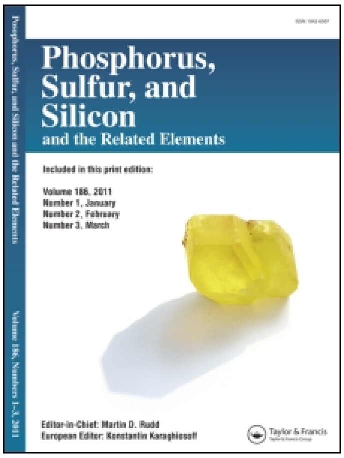


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Crystal Structure of a New Class of Oxygen Bridged Bicyclic Tetraphosphazanes

M. Murray[a]; G. Woodward[a]
[a] Department of Chemistry, University of Bristol, Cantocks Close, Bristol, England

To cite this Article Murray, M. and Woodward, G.(1990) 'Synthesis and Crystal Structure of a New Class of Oxygen Bridged Bicyclic Tetraphosphazanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 476
To link to this Article: DOI: 10.1080/10426509008041000
URL: http://dx.doi.org/10.1080/10426509008041000

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 476
Reprints available directly from the publisher
Photocopying permitted by license only

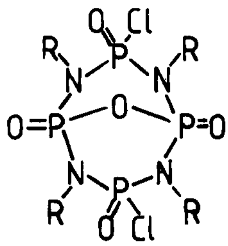
SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW CLASS OF OXYGEN BRIDGED BICYCLIC TETRAPHOSPHAZANES

M.MURRAY, G.WOODWARD
Department of Chemistry, University of Bristol,
Cantocks Close, Bristol, BS8 1TS, England

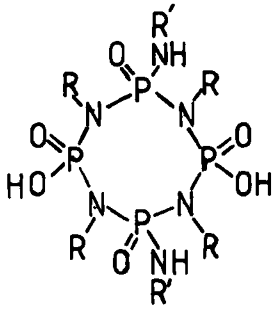
The reaction of primary amine hydrochlorides with phosphorus oxychloride in the presence of 1/4 mole of H_2O yields the title compounds I (R = C_6H_5-, 4-$CH_3C_6H_4$-, 4-$CH_3OC_6H_4$-, 3-$CH_3C_6H_4$-, CF_3CH_2-). Hydrochlorides of more basic amines do not yield any cyclic material. The compound I (R = C_6H_5) was isolated as one isomer. An X-ray crystallographic study has shown an open ring structure in which the two chlorine atoms are positioned on the same face of the P_4N_4 ring as the P-O-P bridge.

An initial study of the reactivity of this ring system has shown similarities to that of $[C_6H_5NPOCl]_3$. The P-O-P bridge can be selectively hydrolysed, e.g. H_2O/primary aliphatic amine yields compounds of type II, but reaction with stronger nucleophiles such as sodium ethoxide in ethanol yields polymeric material.

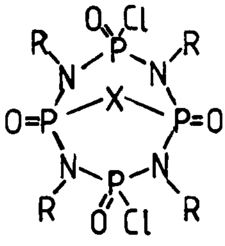
This chemistry could provide a useful route to cyclotetraphosphazane ring systems and may also yield new bicyclic ring systems e.g. III.



(I)



(II)



(III)

(R=aryl, R'=alkyl, X=CH_2 or NR')