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Medium-sized cyclic bis(anisylphosphonothioyl)-disulfanes and their corresponding cyclic sulfane-structures and most characteristic reactions†

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Cyclic 8-, 9-, 10-, and 12-membered bis(anisylphosphonothioyl)disulfanes were synthesized. Next, structurally related 7 to 9-membered *cis* and *trans* sulfanes were isolated as a result of sulfur atom extrusion from the parent cyclic disulfanes. The results of the desulfurization of the disulfanes using triphenylphosphine were compared to the results obtained for desulfurization of the respective bis(anisylphosphodithioates) with the aid of 2-chloro-*N*-methylpyridinium iodide. Cyclic disulfanes predominantly provide *trans*-sulfanes, and the expansion of their ring sizes causes the *cis/trans* isomer ratio of the cyclic sulfanes to increase. Moreover, bis(anisylphosphodithioates) mainly afford *cis*-sulfanes, and the *cis/trans* isomer ratio is greater than 3:1. Mechanistic and stereochemical aspects of cyclic disulfane desulfurization have been presented to elucidate the above findings. Although it was suggested by calculations that *cis*-sulfanes are more thermodynamically stable than their respective *trans* isomers, the cyclisation is a kinetically controlled reaction, which results in predominance of *trans*-sulfanes in the case of *trans*-disulfane desulfurization. Disulfanes exhibit thermal and solvolytic stability (except in wet DMSO). A characteristic persistent deep-blue coloration of methanolic ammonia solutions is an unusual feature of cyclic disulfanes. The mechanism of their ammonolysis has been studied and has been compared to that of the respective reaction performed on acyclic disulfanes. Ammonia solution of an acyclic disulfane is colourless and contains phosphosulfenamide and dithiophosphate, while the respective mixture of cyclic disulfane consists of thiophosphonoamide-phosphonodithioate, *O*-methyl thiophosphonate-phosphonodithioate and deep blue sulfur-ammonia species. Detailed X-ray structural analysis was performed for all *trans*-disulfanes and *cis*- and *trans*-sulfanes. They were compared to each other and to their acyclic or cyclic known analogs that comprise common subunits. 8-, 9-, 10-, and 12-membered disulfanes exist as *trans* isomers exclusively both in the solid state and in solution. They are significantly more stable than their hypothetical *cis* isomers, as shown by DFT calculations. The PSSP torsion angles of cyclic disulfanes lie in the range of 94° to 125° and increase with the size of the ring. These values are greater than the typical torsion angles found for the respective non-cyclic disulfanes. The greater stability of the *cis*-sulfanes was confirmed by calculations and can be ascribed mainly to the characteristic anisyl–anisyl stacking. Special attention was paid to the importance and the role of weak hydrogen bonds (CH...O/S) in conformational stabilization and intermolecular interactions. The conformations of cyclic disulfanes and cyclic sulfanes found in the crystalline state were also preserved in solution (variable temperature NMR). A Karplus relationship has been established between the dihedral angles and vicinal H–P coupling constants for all disulfanes and sulfanes. The effects of solvent on the ¹H NMR chemical shifts (ASIS) were determined and were associated with the dipole moments of the sulfanes.

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