Table 1) are similar to those in **4a**^{•+}. The recorded spectrum when tetraoxoheptacene **5** in TFA was treated with TTA (Fig. 2b) consisted of a very strong multiplet centered at lower *g*-value with the hfs values showed in Table 1. The assignment of the hfs values to the different hydrogens of the radical cation species in Table 1 has been carried out by considering our previous work on azatetrathiopentacenes.^{5,6}

A comparative analysis of the spectra of **4a**^{•+} and **4b**^{•+}, with the spectrum of **5**^{•+} shows a clear difference in the electron coupling with the nitrogen and the hydrogen of the pyridine ring, this coupling being higher in **5**^{•+}. On the other hand, the high values of coupling with the sulfur atoms in **4a**^{•+} and **4b**^{•+} suggest that the major spin density in these radical



Scheme 2

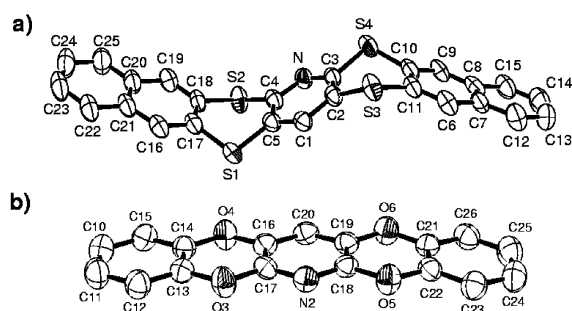


Fig. 1 (a) Molecular structure of **4b** (butyl substituent has been omitted to clarify the difference in the dihedral angles between the structures of **4b** and **6**). (b) Molecular structure of **6**.

cations resides in these heteroatoms and, consequently, they show greater g values than 5^{+} (Table 1).

All these results are in good agreement with theoretical calculations.⁹ Thus, complete geometry optimization of $4a^{+}$ led to an almost planar conformation. The interplanar angles found for this minimum were 174.6 and 175.2°, the reduction with respect to the neutral compound being about 24°. Fig. 3 shows atomic coefficients in the SOMO computed for $4a^{+}$ and 5^{+} . The orbital is mainly located in the S-containing rings in $4a^{+}$, while in 5^{+} the orbital is distributed along the whole molecule.

Cyclic voltammogram of **4a**, **4b** and **5** in CH_2Cl_2 :TFA (1:1) containing tetrabutylammonium perchlorate exhibited at a scan rate (v) ranging from 20 mV s^{-1} to 200 mV s^{-1} and at 25 °C a quasi-reversible redox pair O_1/R_1 with anodic peak potentials (E_a^1) and standard potentials (E°) as depicted in Table 2. These couples are ascribed to the equilibrium between neutral species and their radical cations and they are indicative of the stability of these radical cations in the medium. When the scan potential was increased a second oxidation peak O_2 appeared at $v = 200 \text{ mV s}^{-1}$ with anodic peak potentials (E_a^2) also shown in Table 2. These second irreversible processes should correspond to the oxidation of the radical cations to their dications which are not stable in the medium. No significant differences were observed in cyclic voltammetry

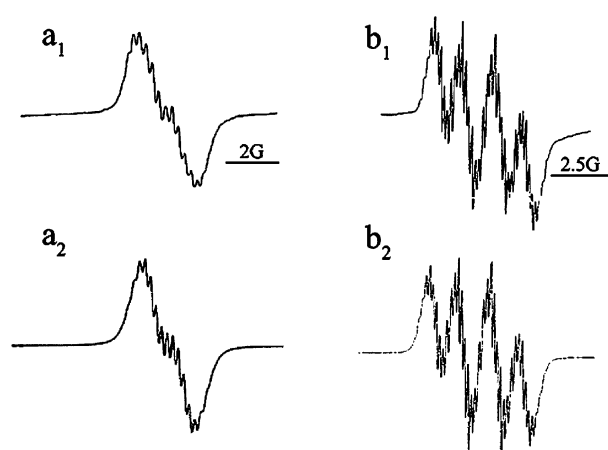
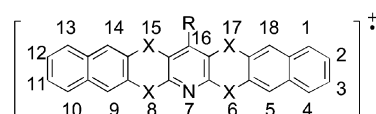


