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

Carlos Troya,^a Albert Vidal,^b Enric Brillas,^c Jordi Rius,^d Xavier Torrelles,^d Carlos Alemán,^e Jordi Casanovas^f and Luis Juliá^{*a}

- ^a Departament de Química Orgànica Biològica, Centre d'Investigació i Desenvolupament (CSIC), Jordi Girona 18-26, 08034, Barcelona, Spain
- ^b Departament de Química Orgànica, CETS Institut Químic de Sarrià, Universitat Ramon Llull, 08017, Barcelona, Spain
- ^c Departament de Química Física, Universitat de Barcelona, Diagonal 647, 08028, Barcelona, Spain
- ^d Institut de Ciència de Materials (CSIC), Campus de la U.A.B., 08193, Bellaterra, Spain
- ^e Departament d'Enginyeria Química, ETS d'Enginyers Industrials de Barcelona, Universitat Politécnica de Catalunya, Diagonal 647, 08048, Barcelona, Spain
- ^f Departament de Química, Escola Universitaria Politécnica, Universitat de Lleida, Jaume II 69, 25001, Lleida, Spain

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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-



Scheme 1

lar behaviour in EPR, the splittings in the spectrum of its radical cation are practically equal to those found in $1^{\bullet+}$ 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° .⁵ In the EPR spectrum of $3^{\bullet+}$, 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]dioxino[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,

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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 $(135^{\circ})^{\circ}$ and between peripheral and central benzenes in tetrathiapentacene 11 $(131.5^{\circ})^{8}$ (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 $[I(^{33}S) = 3/2]$, the two $M_S = \pm 1/2$ groups being lost into the very intense central multiplet. Likewise, the spectrum of $4b^{\cdot+}$ 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 assignation 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 $4a^{\cdot+}$ and $4b^{\cdot+}$, with the spectrum of $5^{\cdot+}$ shows a clear difference in the electron coupling with the nitrogen and the hydrogen of the pyridine ring, this coupling being higher in $5^{\cdot+}$. On the other hand, the high values of coupling with the sulfur atoms in $4a^{\cdot+}$ and $4b^{\cdot+}$ 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 CH₂Cl₂: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 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: (t₀) 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** (~10⁻³ M) in carefully dried CH₂Cl₂ (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 welldefined but irreversible oxidation peak O₁, with an anodic peak potential $E_p^{a}(O_1) = 1.24$ 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^{++}

[12 [11	13 10	14 9	15 X X 8	R 16 N 7	17 X X 6	18 >> 5	1 4	2 3	+•
4a ⁺ ,∶ X=S, R=H									

4b⁺ : X=S, R=C₄H₉ 5 • : X=O, R=H

	a _H	$a_{ m N}$	as	g	$\Delta H_{ m pp}$
4a*+	$\begin{array}{c} 0.46(0.031)(1\mathrm{H})^{a} \\ 0.24(0.041)(4\mathrm{H})^{b} \end{array}$	0.82(0.090)(1N)	4.7(0.136)(4S)	2.0077	0.2
	$0.24(0.048)(4H)^c$ < 0.1(0.040)(4H)				
4 b •+	$0.42(2H)^{a}$ $0.21(8H)^{b \ c}$	0.79(1N)	4.6(4S)	2.0079	0.18
5 •+	$< 0.1(4H)^{a}$ 1.0(0.041)(1H) ^a 0.31(0.036)(4H) ^b	1.48(0.095)(1N)		2.0036	0.11
	$0.18(0.036)(4H)^{c}$				

^{*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^{•+} and 5^{•+}.

