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1,4-Dihydro-1,4-diphosphinine fused with two tetrathiafulvalenes†

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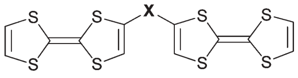
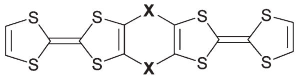
Electrochemical and theoretical investigations demonstrate through-bond interactions between two TTF moieties fused to a 1,4-dihydro-1,4-diphosphinine, for which the single crystal X-ray structure of the *cis* isomer is described together with that of a mixed-valent, charge-localized, radical cation salt with $Mo_6O_{19}^{2-}$, obtained upon electrocrystallization of the same *cis* isomer.

In multi-electron donor systems such as dimeric and higher oligomers of tetrathiafulvalenes (TTF),[1] the control of intramolecular through-bond and/or through-space interactions between the TTF units is of paramount importance to allow for multi-stage redox behavior, as well as their consequences on the stoichiometry and band structure patterns within the corresponding radical cation salts.[2,3] In that respect, main group elements offer the unique opportunity to link in a close vicinity two TTF units whose mutual orientation and degree of interaction depend on the nature of the bridging heteroatom. Most of these derivatives are of $X(TTF)_2$ type (X = S,[4] Se,[4] Te,[5] $SiMe_2$,[6a] Hg[6a]), thus presenting a flexibility due to the free rotation around the $X–C_{TTF}$ simple bonds, which strongly limits the intramolecular through-bond interactions. Enhancement of the molecular rigidity has been achieved with donors formulated as $X_2(TTF)_2$ in which two TTF units are fused to a 1,4-dithiine (X = S)[7] or 1,4-ditellurine (X = Te).[8]



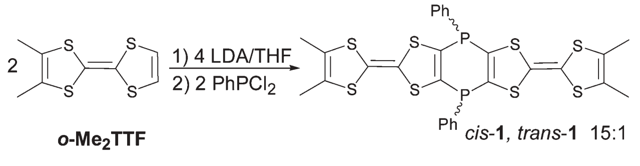
$X(TTF)_2$
X = S, Se, Te, $SiMe_2$, PPh, Hg



$X_2(TTF)_2$ X = S, Te

Of particular interest is also the use of the phosphorus(III) atom as a bridge between two or three TTF units, as in the flexible $PhP(TTF)_2$[6b] and $P(TTF)_3$[9] derivatives, since it can also easily coordinate a metallic center, as demonstrated with chelating diphosphines bearing a single TTF unit[10] and their radical cation salts.[11] We report herein the first example of a $(PPh)_2(TTF)_2$ system which combines the rigidity of the $X_2(TTF)_2$ model with the coordination ability of the phosphines, that is, two TTF moieties fused to a 1,4-dihydro-1,4-diphosphinine heterocycle.

The synthesis of the redox active 1,4-dihydro-1,4-diphosphinine (**1**) was achieved in a one-pot procedure, by bis-lithiation of *o*-dimethyltetrathiafulvalene (*o*-DMTTF) with LDA, followed by trapping the resulting dianion with one equivalent of phenyldichlorophosphine ($PhPCl_2$), as depicted in Scheme 1.† The molecule is thus obtained as a *cis–trans* mixture, in which the *cis* isomer is largely predominant, in a *cis* : *trans* ratio of about 15 : 1, as determined by ^{31}P NMR spectroscopy. Although the phosphorus atoms are constrained in a rigid conformation, their resonances appear in the ^{31}P NMR spectrum at chemical shifts (−21.5, −25.6 ppm) comparable to those of flexible bis(TTF)-phosphines such as $(o\text{-DMTTF})_2PPh$ (−23.2 ppm).[6a] The ultimate proof for the *cis–trans* attribution was provided by an X-ray analysis on single crystals obtained by recrystallization of the isomers mixture from THF or toluene. Note that *trans*-**1** seems to be more soluble and, because of the low amount, its isolation in a pure analytical form was not possible. The THF solvate of *cis*-**1** crystallizes in the triclinic system, space group $P\bar{1}$,‡ with one independent molecule in a general position (Fig. 1). The central dihydrodiphosphinine ring is weakly folded along the P(1)–P(2) hinge by 30.4(1)°, within a boat type conformation. Notice that this folding is much weaker than that reported for the 1,4-ditellurine counterpart (67.8°).[8b]



Scheme 1 One-pot synthesis of **1**.