Fig. 2 (a) EPR spectra of dinaphtho[2,3':5,6][1,4]dithiino[2,3-b:2,3-e]pyridine radical cation ($4a^{+}$) generated from the neutral compound in benzene containing TFA (10% v/v) with thallium(III) trifluoroacetate at rt: (a₁) experimental, (a₂) simulated spectrum using the hfs values given in the text. (b) EPR spectra of dinaphtho[2,3':5,6][1,4]dioxino[2,3-b:2,3-e]pyridine radical cation (5^{+}) generated from the neutral compound in TFA with thallium(III) trifluoroacetate at rt: (b₁) experimental, (b₂) simulated spectrum using the hfs values given in the text.

(CV) among the first anodic peak potentials of tetrathioheptacenes **4a**, **4b** and tetraoxoheptacene **5**, but the second anodic potential of **5** is shifted to less positive potentials relative to those of **4a** and **4b**. Values of ΔE_a (Table 2) are a measure of the intramolecular coulombic repulsion resulting from two positive charges in the molecule. The lowest value of ΔE_a in **5** is in agreement with the fact that charges in 5^{2+} are further apart from each other than in $4a^{2+}$ and $4b^{2+}$. CV of **4b** ($\sim 10^{-3}$ M) in carefully dried CH_2Cl_2 (twice distilled from phosphorus pentoxide) with alumina suspended in the solution and containing 0.1 M tetrabutylammonium hexafluorophosphate at v ranging from 20 mV s^{-1} to 200 mV s^{-1} exhibited one well-defined but irreversible oxidation peak O_1 , with an anodic peak potential $E_p^a(\text{O}_1) = 1.24 \text{ V vs. SCE}$ at 100 mV s^{-1} . The loss of reversibility of this process may be attributed to an

Table 1 Experimental hyperfine coupling constants (a) in Gauss, calculated spin densities in parentheses and other EPR parameters for radical cations $4a^{+}$, $4b^{+}$, and 5^{+}



$4a^{+}$: X=S, R=H
 $4b^{+}$: X=S, R=C₄H₉
 5^{+} : X=O, R=H

	a_H	a_N	a_S	g	ΔH_{pp}
$4a^{+}$	0.46(0.031)(1H) ^a 0.24(0.041)(4H) ^b 0.24(0.048)(4H) ^c < 0.1(0.040)(4H)	0.82(0.090)(1N)	4.7(0.136)(4S)	2.0077	0.2
$4b^{+}$	0.42(2H) ^a 0.21(8H) ^{b,c} < 0.1(4H) ^d	0.79(1N)	4.6(4S)	2.0079	0.18
5^{+}	1.0(0.041)(1H) ^a 0.31(0.036)(4H) ^b 0.18(0.036)(4H) ^c	1.48(0.095)(1N)		2.0036	0.11

^a Hydrogens in position 16. ^b Hydrogens in positions 5, 9, 14, and 18. ^c Hydrogens in positions 2, 3, 11, and 12. ^d Hydrogens in positions 1, 4, 10, and 13.

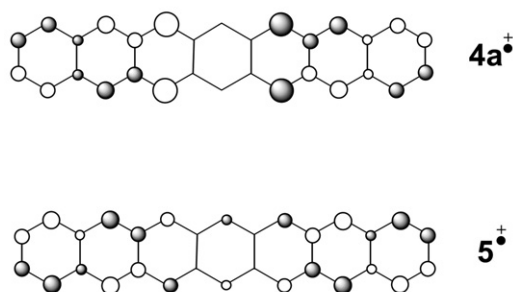


Fig. 3 Atomic coefficients in the SOMO computed for $4a^{\bullet+}$ and $5^{\bullet+}$.

ion-pairing effect based on the irreversible interaction of the hexafluorophosphate counterion with the radical cation.

