

Sb ··· S and S ··· S interactions in the first neutral and oxidized diphenylstibino (Ph₂Sb–) derivatives of the redox active tetrathiafulvalene (TTF) core

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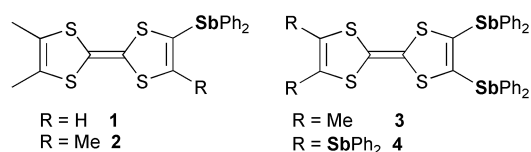
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The preparation of the monostibines *o*-Me₂TTF–SbPh₂ (**1**) and Me₃TTF–SbPh₂ (**2**), the *ortho* distibine *o*-Me₂TTF–(SbPh₂)₂ (**3**) and the tetrastibine TTF(SbPh₂)₄ (**4**) is described together with their electrochemical properties and the X-ray crystal structures of the neutral **1** and **3**. In the former, one intermolecular Sb ··· S contact completes the co-ordination sphere of the antimony atom while in **3** the TTF moieties stack on top of each other with no evidence for Sb ··· S interactions. Electrocrystallisation of **2** in the presence of [*n*-Bu₄N]₂[Mo₆O₁₉] affords a 2 : 1 salt, [2]₂[Mo₆O₁₉] where the 2⁺ cation radical species are associated into diamagnetic [2]₂²⁺ dyads through a strong HOMO ··· HOMO overlap interaction, separated from each other by the [Mo₆O₁₉]²⁻ counter ions.

Introduction

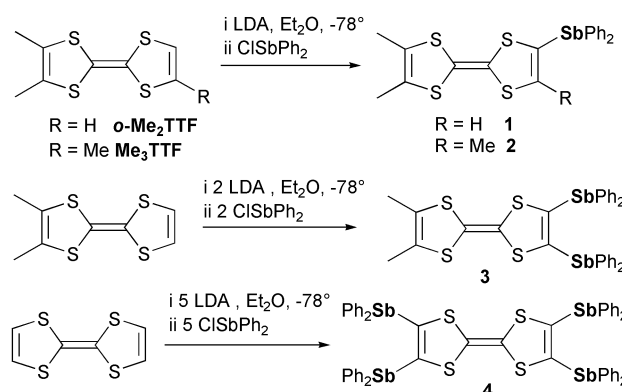
The preparation of several tertiary phosphines and *o*-diphosphines bearing a redox active group such as the tetrathiafulvalenyl moiety^{1,2} has recently opened new perspectives toward the elaboration of hybrid systems associating open-shell species of organic and inorganic character. For example the chelating *o*-Me₂TTF(PPh₂)₂ or TTF(PPh₂)₄ have been employed^{3–5} in various metal complexes where both the TTF π-redox core and the metal fragment are susceptible to oxidation to open-shell species. On the other hand, attempts to electro-oxidize the free phosphines in the presence of various anions invariably led in our hands to the formation of phosphine oxides, probably upon reaction of the formed cation radical with traces of water. A salt of [Me₃TTF–P(O)PPh₂]⁺ was even isolated in crystalline form from the electrocrystallisation of the Me₃TTF–PPh₂ phosphine.⁶ In order to circumvent this drawback, we postulated that the analogous tetrathiafulvalenyl stibines, where Sb substitutes for P in the above described phosphines, would be adequate candidates for the elaboration of stable cation radical salts. Indeed, it is well established in Group 15 chemistry that Sb^{III} derivatives such as stibines are harder to oxidize to the Sb^V stibine oxides than the corresponding phosphines. Furthermore, the larger spatial extension of the antimony lone pair offers the possibility for electronic delocalisation through intermolecular Sb ··· Sb and Sb ··· S interactions.⁷ We describe here the synthesis of several tetrathiafulvalenyl stibines, investigate their electrochemical properties by comparison with the phosphorus analogues and describe the X-ray crystal structures of several neutral donor molecules as well as the first cation radical salt of diphenylstibino-trimethyl-tetrathiafulvalene Me₃TTF–SbPh₂ with the dianionic Mo₆O₁₉²⁻ counter ion.



