

Crystal structures of eight- and ten-membered cyclic bisanisylphosphonothioyl disulfanes and comparison with their *P*-ferrocenyl analogues

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Two new crystal structures of eight- and ten-membered cyclic bisanisylphosphonothioyl disulfanes, namely 2,5-bis(4-methoxyphenyl)-1,6,3,4,2λ⁵,5λ⁵-dioxadithiadiphosphocane-2,5-dithione, C₁₆H₁₈O₄P₂S₄, and 2,5-bis(4-methoxyphenyl)-1,6,3,4,2λ⁵,5λ⁵-dioxadithiadiphosphocane-2,5-dithione, C₁₈H₂₂O₄P₂S₄, have been determined and compared to structures of the ferrocenyl analogues. The eight-membered rings have similar conformations (TBC) but the ten-membered macrocycles are differently puckered. Structural parameters of the relevant SPSSPS motif have been analysed and are discussed in detail. Compound **1** was refined as an inversion twin and **2** was refined as a two-component rotational twin.

1. Chemical context

The most widely used sulfur-transfer agents for thionation of carbonyl compounds are the four-membered 2,4-dianisyl-1,3-dithiadiphosphetane disulfide dimer [AnP(μ-S)]₂ and the 2,4-diferrocenyl-1,3-dithiadiphosphetane disulfide dimer [FcP(μ-S)]₂, *i.e.* Lawesson reagent LR (Jesberger *et al.*, 2003) and ferrocenyl Lawesson reagent fLR (Foreman *et al.*, 1996). However, thiophosphine oxides (AnPSO or FcPSO) separating as cyclic trimers during thionation reactions are usually unwanted side-products. On the other hand, the corresponding alkoxyphosphinodithioic acids, *i.e.* An(RO)P(S)SH and Fc(RO)P(S)SH, obtained in a simple reaction between LR or fLR and alcohols, are of considerable interest because they form a plethora of structurally interesting chelate complexes with metal ions (van Zyl & Woollins, 2013).

The reactions between Lawesson's reagent and diols/diphenols have been successfully involved in the preparation of bis(anisylphosphonodithioic) acid derivatives and among them the unique eight-, nine- and ten-membered cyclic bisanisylphosphonothioyl disulfanes (Przychodzeń, 2004). A high-yielding formation of these medium-sized cyclic disulfanes upon oxidation of bis(anisylphosphonodithioic) acid salts by iodine proceeding without oligomeric by-products may be attributed to their fixed structure, containing the most preferred a zigzag motif of the SPSSPS unit. Slightly modified procedures with respect to the original method have recently been applied for the synthesis of related cyclic bis(ferrocenylphosphonothioyl)disulfanes, *e.g.* eight-membered **1a** (Pillay *et al.*, 2015) and ten-membered **2a** (Hua *et al.*, 2017) and their crystal structures have been determined. Here we report