Absorption peaks in the visible region for the electronic spectra of solutions of **4a** and **4b** in TFA were at λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 417 (9900) and 401 (11450), respectively. In the presence of TTA, absorption peaks appeared at λ_{\max} 411 and 868 nm, and at 411 and 872 nm, attributed to $4a^{\bullet+}$ and $4b^{\bullet+}$, respectively. From the decay of the intensities of these absorbance peaks with time, the half lifetimes of both charged species could be estimated to be $\theta \sim 30$ min. We have no satisfactory results from **5** due to its poor solubility. In the presence of SbCl_5 solutions of **4b** in CHCl_3 yielded a yellow and stable salt characterized as $4b^{2+} \cdot 2\text{SbCl}_6^-$. All attempts to get crystals for an X-ray analysis of this salt proved to be unsuccessful.

Attempts to obtain adducts from dilute solutions of **4a**, **4b** and **5**, with a good electron acceptor such as 2,3-dichloro-5,6-dicyanoquinone (DDQ), were not successful due to the low solubilities of these compounds in most organic solvents; however, the electronic spectrum of mixtures of **4b** and DDQ showed a very weak and broad band at $\lambda_{\max} = 655$ nm, characteristic of the presence of a charge transfer complex. Work is now in progress to introduce substituents in these new heterocycles to improve their solubilities.

Experimental

Melting points were obtained by using a K f ler microscope ‘‘Reichert’’ and are uncorrected. The IR spectra were recorded with a FT-IR ‘‘Bomem-Michalson’’ model MB-120 spectrophotometer. ^1H NMR spectra were determined at 200 MHz and 300 MHz with Varian Gemini 200HC and XL-300 spectrometers, respectively. ^{13}C NMR spectra at 75 MHz were obtained with a Varian Gemini 300HC spectrometer. The electronic spectra were recorded with a Perkin-Elmer Lambda Array 3840 Spectrometer coupled with a Perkin-Elmer 7300 computer. DMF was used as received. CHCl_3 was dried over calcium chloride and distilled. Naphthalene-2,3-dithiol [^1H NMR (300 MHz, CDCl_3) δ 7.90 (s, 2H), 7.66 (dd, 2H, $J = 6.0$ Hz, $J' = 3.3$ Hz), 7.42 (dd, 2H, $J = 6.0$ Hz, $J' = 3.3$ Hz), 3.88 (s, 2H)] was prepared from 1-butanethiol and 2,3-dibromonaphthalene as described.¹³

Electrochemical measurements

The cyclic voltammetric (CV) experiments were carried out in a three-electrode cell. A platinum (Pt) disk with an area of

0.093 cm^2 was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a calomel electrode (SSCE) with a NaCl-saturated aqueous solution, submerged in a salt bridge of the same electrolyte, which was separated from the cell by a Vycor membrane. Solutions of **4b** ($\sim 10^{-3}$ M) in CH_2Cl_2 or in $\text{CH}_2\text{Cl}_2\text{:TFA}$ (1:1) containing tetrabutylammonium perchlorate (0.1 M) as background electrolyte were studied by CV. The volume of all test solutions was 25 mL. The CV measurements were performed with a standard equipment consisting of a PAR 175 universal programmer, an Amel 551 potentiostat, and a Phillips 8043 X–Y recorder. Cyclic voltammograms of all solutions were recorded with scan rates (v) ranging from 20 to 200 mV s^{-1} .

EPR experiments

EPR spectra were recorded with a Varian E-109 Spectrometer working in the X band using a Varian E-257 temperature controller. Solutions ($\sim 10^{-3}$ M) of compounds **4a**, **4b** and **5** in trifluoroacetic acid (TFA) or in mixtures of TFA and CH_2Cl_2 , with or without thallium(III) trifluoroacetate (TTFA) being added as oxidant, were placed in quartz EPR tubes and deoxygenated by bubbling argon through them for 5 min and then transferred to the EPR cavity.