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 ($\varepsilon/dm^3 mol^{-1} cm^{-1}$) = 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**^{•+} and **4b**^{•+}, 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 SbCl₅ solutions of **4b** in CHCl₃ yielded a yellow and stable salt characterized as **4b**²⁺·2SbCl₆⁻. 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 Köfler 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. ¹³C NMR spectra at 75 MH were obtain with a Varian Gemini 300HC spectrometer. The electronic spectra were recorded with a Perkin-Elmer Lambda Array 3840 Spectrometer coupled with a Perkin-Elmer T300 computer. DMF was used as received. CHCl₃ was dried over calcium chloride and distilled. Naphthalene-2,3-dithiol [¹H NMR (300 MHz, CDCl₃) 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 2,3dibromonaphthalene 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

Table 2 Values of anodic peak potentials (E_a) ($v = 200 \text{ mV s}^{-1}$) and redox potentials (E°) in CH₂Cl₂:TFA (1:1) with PTBA as electrolyte

	$E_{\mathrm{a}}^{-1}(E^{\circ})/\mathrm{V}$	$E_{\rm a}{}^2/{ m V}$	$\Delta E_{ m a}/{ m V}$	
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	

0.093 cm² 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 CH₂Cl₂ or in CH₂Cl₂: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 CH₂Cl₂, 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 CCl₄ to give: (a) 2,2'-(naphthalene-2,3-dithio)bis(3,5,6-trichloropyridine) (9a) (0.19 g, 30%); $\delta_{\rm H}$ 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%); $\delta_{\rm H}$ 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) v_{max}/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 C₁₅H₇C₁₂NS₂: 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 CCl₄–CHCl₃ to give 4a (0.20 g; 49%) m.p. 390 °C; $\delta_{\rm H}$ 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) $\nu_{\rm max}/$ 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 C₂₅H₁₃NS₄: 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 CCl₄ to give **4a** (0.66 g; 63%). 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 Na₂SO₄, 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); $\delta_{\rm H}$ 3.04–2.96 (m, 2H), 1.51 (m, 4H), 0.98 (t, 3H, J = 7 Hz); IR (KBr) $v_{\rm max}/\rm cm^{-1}$ 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), 4butyl-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 CCl₄-CHCl₃ (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; $\delta_{\rm H}$ 8.27 (s, 2H), 7.90–7.87 (m, 2H), 7.61–7.58 (m, 2H), 2.93–288 (m, 4H), 1.57–1.42 (m, 8H), 0.97 (t, 6H, J = 7.2 Hz); $\delta_{\rm C}$ 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 C₂₈H₂₄Cl₆ N₂S₂: 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; CDCl₃) 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 = 7.2Hz); ¹³C 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) v_{max}/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 C19H15Cl2NS2: 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 CCl_4 -CHCl₃ (5:1) to give: (a) 7b (0.064 g; 10%); (b) **4b** (0.26 g; 53%): m.p. 317.5 °C by DSC; $\delta_{\rm H}$ 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); $\delta_{\rm C}$ 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) $v_{\rm max}/{\rm cm}^{-1}$ 3040 (w), 2950 (w), 2920 (w), 2880 (w), 1570 (w), 