Results and discussion

Syntheses

1–4 were prepared as previously described for the phosphorus analogues from the reaction of the lithium derivative of the chosen tetrathiafulvalene with ClSbPh₂ as illustrated in Scheme 1. The four stibines are air stable and were obtained in crystal-



Scheme 1 Preparation of **1–4**.

line form (see below). In the mass spectra, loss of a diphenylstibino (–SbPh₂) fragment was identified only in the *o*-distibines **3** and **4**. Cyclic voltammetry experiments show the systematic presence of two reversible, one-electron waves associated with the oxidation of the TTF redox core to the mono- and di-cation respectively (Table 1). Comparison with the analogous phosphines as well as with the unsubstituted TTFs demonstrate the electron rich character of the diphenylstibino substituent whose influence on the redox properties is comparable or even better to that of the PPh₂ moiety. Indeed, we observed that the tetra-substituted TTF(SbPh₂)₄, **4**, even oxidises at a lower potential than **1** or **2**. Accordingly, these new donor molecules are excellent candidates for electrocrystallisation experiments and first attempts performed with **2** in the presence of Mo₆O₁₉²⁻ afforded a 2 : 1 salt, formulated as [2]₂[Mo₆O₁₉].

Table 1 Electrochemical data for the newly prepared donor molecules and the analogous phosphines

Donor molecule	$E_{1/2}^a/V$	$E_{1/2}^b/V$	Ref.
1	0.35	0.90	This work
2	0.34	0.87	This work
3	0.305	0.83	This work
4	0.28	0.76	This work
<i>o</i> -Me ₂ TTF-PPh ₂ ^b	0.32	0.70	13
Me ₃ TTF-PPh ₂	0.23	0.74	6
<i>o</i> -Me ₂ TTF(PPh ₂) ₂ ^a	0.27	0.81	5
TTF(PPh ₂) ₄ ^a	0.33	0.73	5

^a In CH₂Cl₂ vs. SCE. ^b In CH₃CN vs. SCE.

Analysis of the structural organisation

Neutral **1** crystallises in the monoclinic system, space group $P2_1/c$ with one molecule in a general position in the unit cell (Fig. 1). Bond lengths within the TTF core are in the usual

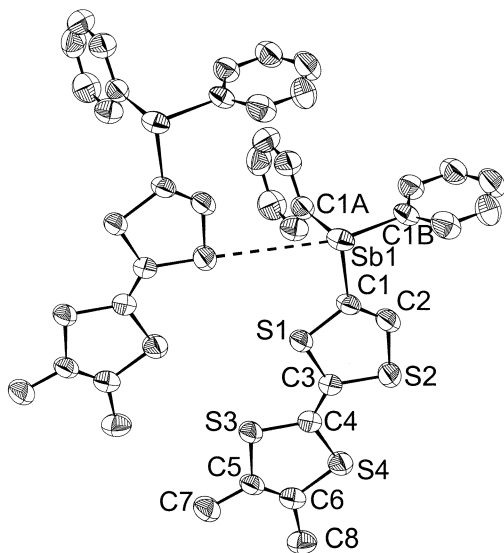


Fig. 1 The coordination sphere of the antimony atom in **1** (ORTEP¹⁸ drawing with thermal ellipsoids at 50% probability).

range for neutral TTF moieties (Table 2). Sb–C distances [2.143(5), 2.150(4), 2.161(4) Å] and C–Sb–C angles [96.01(16), 94.61(16), 93.95(15)°] also compare with those described for the tertiary Ph₃Sb stibine for example [av. Sb–C: 2.155(9), C–Sb–C: 95.1(3)–98.0(3)°].⁸ In the solid state (Fig. 1), the antimony atom completes its coordination sphere through one Sb···S contact at 4.01(5) Å, slightly above the sum of the van der Waals radii⁹ which amounts to 1.80 (S) + 2.12 (Sb) = 3.92 Å, and involving one sulfur atom pertaining to a neighbouring

molecule by translation along the *z* axis. As a consequence, the geometry around the Sb atom, taking into account its lone pair, can be considered as intermediate between a trigonal bipyramid and square pyramid depending on the location of the lone pair.