2,3-Dichloronaphtho[2',3':5,6][1,4]dithiino[2,3-*b*]pyridine (**7a**)

A mixture of naphthalene-2,3-dithiol (0.44 g; 2.31 mmol), 2,3,5,6-tetrachloropyridine (0.5 g; 2.31 mmol), sodium bicarbonate (0.82 g), and DMF (25 mL) was stirred under argon at 100°C for 2.5 h and then refluxed for 4 h. The mixture was cooled, poured into water, acidified with hydrochloric acid and filtered. The precipitate was chromatographed (silica gel) and eluted with CCl_4 to give: (a) 2,2'-(naphthalene-2,3-dithio)-bis(3,5,6-trichloropyridine) (**9a**) (0.19 g, 30%); δ_{H} 8.29 (s, 2H), 7.92–7.88 (m, 2H), 7.63 (s, 2H), 7.64–7.60 (m, 2H). (b) **7a** (0.39 g; 51%); δ_{H} 7.95 (s, 1H), 7.94 (s, 1H), 7.79 (s, 1H), 7.74–7.78 (m, 2H), 7.53–7.47 (m, 2H); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3030 (w), 1510 (w), 1485 (w), 1360 (s), 1340 (m), 1310 (m), 1220 (m), 1155 (m), 1110 (w), 1065 (m), 1055 (w), 885 (m), 870 (m), 735 (m), 715 (w), 620 (m). Anal. Calc. for $\text{C}_{15}\text{H}_7\text{Cl}_2\text{NS}_2$: C, 53.6; H, 2.1; Cl, 21.1; N, 4.2; S, 19.1. Found: C, 53.5; H, 2.0; Cl, 21.6; N, 4.1; S, 19.1%.

Dinaphtho[2',3':5,6][1,4]dithiino[2,3-*b*:2,3-*e*]pyridine (**4a**)

(i) **From 2,3-dichloronaphtho[2',3':5,6][1,4]dithiino[2,3-*b*]pyridine (**7a**)**. A mixture of naphthalene-2,3-dithiol (0.21 g; 1.09 mmol), **7a** (0.30 g; 0.89 mmol), sodium bicarbonate (0.40 g), and DMF (12 mL) was stirred under argon at 100°C for 1.5 h and then refluxed for 5 h. The mixture was cooled, poured into water, acidified with hydrochloric acid and filtered. The precipitate was extracted by a mixture of $\text{CCl}_4\text{--CHCl}_3$ to give **4a** (0.20 g; 49%) m.p. 390°C ; δ_{H} 7.97 (s, 2H), 7.95 (s, 2H), 7.77 (s 1H), 7.77–7.74 (m, 4H), 7.50–7.46 (m, 4H); IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3050 (w), 1490 (w), 1430 (w), 1365 (m), 1350 (s), 1310 (w), 1220 (w), 1190 (w), 1160 (m), 1140 (w), 1110 (m), 900 (w), 870 (s), 750 (w), 730 (s), 660 (w), 630 (w). Anal. Calc. for $\text{C}_{25}\text{H}_{13}\text{NS}_4$: C, 65.9; H, 2.9; N, 3.1; S, 28.1. Found: C, 65.9; H, 2.8; N, 3.1; S, 28.1%.

(ii) **From 2,3,5,6-tetrachloropyridine**. A mixture of naphthalene-2,3-dithiol (0.89 g; 4.6 mmol), 2,3,5,6-tetrachloropyridine (0.50 g; 2.3 mmol), sodium bicarbonate (1.68 g), and DMF (50 mL) was allowed to react as described in (i). The reaction mixture was treated as before, and the crude product was extracted by CCl_4 to give **4a** (0.66 g; 63%).

Table 2 Values of anodic peak potentials (E_a) ($v = 200 \text{ mV s}^{-1}$) and redox potentials (E°) in $\text{CH}_2\text{Cl}_2\text{:TFA}$ (1:1) with PTBA as electrolyte

	$E_a^1(E^\circ)/\text{V}$	E_a^2/V	$\Delta E_a/\text{V}$
4a	1.16 (1.11)	1.74	0.58
4b	1.21 (1.08)	1.84	0.63
5	1.08 (1.04)	1.52	0.44

