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FIRST PHOSPHORUS MACROCYCLES INCORPORATING TETRATHIAFULVALENE (TTF) MOIETIES

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Summary : Reaction of phosphodihydrazides ***1a-b*** *with the [Z]- isomer of the diformyl-tetrathiafulvalene (TTF) derivative* ***4*** *leads to the 26-membered macrocycles* ***5a,b*** *incorporating two TTF moieties.*

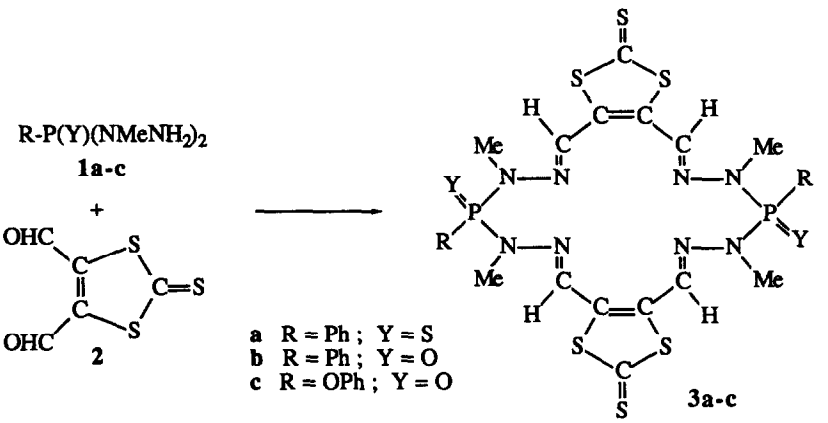
Since the discovery of the high electrical conductivity of cation-radical salts derived from tetrathiafulvalene (TTF), subtle structural modifications of this heterocycle have allowed to reach organic superconductors[1], and many efforts are still devoted[2-4] in order to raise their Tc (present record 11.6 K.[5]). An attractive trend in this area has consisted in incorporating the TTF moiety in a host-cage structure (e.g. polyoxa[6]-aza- and thia-macrocycles.[7,8]).

Recent papers[6,7] prompt us to report our findings in this topic, i.e. the synthesis of compounds **5a,b** having two TTF moieties incorporated into a polyazaphosphorus macrocycle.

We have previously shown that the [2+2] cyclocondensation of two phosphodihydrazides (such as **1a-c**) and two dialdehydes OHC-X-CHO afforded 18, 20 and 22 atoms polyazaphosphorus macrocyclic compounds[9,10] ; moreover the later were shown to exhibit good cation binding properties.[9,10] Therefore we decided to apply our synthetic strategy to the [Z]- and [E]-[11] diformyl TTF derivatives **4** and **4'**[12], and to their precursor, the diformyl dithiole thione **2**.[12]

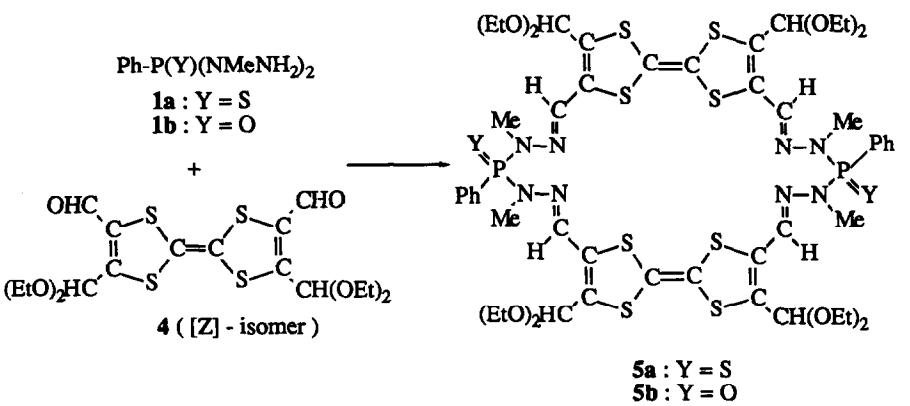
Simultaneous slow addition of a methanolic solution of phosphodihydrazides **1a-c** (1 eq.) and a methanolic solution of the diformyl dithiole thione **2** (1 eq.) to methanol leads to the formation of original 18-

membered rings **3a-c** in near quantitative yield(Scheme I).[13]



Scheme I

In the same way, treatment of phosphodihydrazides **1a-b** with the diformyl tetrathiafulvalene **4** leads to macrocycles **3a** or **3b** respectively in 60 and 80% yield (scheme II).



