SUPPORTING INFORMATION

EXPERIMENTAL DETAILS

All reactions were carried out under inert gas atmosphere using Schlenk techniques. Argon (Messer Griesheim, purity 4.6 in 50 l steel cylinder) was used as inert gas. The glass vessels used were stored in a 130 °C drying oven, and flame-dried in vacuum at 10^{-3} mbar. Pyridine was dried using commonly known drying methods. P_4S_{10} and elemental sulfur (Aldrich) were used as received.

NMR spectra were recorded using a Jeol EX 400 Eclipse instrument operating at 161.997 MHz. The ^{31}P NMR chemical shift is referred to 85 % H_3PO_4. MS: Jeol MStation JMS-700; in *m/z* (rel.). IR: Perkin-Elmer Spectrum One FT-IR; KBr pellet. Raman: Bruker MULTIRAM 1064 2000R NIR FT, with Nd-YAG laser (1064 nm). The molecular structure of $py_2P_2S_7$ in the crystalline state was determined using an Oxford Xcalibur3 diffraction instrument with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD detector with a X-ray radiation wavelength of 0.71073 Å. The data collection was performed with the CrysAlis CCD software, the data reduction with the CrysAlis RED software.[1,2] The structure was solved with SHELXS-97, refined with SHELXL-97 and finally checked using PLATON.[3-6] The absorptions were corrected by SCALE3 ABSPACK multi-scan method.[7]

Synthesis of $py_2P_2S_7$: 1 mmol P_4S_{10} (442 mg) and 4 mmol elemental sulfur (128 mg) were suspended in 8 mL of pyridine. The reaction mixture was refluxed for two hours, yielding a yellow solution. $py_2P_2S_7$ crystallizes out of the reaction during cooling down to ambient temperature. The crystals were separated from the solution using a G4 frit. Yield: 0.26 g (0.585 mmol) $py_2P_2S_7$ (58.5 % with respect to P_4S_{10}). m.p.: 296 °C (decomposition).

$^{31}P\{^1H\}$ NMR (pyridine, r.t.) = 84.2 ($py_2P_2S_7$); 104.8 ($py_2P_2S_5$)[8].

MS: (EI+): *m/z* = 63.1 (PS), 79.1 (pyridine), 285.9 (P_2S_7), 443.0 ($py_2P_2S_7$).

MS: (DEI+): *m/z* (I_{rel}) = 39 (9), 43 (6), 49 (7), 50 (36), 51 (49), 52 (100), 53 (12), 63 (37, PS), 64 (27), 78 (30), 79 (100, pyridine), 80 (15), 95 (9), 96 (10), 128 (14), 156 (23), 160 (7), 190 (11), 254 (14).

IR-spectrum: (200 mW, RT): $\tilde{\upsilon}$ [cm^{-1}] = 3088 (17), 3060 (18), 1633 (48), 1606 (20), 1532 (46), 1484 (48), 1470 (45), 1452 (4), 1330 (45), 1262 (50), 1194 (37), 1154 (52), 1093 (56), 1053 (19), 1044 (15), 1011 (22), 762 (23). 734 (5), 673 (8), 655 (32), 642 (41), 574 (5), 482 (70), 471 (55), 461 (35), 453 (28), 435 (51), 423 (42).

Raman spectrum (200 mW, RT): $\tilde{\upsilon}$ [cm^{-1}] = 3068(47), 1688(21), 1609(40), 1567(24), 1290(23), 1197(47), 1013(100), 899(21), 738(39), 580(64), 482(80), 461(33), 436(65), 426(8), 413(12), 396(13), 333(41), 310(23), 281(28),259(12), 239(62), 226(30), 187(30), 173(29), 146(20), 126(7).

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CRYSTALLOGRAPHIC DETAILS

$C_{10}H_{10}N_2P_2S_7$; M_r = 444.63; 0.179 x 0.101 x 0.043 mm; monoclinic; $P2_1/c$; a = 13.000(3), b = 8.0185(16), c = 17.332(4) [Å]; β = 97.68(3)°; V = 1790.5(6) Å^3; Z = 4; ρ_{ber} = 1.649 cm^{-3}; μ = 1.051 mm^{-1}; MoK\α radiation; T = 200 K; $2\theta_{max}$ = 25.35; reflns collected: 11002; reflns unique = 3259; R_{int} = 0.0617; $R1/wR2$ (2σ data) = 0.0421/0.8888; max diff peak/hole = 0.375/-0.455.