4-Butyl-2,3,5,6-tetrachloropyridine

A solution of butylmagnesium bromide [from magnesium (1.22 g; 0.05 mol) and butylbromide (8.23 g; 0.06 mol) in diethyl ether] was added dropwise to a solution of pentachloropyridine (6.28 g; 0.025 mol) in diethyl ether (50 mL). The mixture was stirred under argon at rt for 12 h. The reaction mixture was poured into hydrochloric acid (20%) and extracted with more ether. The ethereal solution, washed with water and dried over Na_2SO_4 , was evaporated under reduced pressure to give a residue which was filtered through silica gel. Elution with hexane gave 4-butyl-2,3,5,6-tetrachloropyridine (3.49 g; 52%): bp 138–144 °C/3 mmHg (lit.¹⁴ 140–145 °C/3 mmHg); δ_{H} 3.04–2.96 (m, 2H), 1.51 (m, 4H), 0.98 (t, 3H, $J = 7$ Hz); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 2960 (s), 2930 (m), 2870 (m), 2860 (m), 1570 (s), 1470 (m), 1460 (m), 1330 (s), 660 (m).

4-Butyl-2,3-dichloronaphtho[2',3':5,6][1,4]dithiino[2,3-*b*]pyridine (7b)

A mixture of naphthalene-2,3-dithiol (0.79 g; 4.0 mmol), 4-butyl-2,3,5,6-tetrachloropyridine (1.09 g; 4 mmol), sodium bicarbonate (1.5 g), and DMF (45 mL) was stirred under argon at 100 °C for 1.5 h and then refluxed for 6 h. The mixture was cooled, poured into water, acidified with hydrochloric acid and filtered. The precipitate was chromatographed (silica gel) and eluted with $\text{CCl}_4\text{--CHCl}_3$ (5:1) to give: (a) 2,2'-(naphthalene-2,3-dithio)bis(4-butyl-3,5,6-trichloropyridine) (9b) (0.49 g; 18%) m.p. 191–193 °C; δ_{H} 8.27 (s, 2H), 7.90–7.87 (m, 2H), 7.61–7.58 (m, 2H), 2.93–2.88 (m, 4H), 1.57–1.42 (m, 8H), 0.97 (t, 6H, $J = 7.2$ Hz); δ_{C} 155.7, 149.6, 146.8, 137.8, 134.0, 131.2, 127.9, 127.6, 127.0, 126.6, 32.3, 29.3, 22.8, 13.8. Anal. Calc. for $\text{C}_{28}\text{H}_{24}\text{Cl}_6\text{N}_2\text{S}_2$: C, 50.5; H, 3.6; N, 4.2; S, 9.6. Found: C, 50.4; H, 3.6; N, 4.2; S, 9.6%; (b) 7b (0.88 g; 56%) m.p. 159–161 °C; ^1H NMR (300 MHz; CDCl_3) δ 8.01 (s, 1H), 7.97 (s, 1H), 7.78–7.74 (m, 2H), 7.52–7.48 (m, 2H), 3.11–3.06 (m, 2H), 1.62–1.49 (m, 4H), 1.03 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR 154.7, 150.8, 147.2, 132.7, 132.5, 132.0, 131.0, 129.9, 128.9, 127.5, 127.4, 127.2, 127.2, 127.1, 127.1, 32.9, 30.2, 22.8, 13.8; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3050 (w), 2950 (w), 2930 (w), 2870 (w), 1570 (w), 1520 (m), 1510 (w), 1490 (w), 1320 (m), 880 (s), 750 (s), 640 (s). Anal. Calc. for $\text{C}_{19}\text{H}_{15}\text{Cl}_2\text{NS}_2$: C, 58.2; H, 3.9; N, 3.6; S, 16.3. Found: C, 58.1; H, 3.9; N, 3.5; S, 16.4%.

16-Butyldinaphtho[2',3':5,6][1,4]dithiino[2,3-*b*:2,3-*e*]pyridine (4b)

