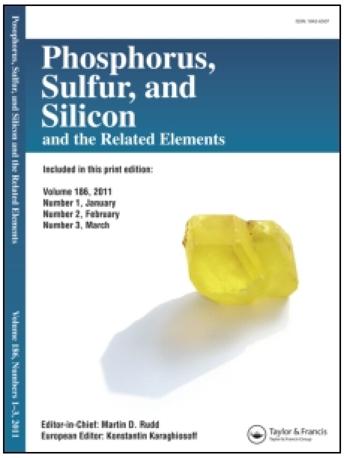


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Cyclotriphosphazane-Trisulfide from the Sulfuration of a 1,2,4,3-Triazaphosphole

Alfred Schmidpeter[a]; Franz Steinmüller[a]
[a] Institut für Anorganische Chemie der Universität München Meiserstrasse 1, München, Germany

To cite this Article Schmidpeter, Alfred and Steinmüller, Franz(1994) 'A Cyclotriphosphazane-Trisulfide from the Sulfuration of a 1,2,4,3-Triazaphosphole', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 383 — 384
To link to this Article: DOI: 10.1080/10426509408021867
URL: http://dx.doi.org/10.1080/10426509408021867

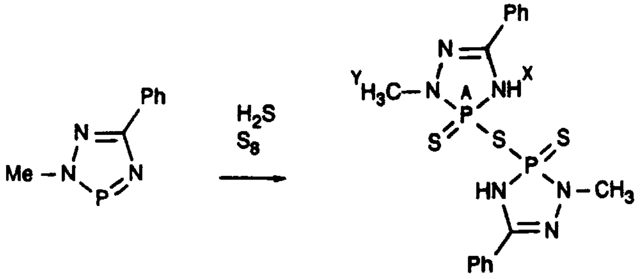
Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 383–384
Reprints available directly from the publisher
Photocopying permitted by license only

A Cyclotriphosphazane-trisulfide from the Sulfuration of a 1,2,4,3-Triazaphosphole

Alfred Schmidpeter and Franz Steinmüller

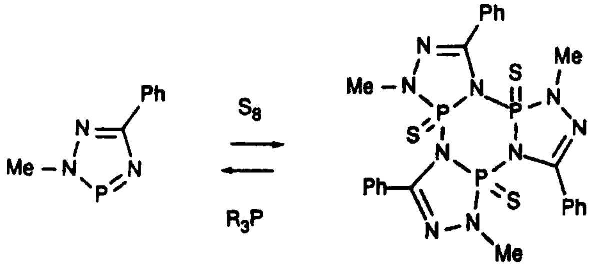
Institut für Anorganische Chemie der Universität München
Meiserstrasse 1, D-80333 München, Germany

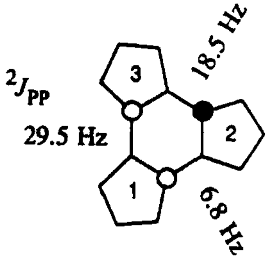
The two-coordinate phosphorus of azaphospholes is typically inert to chalcogen oxidation. In general it reacts with sulfur only if a protic reagent as a third component is added simultaneously [1]. Hence the 2-methyl-5-phenyl-1,2,4,3-triazaphosphole adds sulfur in the presence of HCl or H_2S, resulting in an azaphospholine sesquisulfide in the latter case [2]. The compound is obtained as a 55:45 mixture of diastereomers. Their structure is illustrated by their ^{31}P- and ^{1}H-NMR spectra of AA'XX'Y_3Y'$_3$ type.



δ^{31}P	64.9	65.5
$^2J_{PP}$	21.5	18.0 Hz
$^2J_{PH}$	23.0	23.0 Hz
$^3J_{PH}$	10.5	10.7 Hz

While azaphospholes are said not to react with sulfur alone, we find that in hot pyridine a slow direct sulfuration of the triazaphosphole can be achieved. It leads to a trimeric product with a central cyclotriphosphazane-trisulfide ring [2].

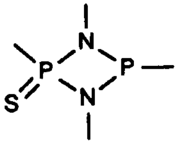


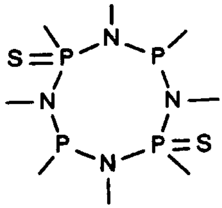


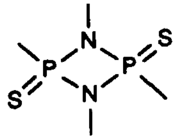
Its *cis*-substituted form would just give a single ^{31}P-NMR signal. The exclusively observed ABC spin system therefore indicates the *trans*-substitution. A model suggests a boat-like conformation of the central six-membered ring with rather different S–P–N–P dihedral angles paralleled by the large differences in $^2J_{PP}$ coupling.

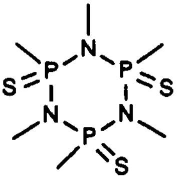
On desulfuration by tributylphosphine the monomeric triazaphosphole reforms. This is reminiscent of the reversible tetramerization of a triazaphosphole by complex formation and decomplexation [3].

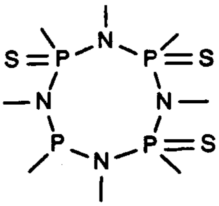
While sulfides of cyclodiphosphazanes are common [4], those of cyclotriphosphazanes [5] (and also of cyclotetraphosphazanes [6]) are rare.











In case of the azaphosphole derived cyclophosphazane sulfide the ring size is governed by the need of coplanar pairs of exocyclic bonds at adjacent P and N ring members.

1. A. Schmidpeter, K. Karaghiosoff in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (M. Regitz, O.J. Scherer, eds.), Thieme, Stuttgart, 1990, p.258.
2. A. Schmidpeter, F. Steinmüller, K. Karaghiosoff, *Heteroatom Chem.* **5** (1994).
3. A. Schmidpeter, H. Tautz, J. von Seyerl, G. Huttner, *Angew. Chem.* **93**, 420 (1981); *Angew. Chem. Int. Ed. Engl.* **20**, 408 (1981).
4. R. Keat in *The Chemistry of Inorganic Homo- and Heterocycles* (I. Haiduc, D.B. Sowerby, eds.), Academic Press, London, 1987, p.467.
5. W. Zeiss, H. Klehr, *Z. Naturforsch. B* **35**, 1179 (1980).
6. W. Zeiss, H. Henjes, *Chem. Ber.* **111**, 1655 (1987); W. Zeiss, W. Schwarz, H. Hess, *Z. Naturforsch. B* **35**, 959 (1980); J.M. Barendt, E.G. Bent, R.C. Haltiwanger, A.D. Norman, *J. Am. Chem. Soc.* **111**, 6883 (1989).