The cyclic voltammetry of *cis*-**1** (Fig. 2) shows unambiguously the presence of four reversible oxidation waves, very likely corresponding to the series radical cation ($E_{1/2}{}^1$ = 0.43 V), dication ($E_{1/2}{}^2$ = 0.55 V), trication ($E_{1/2}{}^3$ = 0.93 V) and tetracation ($E_{1/2}{}^4$ = 1.05 V).

Of particular note is the large potential differences between the first and second (120 mV), but also between the third and fourth waves (120 mV), in sharp contrast with the previously described flexible $(o\text{-DMTTF})_2PPh$ phosphine[6] or the rigid, but strongly folded, dithiine[7] and ditellurine[8a] derivatives where oxidations to the tri- and tetracationic states could not be separated under those conditions. On the other hand, they favorably compare with those described for TTF dimers with fully conjugated bridges such as benzo[12] or pyrazino[13] rings. Therefore, the striking splitting of both

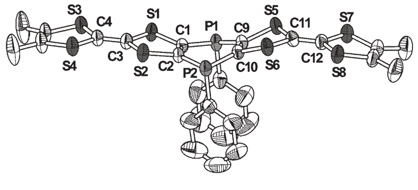


Fig. 1 ORTEP view of *cis*-**1**.

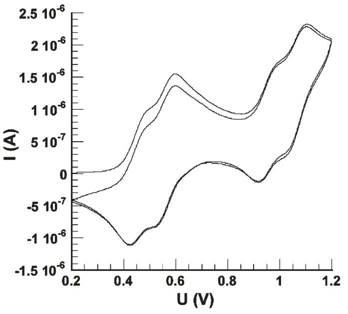


Fig. 2 Cyclic voltammetry of *cis*-**1** (ref. Ag/AgCl, 0.2 M $TBAPF_6$ in CH_2Cl_2, 0.1 V s^{-1}).

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† Electronic supplementary information (ESI) available: detailed synthesis of **1**. See http://www.rsc.org/suppdata/cc/b4/b412193g/

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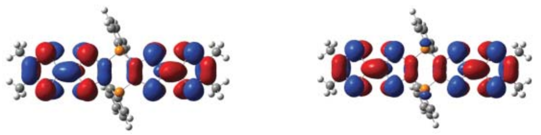

Fig. 3 HOMO (left) and HOMO-1 (right) of *cis*-**1** (B3LYP/6-31G*).

oxidation waves in *cis*-**1** is very likely due to a significant interaction between the two TTF moieties through the almost planar dihydrodiphosphinine ring, since a through-space interaction should be negligible when considering the rigidity of the central ring, an original feature not encountered in the few $X_2(TTF)_2$ systems described so far.

In order to check this assumption, we have undertaken theoretical calculations at DFT (B3LYP/6-31G*) level, aimed at optimizing the geometry of *cis*- and *trans*-**1**, and, subsequently, at generating the sequence of molecular orbitals. For both isomers, geometry optimizations lead to symmetrical structures, with a calculated folding of the diphosphinine along the P(1)–P(2) hinge in *cis*-**1** of only 2.3° and an essentially planar diphosphinine in *trans*-**1**. The difference between the equilibrium structure energies of *cis*- and *trans*-**1** (0.16 kcal mol^{-1}) indicates that the *cis* isomer is more stable than the *trans* one, as experimentally observed. As emphasized in Fig. 3, the HOMO consists of the antisymmetrical combination of two TTF π-orbitals with a nodal plane running through the phosphorus atoms, whereas the HOMO-1 is the corresponding symmetrical combination with a sizeable contribution from the phosphorus atoms and the corresponding adjacent *ipso* C atoms,[14] at the origin of the non-degeneracy of HOMO and HOMO-1 orbitals. Indeed, the molecular orbital diagram of *cis*-**1** shows an energy gap of 41.6 meV between the HOMO and HOMO-1.[15] Thus, the formally anti-aromatic 1,4-dihydrodiphosphinine behaves here as a delocalized bridge between the two redox active moieties.

As a confirmation of the electrochemical behavior of our redox active diphosphinine, the electrocrystallization of *cis*-**1** in the presence of the Linquist anion $Mo_6O_{19}^{2-}$ provided single crystals of a mixed valence salt, formulated as $[(o\text{-DMTTF})_2(PhPO)_2]_2Mo_6O_{19}\cdot 2H_2O$, that is a salt of the radical cation and not the dication.