The neutral *ortho* distibine **3** crystallises in the monoclinic system, space group $C2/c$ with one molecule in a general position in the unit cell (Fig. 2). Bond lengths and distances within

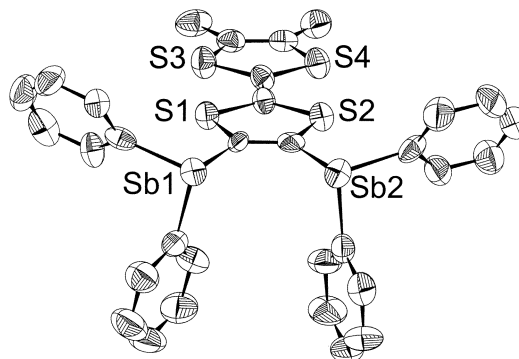


Fig. 2 ORTEP view of the distibine **3** showing the relative orientation of the two SbPh₂ groups.

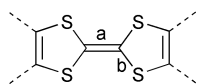
the TTF core and around the antimony atom are in the expected range (Table 2). Of particular interest is the relative orientation of the two diphenyl stibino groups. As shown in Fig. 2, the lone pairs of the two Sb atoms point towards rather than away from each other and are therefore essentially localised within the TTF mean plane. This orientation differs from what is observed in the only other structurally characterised *o*-distibine, *i.e.* 2,3-bis(diphenylstibino)maleic anhydride,¹⁰ where the lone pair of one of the SbPh₂ groups are oriented almost perpendicular to the maleic anhydride mean plane. In the solid state (Fig. 3), the molecules of the *ortho* distibine **3** are organised into stacks along the *b* axis where the TTF moiety fits in between the two SbPh₂ arms of the molecules with the shortest Sb···S intermolecular contacts observed at 4.04–4.08 Å. It is hoped that such an organisation could be maintained in cation radical salts of **3** since it would allow for an effective electronic delocalisation through the HOMO···HOMO overlap of the TTF moieties. However, no such salts with **3** could be isolated up to now; only with the monostibine **2**, *i.e.* Me₃TTF–SbPPh₂, as described below.

The electrocrystallisation of **2** in the presence of the tetrabutyl ammonium salt of the Linquist anion [Mo₆O₁₉]²⁻, [n-Bu₄N]₂[Mo₆O₁₉], afforded indeed a 2 : 1 salt, formulated as [2]₂[Mo₆O₁₉]. It crystallises in the monoclinic system, space group $C2/c$ with one [Mo₆O₁₉]²⁻ anion located on an inversion centre while the donor molecule is in a general position in the unit cell (Fig. 4). Bond distances within the TTF core exhibit the

Table 2 Geometrical characteristics of the TTF core and the Sb environment in the neutral and oxidised donor molecules (The range of values is given together with the averaged value in italics)

	C=C bond (a)/Å	C–S bonds (b)/Å	Sb–C bonds/Å	C–Sb–C°
1	1.337(5)	1.749(4)–1.767(4) <i>1.757</i>	2.143(5)–2.161(4) <i>2.152</i>	93.9(1)–96.0(1) <i>94.8</i>
3	1.368(11)	1.749(8)–1.761(8) <i>1.754</i>	2.116(9)–2.142(9) <i>2.130</i>	93.3(3)–99.3(3) <i>96.4</i>
2⁺⁺ ^a	1.390(6)	1.707(5)–1.727(5) <i>1.716</i>	2.148(5)–2.177(5) <i>2.159</i>	93.8(2)–99.0(2) <i>95.5</i>

^a In [2]₂[Mo₆O₁₉].



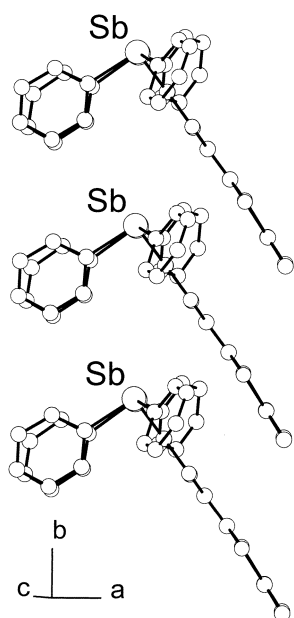


Fig. 3 The stacking of the neutral distibine **3** along the *b* axis.