Scheme II

Such [2+2] condensation reactions do not necessitate high dilution techniques. Simple filtration affords pure compounds as red powders. Their structures were determined by NMR and I.R. spectroscopies, cryoscopic measurements as well as microanalysis.[13] ^{31}P NMR chemical shifts (**5a** $\delta^{31}P = 78.6$; **5b** $\delta^{31}P = 23.8$ ppm) are in the expected range for such species.[9a,b] Indeed upfield shifts of 6-7 ppm are characteristic of the cyclisation of phosphodihydrazides into macrocycles.[9] Noteworthy is the fact that the ring size has no direct in-

fluence on the value of the ^{31}P chemical shift.[9b]

^{1}H NMR spectra exhibit singlets at 8.2 (**5a**) and 8 (**5b**) ppm due to imino protons. Moreover ^{13}C NMR spectra reflect the structure of these macrocycles and are fully consistent with the presence of imino carbon atoms. None of the IR spectra exhibits any absorption at 3250-3400 cm^{-1} that could be attributed to unreacted hydrazine.

Mass spectrometry (field desorption, chemical ionisation or FAB) is consistent with the proposed structures even if the molecular peak is not detected (for ex: **5a** $M^{+\cdot}-(EtO)_2 = 1226$; $M^{+\cdot}-2(EtO)_2 = 1136$; $M^{+\cdot}-3(EtO)_2 = 1046$; $M^{+\cdot}-4(EtO)_2 = 936$ etc...).

The π-donor ability of **5b** was measured by cyclic voltammetry, with two poorly reversible peaks at E^1_p = + 0.61 V and E^2_p = + 1.05 V/S.C.E (S.C.E = standard calomel electrode) at 20°C [1,1,2-trichloroethane, $Bu^n_4ClO_4$ (0.1 M), **5b** (10^{-3}M)] (+ 0.84 V and + 1.24 V respectively for **4**).

A mixture of two main phosphorus species ($\delta^{31}P$ = 81.1 and 78.6 ppm) was obtained when the reaction was performed under the same experimental conditions with solutions of the diformyltetrathiafulvalene **4**, **4'** (mixture of [Z] and [E]-isomers) and phosphodihydrazide **1a**. Macrocycle **5a** was isolated from this mixture in 20% yield.

$$\mathbf{1a} + [\,\mathbf{4} + \mathbf{4'}\,] \rightarrow \mathbf{5a} + \text{polymers}$$

On the other hand, cyclisation does not occur when the [E]-isomer **4'** is reacted with **1a**. The ^{31}P NMR spectrum reveals a signal at 81.1 ppm besides that of the starting compound **1a** (86.6 ppm). Stirring for four additional days allows to get only a poorly soluble polymeric material ($\delta^{31}P$ = 81.1 ppm).

$$\mathbf{1a} + \mathbf{4'} \rightarrow \text{polymers}$$

In conclusion only the [Z]-isomer **4** allows the synthesis of new 26-membered rings possessing 2 TTF moieties whose π-donor ability has been evaluated. Full characterisation of oligomeric species obtained from **4'** as well as investigations of the properties of phosphorus macrocycles **3a-c**, **5a-b** are underway.

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13 **3a)** ^{31}P NMR ($CDCl_3$): δ=79.36; ^{1}H NMR ($CDCl_3$): δ=3.16 (br. s, 12H, P-N-CH_3) 7.4-7.6 (m, 10H C_6H_5) 7.91 (v.br. s, 4H, HC=N). ^{13}C NMR ($CDCl_3$): δ=32.6 (br. s, P-N-CH_3) 139.3 (s, HC=N) 212. (s, C=S). IR (KBr) 1640 (νC=N)cm^{-1}. Mass spectrum m/e: 768. Anal. Calcd. for $C_{26}H_{26}N_8P_2S_8$: C 40.63; H, 3.41; N, 14.59. Found: C, 40.48; H, 3.31; N, 14.42.