(i) From 4-butyl-2,3-dichloronaphtho[2',3':5,6][1,4]dithiino[2,3-*b*]pyridine (7b). A mixture of naphthalene-2,3-dithiol (0.19 g; 0.96 mmol), 7b (0.38 g; 0.96 mmol), sodium bicarbonate (1.0 g), and DMF (15 mL) was stirred under argon at 110 °C for 1 h and then at reflux for 6 h. The mixture was cooled, poured into water, acidified with hydrochloric acid and filtered. The precipitate was chromatographed (silica gel) and eluted with $\text{CCl}_4\text{--CHCl}_3$ (5:1) to give: (a) 7b (0.064 g; 10%); (b) 4b (0.26 g; 53%): m.p. 317.5 °C by DSC; δ_{H} 8.02 (s, 2H), 7.98 (s, 2H), 7.79–7.73 (m, 4H), 7.53–7.45 (m, 4H), 3.13–3.05 (m, 2H), 1.56 (m, 4H), 1.03 (t, 3H, $J = 7.0$ Hz); δ_{C} 155.6, 149.5, 132.8, 132.8, 132.6, 130.8, 129.8, 127.4, 127.4, 127.3, 127.2, 127.0, 126.9, 32.6, 31.4, 22.9, 14.0; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3040 (w), 2950 (w), 2920 (w), 2880 (w), 1570 (w), 1510 (m), 1490 (m), 1310 (s), 880 (s), 740 (s). Anal. Calc. for $\text{C}_{19}\text{H}_{21}\text{NS}_4$: C, 68.1; H, 4.1; N, 2.7; S, 25.1. Found: C, 68.1; H, 3.9; N, 2.8; S, 25.0%.

(ii) From 4-butyl-2,3,5,6-tetrachloropyridine. A mixture of naphthalene-2,3-dithiol (1.42 g; 7.4 mmol), 4-butyl-2,3,5,6-tetrachloropyridine (0.80 g; 3.0 mmol), sodium bicarbonate (2.5 g), and DMF (90 mL) was stirred under argon at 105 °C

for 1.5 h and then at reflux for 5 h. The reaction mixture was worked up as before to give: (a) 7b (0.16 g; 8%) and (b) 4b (1.28 g; 85%).

2,3-Dichloro[1,4]benzodioxino[2,3-*b*]pyridine (8)

A mixture of benzene-1,2-diol (2.06 g; 18.7 mmol), 2,3,5,6-tetrachloropyridine (3.96 g; 18.2 mmol), sodium carbonate (4.2 g), and DMF (40 mL) was stirred at reflux under argon for 6 h. The mixture was cooled, poured into water, acidified with hydrochloric acid and extracted with diethyl ether. The ethereal solution was washed with water, dried over Na_2SO_4 and finally distilled at reduced pressure, to yield a residue which was chromatographed (silica gel). Elution with CCl_4 gave: (a) 2,2'-(1,2-phenylenedioxy)bis(3,5,6-trichloropyridine) (10) (0.76 g; 18%); δ_{H} 7.73 (s, 2H), 7.31–7.41 (m, 4H); δ_{C} 155.1, 143.9, 143.7, 140.5, 126.5, 123.9, 123.6, 117.2; (b) 8 (3.18 g; 69%), m.p. 164–165 °C (from $\text{CHCl}_3\text{--hexane}$); δ_{H} 6.84–7.01 (m, 5H); δ_{C} 146.9, 140.9, 140.3, 139.0, 137.2, 126.3, 125.2, 125.0, 117.3, 116.4; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3065 (w), 1570 (m), 1495 (s), 1440 (s), 1375 (m), 1300 (m), 1260 (m), 1195 (m), 1155 (m), 1100 (w), 980 (m), 880 (s), 860 (m), 750 (s), 720 (w). Anal. Calc. for $\text{C}_{11}\text{H}_5\text{Cl}_2\text{NO}_2$: C, 51.9; H, 2.0; Cl, 27.9; N, 5.5. Found: C, 51.9; H, 2.0; Cl, 28.1; N, 5.5%.