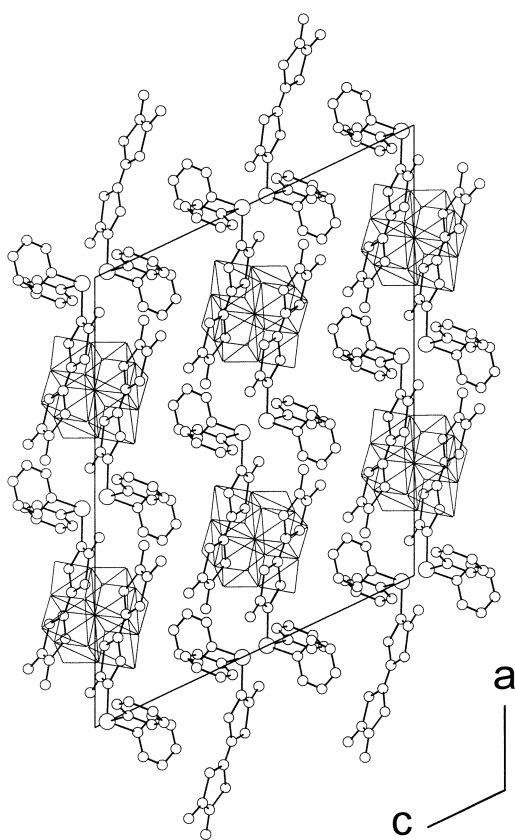


Fig. 4 A view of the unit cell of $[2]_2[Mo_6O_{19}]$ showing the mixed organic-inorganic (*b,c*) slabs. The detail of one of those slabs is shown in Fig. 5.

usual C=C lengthening and C-S shortening by comparison with the neutral **1** (Table 2), a signature of the cation radical state of the donor molecule. In the solid, the donor molecules are associated into inversion-centred dyads with a very short interplanar distance observed at 3.363(1) Å. Those dyads alternate with the inorganic moieties in the *bc* planes, as shown in Fig. 5 where one of those hybrid slabs is represented. The short interplanar distance and the almost eclipsed interaction within the dyads are the signature of a strong bonding interaction between the two $[Me_3TTF-SbPh_2]^+$ radical species, as also confirmed

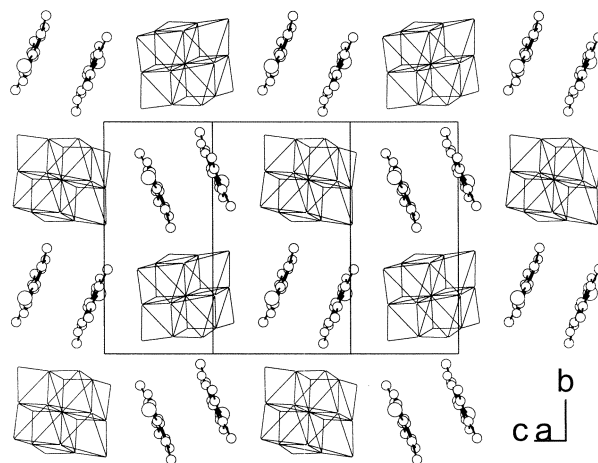


Fig. 5 A view of one of the *b,c* planes in $[2]_2[Mo_6O_{19}]$ showing the facet-to-face arrangement of the organic dyads.

by the large calculated $\beta_{HOMO \dots HOMO}$ interaction energy within the dyad, found here at 1.15 eV. As a consequence the two radicals are associated in the bonding combination of the two HOMO to afford isolated diamagnetic $[2]_2^{2+}$ dyads, separated from each other by the $[Mo_6O_{19}]^{2-}$ dianions. Of particular note is the absence of short Sb \dots Sb or Sb \dots S intermolecular distances in $[2]_2[Mo_6O_{19}]$ where the SbPh₂ moieties fill the space inbetween the hybrid slabs identified above; the behaviour is dominated here by the S \dots S overlap interactions of the open-shell species. It should be stressed that the isolation of this cation radical salt fulfils our expectations about the increased stability of stibines relative to phosphines toward the one-electron oxidation of the TTF core. In order to decrease the steric demand of the phenyl substituents, we are now considering the preparation of monostibines incorporating two or three TTF moieties.