3b) ^{31}P NMR ($CDCl_3$): δ=24.9 ppm; ^{1}H NMR ($CDCl_3$): δ=3.15 (br. s, 12H, P-N-CH_3), 7.4-7.6 (m 10H, C_6H_5) 7.85 (br. s, 4H, HC=N). ^{13}C NMR ($CDCl_3$): δ= 31.89 (s. P-N-CH_3) 139.1 (s, HC=N 212.07 (s, C=S). IR (KBr) 1650 (w, νC=N) cm^{-1}. Mass spectrum m/e: 736. Anal. Calcd. fo $C_{26}H_{26}N_8O_2P_2S_6$: C, 42.39; H, 3.56; N 15.28. Found: C, 42.21; H, 3.51; N 15.11.

3c) ^{31}P NMR ($CDCl_3$): δ=0.1; ^{1}H NMR ($CDCl_3$): δ=3.2 (br. s, 12H, P-N-CH_3) 7.2 (m, 10H, C_6H_5) 7. (v. br. s, HC=N); ^{13}C NMR ($CDCl_3$): δ=33.2 (s. P-N-CH_3) 138.8 (br. s, HC=N) 210.9 (broad s. C=S). IR (KBr) 1660 (νC=N)cm^{-1}. Mass spectrum m/e: 768. Anal. Calcd. for $C_{26}H_{26}N_8O_4P_2S_6$: C, 40.63; 3.41; N, 14.59. Found: C, 40.41; H, 3.28; N, 14.39.

5a) ^{31}P NMR ($CDCl_3$): δ=78.6 ppm; ^{1}H NMR ($CDCl_3$): δ=1.21 (br. s, 24H, OCH_2-$\underline{CH_3}$), 3.3 (br. 12H, P-N-CH_3) 3.61 (br. s, 16H, $O\underline{CH_2}CH_3$), 5.5 (s, 4H, $\underline{CH}(OEt)_2$), 7.8 (m, 10H, C_6H_5), 8,2 (s, 4H $\underline{CH}$=N) ppm; ^{13}C NMR ($CDCl_3$): δ=15.4 (s, $OCH_2\underline{CH_3}$), 32.01 (br. s, P-N-$\underline{CH_3}$), 61.3 (s, O-$\underline{CH_2}$-CH_3 98.3 (s, $\underline{CH}(OEt)_2$), 108.7 (s, $S_2\underline{C}$=$\underline{C}S_2$), 128.4-134.7 (m, $\underline{C_6}H_5$, $\underline{C}$=N), 135.0 (s) and 154.5 (s) ($\underline{C}$=$\underline{C}$ ppm. IR (KBr), 1625 (w, νC=N)cm^{-1}. Anal. Calcd. for $C_{52}H_{70}N_8O_8P_2S_{10}$: C, 47, 41; H, 5.36; N, 8.5 Found: C, 46.92; H, 5.02; N, 7.94.

5b) ^{31}P NMR ($CDCl_3$): δ=23.8 ppm; ^{1}H NMR ($CDCl_3$): δ=1.19 (br. s, 24H, $OCH_2\underline{CH_3}$), 3.11 (br. 12H, P-N-$\underline{CH_3}$), 3.59 (br. s, 16H, O-$\underline{CH_2}$-CH_3), 5.5 (s, 4H, $\underline{CH}$(O-CH_2-CH_3)$_2$), 7.6 (m, 10H, $C_6\underline{H_5}$), (s, 4H, $\underline{HC}$=N) ppm; ^{13}C NMR ($CDCl_3$): δ=15.13 (s, O-CH_2-$\underline{CH_3}$), 31.94 (br. s, P-N-$\underline{CH_3}$), 61.3 (s O-$\underline{CH_2}$-CH_3), 97.15 (s, $\underline{CH}$(O-CH_2-CH_3)$_2$), 108.4 (s, S-$\underline{C}$=$\underline{C}$-S), 128-135 (m, $\underline{C_6}H_5$, $\underline{C}$=N), 135.9 and 155.0 (s) ($\underline{C}$=$\underline{C}$)ppm. IR (KBr), 1650 (w, νC=N)cm^{-1}. Anal. Calcd. for $C_{52}H_{70}N_8O_{10}P_2S_8$: C, 48.5 H, 5.45; N, 8.72; Found: C,48.38; H,5.17; N, 8.81.

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