1510 (m), 1490 (m), 1310 (s), 880 (s), 740 (s). Anal. Calc. for C19H21NS4: 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 $105 \,^{\circ}$ 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), 2,3,5,6tetrachloropyridine (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 Na₂SO₄ and finally distilled at reduced pressure, to yield a residue which was chromatographed (silica gel). Elution with CCl₄ gave: (a) 2,2'-(1,2-phenylenedioxo)bis(3,5,6-trichloropyridine) (10) (0.76 g; 18%); $\delta_{\rm H}$ 7.73 (s, 2H), 7.31–7.41 (m, 4H); $\delta_{\rm C}$ 155.1, 143.9, 143.7, 140.5, 126.5, 123.9, 123.6, 117.2; (b) 8 (3.18g; 69%), m.p. 164–165 °C (from CHCl₃–hexane); $\delta_{\rm H}$ 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) v_{max}/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 C₁₁H₅Cl₂NO₂: 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 CCl₄:CHCl₃ (3:1) to give **6** (0.95 g; 41%), m.p. 274–276 °C (from hexane); $\delta_{\rm H}$ 6.79–6.94 (m, 9H); $\delta_{\rm C}$ 141.4, 140.7, 133.8, 124.6, 124.4, 117.1, 116.2, 114.2; IR (KBr) $v_{\rm max}/{\rm cm}^{-1}$ 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 C₁₇H₉NO₄: 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), 2,3,5,6tetrachloropyridine (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) v_{max}/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 C₂₅H₁₃NO₄: 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 SbCl₅ (0.12 mL; 0.98 mmol) was added dropwise by syringe to a stirred solution of **4b** (100 mg; 0.19 mmol) in anhydrous CHCl₃ (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 CHCl₃. The salt, **4b**²⁺·2SbCl₆, was dried at 50 °C (0.5 mmHg) to afford a powder (195 mg; 85%); IR (KBr) v_{max}/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 C₁₉H₂₁Cl₁₀NS₄Sb₂: 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 C₂₉H₂₁NS₄. Molecular weight 511.71. Triclinic, P1, 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, $Z = 2, F(000) = 532, \ D_c = 1.414 \ \text{g cm}^{-3}, \ \mu = 0.41 \ \text{mm}^{-1}, \ \text{crystal}$ 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 MoKa 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 $\omega/$ 2θ 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, $T_{\text{max}} =$ 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 $F^{2} = > 4\sigma(F^{2}), \text{ and } wR^{2} = 25.36\%, \text{ Goof} = 1.050 \text{ for all data,} where <math>R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, wR^{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}; w = 1 / [\sum \delta(F_{o}^{2})^{2} + (0.554P)^{2} + 0.92P]; P = [Max(F_{o}^{2}, 0) + 2F_{c}^{2}] / 3, \text{ Goof} = [(\sum w(F_{o}^{2} - F_{c}^{2})) / (n-p)]^{1/2}$ (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 C₁₇H₉NO₄. Molecular weight 291.25. Monoclinic, $P2_1/n$, no.14. Cell dimensions: $a = 6.090(2), b = 22.542(6), c = 13.823(3) \text{ Å}, \beta = 90.24(3)^{\circ}, V = 1897.6(9) \text{ Å}^3, F(000) = 900, D_c = 1.529 \text{ g cm}^{-3}, \mu =$ 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 MoKa 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 $2.33 \le \theta \le 26.28^{\circ}$ and index ranges $0 \le h \le 7$, $-28 \le k \le 0$, $-17 \le l \le 17$ 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, $T_{\text{max}} = 98.62\%$ and $T_{\text{min}} = 92.88\%$.