Experimental

The solvent Et₂O was freshly distilled under N₂ over sodium and benzophenone before use. SbClPh₂,¹¹ TTF,¹² *o*-DMTTF¹³ and Me₃TTF¹⁴ were prepared according to published procedures. Melting points are uncorrected. ¹HNMR spectra were recorded in CDCl₃, containing TMS as internal standard on a Bruker Avance DRX 500 MHz spectrometer. Mass spectra were obtained by chemical ionization on a Bruker Biflex III mass spectrometer. Elemental analyses were performed at the Institut de Chimie des Substances Naturelles, CNRS, Gif-sur-Yvette, France.

Synthesis

3-Diphenylstibino-3',4'-dimethyltetraathiafulvalene 1. To a solution of *o*-DMTTF (0.465 g, 2 mmol) in dry Et₂O (40 mL) was added successively at -78 °C diisopropylamine (0.31 mL, 2.2 mmol) and *n*-BuLi (2 M solution in hexane, 1.1 mL, 2.2 mmol). A yellow precipitate formed immediately. After stirring at -78 °C for 2 h, the yellow suspension was treated dropwise with chloro(diphenyl)antimony (0.654 g, 2.1 mmol) in dry Et₂O. The resultant solution was slowly warmed to room temperature and stirred overnight. The suspension was filtered through Celite® and silica gel (toluene as eluant) and the solvent was removed. The residue containing **1** and unreacted *o*-Me₂TTF was purified by subliming *o*-Me₂TTF at 75 °C. Recrystallisation of the residue from Et₂O afforded *o*-Me₂TTF-SbPh₂ as orange crystals (0.556 g, 55%), mp 127–128 °C [Calc. (found) for C₂₀H₁₇S₄Sb: C, 47.67 (47.35); H, 3.37 (3.38); S, 25.93 (25.28)%]; δ_H (CDCl₃, TMS) 1.90 (s, 6H, Me), 6.24 (s, 1H, TTF-H), 7.37 (m, 6H, Ph), 7.53 (m, 4H, Ph); MS-CI *m/z* 174 (100), 506 (M⁺, 81).

Table 3 Crystallographic data

	Me ₂ TTF–SbPh ₂ , 1	Me ₂ TTF(SbPh ₂) ₂ , 3	[2] ₂ [Mo ₆ O ₁₉]
Formula	C ₂₀ H ₁₇ S ₄ Sb	C ₃₂ H ₂₆ S ₄ Sb ₂	C ₄₂ H ₃₈ Mo ₆ O ₁₉ S ₈ Sb ₂
Formula mass	507.33	782.27	1922.34
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	7.7888(16)	40.546(4)	24.630(5)
<i>b</i> /Å	38.875(8)	6.3151(4)	13.868(3)
<i>c</i> /Å	6.8578(14)	24.613(2)	19.166(4)
β /°	92.87(3)	99.526(11)	115.83(3)
<i>V</i> /Å ³	2073.9(7)	6215.4(9)	5892(2)
<i>T</i> /K	293(2)	293(2)	293(2)
<i>Z</i>	4	8	4
μ /mm ⁻¹	1.734	2.028	2.486
Data collected	18941	25617	30703
Independent data	4612	6151	5503
<i>R</i> _{int}	0.0558	0.1607	0.0652
Observed data [<i>I</i> > 2σ(<i>I</i>)]	2981	2466	3663
Parameters refined	226	343	349
<i>R</i> (<i>F</i>) _{obs}	0.0339	0.0497	0.0337
<i>wR</i> (<i>F</i> ²) _{all}	0.0867	0.0891	0.0745

3-Diphenylstibino-4,3',4'-trimethyltetrathiafulvalene 2. To a solution of Me₂TTF (0.493 g, 2 mmol) in dry Et₂O (40 mL) was added successively at –78 °C, diisopropylamine (0.31 mL, 2.2 mmol) and *n*-BuLi (2 M solution in hexane, 1.1 mL, 2.2 mmol). A yellow precipitate formed immediately. After stirring at –78 °C for 2 h, the yellow suspension was treated dropwise with chloro(diphenyl)antimony (0.654 g, 2.1 mmol) in dry Et₂O. The resultant solution was slowly warmed to room temperature and stirred overnight. The suspension was filtered through Celite® and silica gel (toluene as eluant) and the solvent was evaporated. Recrystallisation from Et₂O afforded **2** as orange crystals (0.6 g, 59%), mp 140–143 °C [Calc. (found) for C₂₁H₁₉S₄Sb: C, 48.54 (48.38); H, 3.73 (3.67); S, 24.41 (24.60)%]; δ_H (CDCl₃, TMS) 1.90 (bs, 6H, *o*-Me₂), 2.19 (s, 3H, Me), 7.37 (m, 6H, Ph), 7.53 (m, 4H, Ph); MS–CI *m/z* 520 (M⁺).