Di[1,4]benzodioxino[2,3-*b*:2,3-*e*]pyridine (6)

A mixture of benzene-1,2-diol (1.00 g; 9.1 mmol), 8 (2.00 g; 7.9 mmol), sodium bicarbonate (2.2 g) and DMF (40 mL) was stirred at reflux under argon for 16.5 h. The mixture was worked up as before and the residue was chromatographed (silica gel) and eluted with $\text{CCl}_4\text{--CHCl}_3$ (3:1) to give 6 (0.95 g; 41%), m.p. 274–276 °C (from hexane); δ_{H} 6.79–6.94 (m, 9H); δ_{C} 141.4, 140.7, 133.8, 124.6, 124.4, 117.1, 116.2, 114.2; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3065 (w), 1635 (w), 1590 (w), 1500 (m), 1465 (s), 1450 (s), 1315 (w), 1275 (s), 1225 (m), 1180 (w), 1100 (w), 1030 (w), 940 (m), 920 (w), 880 (m), 810 (w), 780 (w), 745 (s), 715 (w). Anal. Calc. for $\text{C}_{17}\text{H}_9\text{NO}_4$: C, 70.1; H, 3.1; N, 4.8. Found: C, 70.1; H, 3.0; N, 4.7%.

Dinaphtho[2',3':5,6][1,4]dioxino[2,3-*b*:2,3-*e*]pyridine (5)

A mixture of naphthalene-2,3-diol (3.85 g; 24.0 mmol), 2,3,5,6-tetrachloropyridine (2.0 g; 9.2 mmol), sodium bicarbonate (4.8 g), and DMF (100 mL) was stirred at 100 °C for 1 h and then at reflux for 11 h. The mixture was cooled, poured into diluted aqueous hydrochloric acid and the precipitate was isolated by filtration, washed with water and dried. The solid, digested from hexane and twice from chloroform, gave 5 (1.86 g; 51.5%), m.p. 441 °C (decomp.); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3055(w), 1625 (w), 1510 (m), 1460 (s), 1395 (m), 1360 (m), 1285 (s), 1240 (m), 1200 (m), 1185 (s), 960 (s), 875 (s), 865 (s), 790 (w), 750 (s), 730 (w), 715 (w). Anal. Calc. for $\text{C}_{25}\text{H}_{13}\text{NO}_4$: C, 76.7; H, 3.35; N, 3.6; O, 16.3. Found: C, 74.6; H, 3.3; N, 3.6; O, 16.5; Cl, 1.7%.

Hexachloroantimonate of 4b²⁺

Neat SbCl_5 (0.12 mL; 0.98 mmol) was added dropwise by syringe to a stirred solution of 4b (100 mg; 0.19 mmol) in anhydrous CHCl_3 (30 mL) under an argon atmosphere. The solution turned yellow and a solid precipitated. The resulting mixture was stirred for 2.5 h. The precipitate was filtered under argon and washed thoroughly with anhydrous CHCl_3 . The salt, $4b^{2+}\cdot 2\text{SbCl}_6^-$, was dried at 50 °C (0.5 mmHg) to afford a powder (195 mg; 85%); IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3080 (w), 2960 (w), 2910 (w), 2860 (w), 1570 (w), 1550 (m), 1420 (m), 1290 (m), 1280 (m), 880 (s), 750 (s). Anal. Calc. for $\text{C}_{19}\text{H}_{21}\text{Cl}_{10}\text{NS}_4\text{Sb}_2$: C, 29.65; H, 1.8; N, 1.2; S, 10.9. Found: C, 29.7; H, 1.8; N, 1.25; S, 10.9%.

X-Ray analysis of 4b

Crystal data. Molecular formula $C_{29}H_{21}NS_4$. Molecular weight 511.71. Triclinic, $P\bar{1}$, no. 2. Cell dimensions $a = 8.813(2)$, $b = 10.229(1)$, $c = 14.309(3)$ Å, $\alpha = 72.49(2)$, $\beta = 78.36(2)$, $\gamma = 82.90(2)^\circ$, $V = 1202.1(4)$ Å³, $Z = 2$, $F(000) = 532$, $D_c = 1.414$ g cm⁻³, $\mu = 0.41$ mm⁻¹, crystal dimensions $0.62 \times 0.16 \times 0.34$ mm, brown coloured.