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 $R = \sum ||F_0| - |F_c|| / \sum |F_0|$, $wR^2 = \sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2|^{1/2}$, $w = 1 / [\sum \delta(F_0^2)^2 + (0.0594P)^2 + 0.00P]$, $P = \sum W(F_0^2)^2 / (0.0594P)^2 + 0.00P]$. $[Max(F_o^2, 0) + 2F_c^2]/3$, $GooF = [(\sum w(F_o^2 - F_c^2))/(n-p)]^{1/2}$ (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 program¹ 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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References

- (a) H. J. Shine and L. Piette, J. Am. Chem. Soc., 1962, 84, 4798; (b) H. J. Shine, C. F. Dair and R. J. Small, J. Chem. Phys., 1963. 38. 569.
- (a) P. D. Sullivan, J. Am. Chem. Soc., 1968, 90, 3618; (b) H. J. Shine and P. D. Sullivan, J. Phys. Chem., 1968, 72, 1390; (c) J. Giordan and H. Bock, Chem. Ber., 1982, 115, 2548; (d) H. Bock, A. Rauschenbach, C. Näther, M. Kleine and Z. Havlas, Chem. Ber., 1994, 127, 2043.
- S. Larson, O. Simonsen, G. E. Martín, K. Smith and S. Puig-Torres, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1984, 40, 103.
- (a) P. Berges, V. Mansel and G. Klar, Z. Naturforsch., Teil B, 1992, 47, 211; (b) W. Hinrichs, P. Berges, G. Klair, E. Sánchez-Martinez and W. Gunsser, Synth. Met., 1987, 20, 357; (c) H. Bock, A. Rauschenbach, K. Ruppert and Z. Havlas, Angew. Chem., Int. Ed. Engl., 1991, 30, 714; (d) S. Hünig, K. Sinzger, R. Bau, T. Metzenthin and J. Salbeck, Chem. Ber., 1993, 126, 465.
- 5 C. Martí, J. Irurre, A. Alvarez-Larena, J. F. Piniella, E. Brillas, Ll. Fajarí, C. Alemán and L. Juliá, J. Org. Chem., 1994, 59, 6200.
- B. Bueno, B. Esteve, J. Irurre, E. Brillas, X. Torrelles, J. Rius, 6 A. Alvarez-Larena, J. F. Piniella, C. Alemán and L. Juliá, J. Chem. Soc., Perkin Trans. 2, 1999, 1503.
- (a) R. S. Dainter, L. Juliá, H. Suschitzky and B. J. Wakefield, J. (d) K. S. Danner, E. Julia, H. Suschitzky and D. J. Wakenera, J. Chem. Soc., Perkin Trans. 1, 1982, 2897; (b) L. Juliá, J. Rius and H. Suschitzky, *Heterocycles*, 1992, **34**, 1539. V. N. Nesterov, V. E. Shklover, Y. T. Struchkov, V. A. Sergeev, V. E. Shklover, Y. T. Struchkov, V. A. Sergeev, M. E. Shklover, Y. T. Struchkov, V. A. Sergeev, M. E. Shklover, Y. T. Struchkov, V. A. Sergeev, M. E. Shklover, Y. T. Struchkov, V. A. Sergeev, M. E. Shklover, Y. T. Struchkov, V. A. Sergeev, M. E. Shklover, Y. T. Struchkov, V. A. Sergeev, M. S. Shklover, Y. T. Struchkov, V. A. Sergeev, M. S. Shklover, Y. T. Struchkov, V. A. Sergeev, M. S. Shklover, Y. T. Struchkov, V. A. Sergeev, M. S. Shklover, Y. Shklover, Y. T. Struchkov, V. A. Sergeev, M. S. Shklover, Y. Sh
- 8 V. I. Nedelkin and I. S. Ivanova, Acta Crystallogr., 1986, 42, 720.
- Molecular geometries, energies and spin densities were computed at the semiempirical MNDO¹⁰ level, which is known to provide good results for the family of compounds investigated in the present work.^{5,6} Calculations for the neutral compounds and the radical cations were performed using the RHF and UHF methods, respectively. Spin densities were computed using the EPR keyword implemented in the MOAC93 Revision 2 program.¹¹
- M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 1985, 107, 3902. 10
- 11 J. J. P. Stewart, MOPAC 93 Revision 2, Fujitsu Limited. The simulation was performed by using the WINSIM program provided by D. Dulog, Public EPR Software Tools, 12
- National Institute of Environmental Health Sciences, Bethesda, MD. 1996. 13
- R. Gleiter and J. Vischmann, J. Org. Chem., 1986, 51, 370.
- S. S. Dua and H. Gilman, J. Organomet. Chem., 1968, 12, 234. 14 15
- CAD4-Express Operating Software, V. 5.1, Enraf-Nonius, Delft Instruments X-Ray Diffraction, Delft, The Netherlands, J. Rius, Acta Crystallogr., Sect. A, 1993, 49, 406. 16
- G. M. Sheldrick, SHELXL-93, A program for the refinement of 17 crystal structures, Göttingen University, 1993.
- A. L. Spek, PLUTON, A program for Display and Analysis of 18 Crystal and Molecular Structures, Utrecht University, 1993.