3,4-Bis(diphenylstibino)-3',4'-dimethyltetrathiafulvalene 3. To a solution of *o*-Me₂TTF (0.697 g, 3 mmol) in dry Et₂O (100 mL) was added successively at –78 °C, diisopropylamine (0.9 mL, 6.2 mmol) and *n*-BuLi (2 M solution in hexane, 3.1 mL, 6.2 mmol). A yellow precipitate formed immediately. After stirring at –78 °C for 1 h and at 25 °C for 30 min, the yellow suspension was treated dropwise with chloro(diphenyl)antimony (1.931 g, 6.2 mmol) in dry Et₂O at –78 °C. The resultant solution was slowly warmed to room temperature and stirred overnight. The suspension was filtered and the solid portion was washed twice with ether and the product was obtained by washing the solid with CH₂Cl₂. Recrystallisation from Et₂O afforded **3** (1.25 g, 53.3%), mp 217–220 °C [Calc. (found) for C₃₂H₂₆S₄Sb₂: C, 48.61 (49.13); H, 3.36 (3.35); S, 16.24 (16.39)%]; δ_H (CD₂Cl₂, TMS) 1.88 (bs, 6H, Me), 7.36–7.39 (m, 12H, Ph), 7.54–7.57 (m, 8H, Ph); MS–CI *m/z* 506 (M⁺ – SbPh₂), 782 (M⁺).

3,3',4,4'-Tetrakis(diphenylstibino)tetrathiafulvalene 4. To a solution of TTF (0.408 g, 2 mmol) in dry THF (40 mL) was added successively at –78 °C, diisopropylamine (1.4 mL, 10 mmol) and *n*-BuLi (2 M solution in hexane, 5 mL, 10 mmol). A yellow precipitate formed immediately. After stirring at –78 °C for 3 h, the yellow suspension was treated dropwise with chloro(diphenyl)antimony (3.1 g, 10 mmol) in dry THF at –78 °C. The resultant solution was slowly warmed to room temperature (colour changes from orange to dark brown and to dark orange) and stirred overnight. THF was removed under vacuum and diethyl ether (~100 mL) was added. The suspension was filtered over Celite® and the solid portion was washed twice with toluene. The solvents were removed, and the solid residue recrystallised from a Et₂O–hexane mixture to afford **4** (2 g, 76.7%), mp 98–100 °C [Calc. (found) for C₅₄H₄₀S₄Sb₄: C,

47.72 (49.73); H, 3.48 (3.09); S, 10.11 (9.83)%]; δ_H (CDCl₃, TMS) 7.32 (m, 3H, Ph), 7.47 (m, 2H, Ph); MS–CI *m/z* 420 (100), 721, 1028 (M⁺ – SbPh₂), 1304 (M⁺).

Electrochemistry

Cyclic voltammetry experiments were performed in CH₂Cl₂ containing 0.1 M *n*-Bu₄NPF₆ as electrolyte at a scan rate of 100 mV s⁻¹ with an Ag⁺/AgCl reference electrode, platinum working and counter electrodes. Electrocrystallisation experiments were performed in two-compartment cells with Pt electrodes (length = 2 cm, diameter = 1 mm) at 25 °C with a current of 1 μA. The electrolyte, (*n*-Bu₄N)₂(Mo₆O₁₉), was prepared according to published procedures¹⁵ and recrystallised before use. Solvents were dried over activated Al₂O₃ and degassed.

X-Ray crystallography

The X-ray single crystal measurements were carried out using a Stoe IPDS with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Details about data collection and structure refinements are given in Table 3. The structures were solved by direct methods (SHELXS)¹⁶ and refined by full-matrix least-squares (SHELXL).¹⁷ The hydrogen atoms were included at idealised positions and not refined (riding model).

CCDC reference numbers 187526–187528.

See <http://www.rsc.org/suppdata/dt/b2/b205594p/> for crystallographic data in CIF or other electronic format.

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