Data collection. The diffractometer was an Enraf Nonius CAD4 with a graphite monochromated MoK α radiation, $\lambda = 0.7103$ Å. Cell parameters were determined from refinement of 25 reflections using the CAD4 Express software.¹⁵ 4614 reflections were measured with $1.0 < 2\theta < 25.0^\circ$ and index ranges $-10 < h < 10$, $-11 < k < 12$, $0 < l < 17$ in $\omega/2\theta$ scan mode, $0.8 + 0.5 \tan(2\theta)$ scanwidth and maximum final scan time of 60 s. 3 standard reflections were measured every 3600 s to check for the intensity variation and 3 more standards were measured every 50 reflections to check the crystal orientation. Intensity decay was 2.7% and was corrected. Absorption corrections were made using 9 psi-scans, $T_{\max} = 99.81\%$ and $T_{\min} = 63.91\%$.

Resolution and refinement. The structure was solved by direct methods using SumF-TF¹⁶ and refined on F^2 with 4232 unique reflections and 323 parameters. Final R factors: $R = 7.83\%$ for $F^2 = > 4\sigma(F^2)$, and $wR^2 = 25.36\%$, Goof = 1.050 for all data, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1 / [\sum \delta(F_o^2)^2 + (0.554P)^2 + 0.92P]$, $P = [\text{Max}(F_o^2, 0) + 2F_c^2] / 3$, Goof = $[\sum w(F_o^2 - F_c^2) / (n - p)]^{1/2}$ (n , number of reflections and p , number of parameters). Final shifts/esd were less than 0.001 in the last cycle, and the maximum and minimum residual electron density in the final Fourier difference were 0.74 and -0.64 e Å⁻³, respectively. The SHELXL-93 program¹⁷ was used for refinement and plots were made with the PLUTON program.¹⁸

X-Ray analysis of 5

Crystal data. Molecular formula $C_{17}H_9NO_4$. Molecular weight 291.25. Monoclinic, $P2_1/n$, no.14. Cell dimensions: $a = 6.090(2)$, $b = 22.542(6)$, $c = 13.823(3)$ Å, $\beta = 90.24(3)^\circ$, $V = 1897.6(9)$ Å³, $F(000) = 900$, $D_c = 1.529$ g cm⁻³, $\mu = 0.111$ mm⁻¹, crystal dimensions $0.77 \times 0.17 \times 0.12$ mm.

Data collection. The diffractometer was an Enraf Nonius CAD4 with graphite monochromated MoK α radiation, $\lambda = 0.71073$ Å. Cell parameters were determined from refinement of 15 reflections using the CAD4 Express software.¹⁵ 4193 reflections were measured with $2.33 \leq \theta \leq 26.28^\circ$ and index ranges $0 \leq h \leq 7$, $-28 \leq k \leq 0$, $-17 \leq l \leq 17$ in $\omega/2\theta$ mode, $0.58 + 0.60 \tan(\theta)$ scanwidth and maximum final scan time of 60 s. 3 standard reflections were measured every 3600 s to check for the intensity variation and 3 more standards were measured every 55 reflections to check the crystal orientation. There was no intensity loss. Absorption correction was made using 9 psi-scans, $T_{\max} = 98.62\%$ and $T_{\min} = 92.88\%$.

Resolution and refinement. The structure was solved by direct methods using SumF-TF¹⁶ and refined on F^2 with 3830 unique reflections and 321 parameters. Final R factors: $[I > 2\sigma(I)]$ $R1 = 0.0419$ and $wR^2 = 0.0975$; R factors (all data) $R1 = 0.1439$ and $wR^2 = 0.1117$. Goodness-of-fit on $F^2 = 0.796$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1 / [\sum \delta(F_o^2)^2 + (0.0594P)^2 + 0.00P]$, $P = [\text{Max}(F_o^2, 0) + 2F_c^2] / 3$, Goof = $[\sum w(F_o^2 - F_c^2) / (n - p)]^{1/2}$ (n , number of reflections and p , number of parameters). Final shifts/esd were less than 0.000 in the last cycle (with conver-

gence to zero), and the maximum and minimum residual electron density in the final Fourier difference were 0.121 and -0.193 e Å⁻³, respectively. The SHELXL-93 program¹⁷ was used for refinement and plots were made with PLUTON programs.¹⁸

CCDC reference numbers 190862 and 190863. See <http://www.rsc.org/suppdata/nj/b2/b202708a/> for crystallographic files in CIF or other electronic format.

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