Note that in the course of the electrocrystallization experiment, the phosphorus atoms were oxidized into phosphine oxide.[16] The salt crystallizes in the monoclinic system, space group *C*2/*m*,‡ with the $Mo_6O_{19}^{2-}$ anion on a 2/*m* site and the organic molecule on the mirror plane. An organic–inorganic segregation occurs along *c*, with slabs of oxidized donors in the *ab* plane, and, within the organic slabs, chains running along *a* (Fig. 4). Moreover, the molecule is totally unsymmetrical, since one TTF moiety is essentially flat, with a folding angle around S(1)–S(1) axis of only 9.49°(35), whereas the other is strongly folded, by 37.49°(66) around the S(3)–S(3) hinge. Within the chains along *a*, the flat TTF moieties of neighboring molecules adopt an eclipsed ring-over-ring configuration with short intermolecular S–S distances (3.36 Å), while the folded TTF moieties adopt a staggered bond-over-ring configuration, with intermolecular S–S distances above 3.79 Å. Extended Hückel calculations of the overlap interaction energies (β) of both configurations indicate the existence of a strong interaction ($\beta = 1.18$ eV) within the eclipsed dyads, with charge localization, and a much weaker one ($\beta = 0.07$ eV) between the slipped neutral dyads, thus confirming the insulating behaviour of the compound ($\sigma < 10^{-5}$ S cm^{-1}).

Hence, the isolation of a radical cation salt of *cis*-**1** further confirms the strong electronic communication between the two redox active moieties through the 1,4-dihydrodiphosphinine ring. The synthesis of this redox active, non-chelating diphosphine also opens wide perspectives towards cyclic bimetallic systems and extended coordination polymers, as well as combination of the mixed-valent $\mathbf{1}^{\cdot+}$ radical cation species with paramagnetic metallic centers.[17] Furthermore, the through-bond interactions

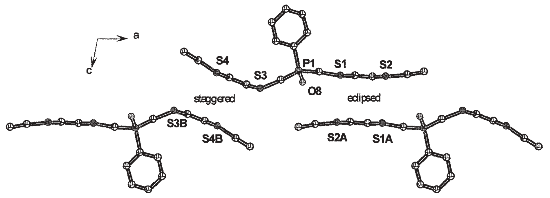

Fig. 4 Interacting radical cations of *cis*-**1**-bis(oxide) in $[(o\text{-DMTTF})_2(PhPO)_2]_2Mo_6O_{19}$ (equivalent positions: $1 - x, y, 1 - z$ (A) and $-x, y, 1 - z$ (B)).

and coordination properties of this rigid $X_2(TTF)_2$ ligand can also be tuned by using different links, either through chemical modifications of the phosphorus bridges (X = PR=S, PR=O, PR_2^+), or by changing the heteroatom nature (X = SbR, SiR_2).

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Notes and references

‡ Crystal data for *cis*-**1**: $C_{28}H_{22}P_2S_8\cdot THF$, $M = 748.98$, triclinic, space group $P\bar{1}$, $a = 12.5674(14)$, $b = 13.0748(14)$, $c = 13.2647(14)$, $\alpha = 62.261(11)$, $\beta = 69.342(12)$, $\gamma = 67.485(12)$, $V = 1741.0(3)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\mu = 0.631$ mm^{-1}, 17474 reflections measured, 6208 unique reflections, $R = 0.041$, $R_w = 0.100$. For $([(cis\text{-}\mathbf{1})O_2]_2Mo_6O_{19}\cdot 2H_2O)$: $C_{56}H_{48}O_{25}P_4S_{16}Mo_6$, $M = 2333.42$, monoclinic, space group *C*2/*m*, $a = 20.573(3)$, $b = 14.086(2)$, $c = 14.0657(15)$, $\beta = 100.809(14)$, $V = 4003.8(9)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\mu = 1.481$ mm^{-1}, 15710 reflections measured, 3917 unique reflections, $R = 0.078$, $R_w = 0.222$. CCDC 239190 and 239193 respectively. See http://www.rsc.org/suppdata/cc/b4/b412193g/ for crystallographic data in .cif or other electronic format.

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