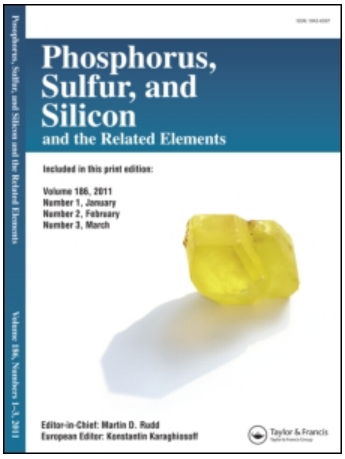

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PREPARATION AND X-RAY STRUCTURE OF 3,4,8-TRIS(T-BUTYL)-1,6-BIS(4-TRIFLUORMETHYLPHENYL)-2,5,7,9-TETRAZA-3λ^3,4λ^5 8λ^3-TRIPHOSPHA [4.3.0]BICYCLONONA-1,4,6-TRIEN (4). STUDY OF THE THERMAL STABILITY OF 4, AND TWO OTHER CICLOCARBOPHOSPHAZENES.

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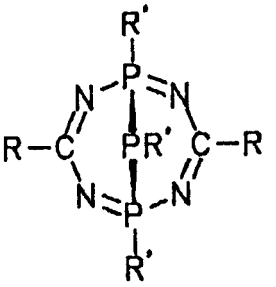
Abstract In this work, we expose the synthesis of the new bicyclocarbophosphazene 4, its x-ray crystall structure and the experimental data obtained. The results of the study of thermal stability of 4 and two related compounds are also presented.

The synthesis of macromolecules containing inorganic elements in the polymer backbone is currently an area of intense investigation.[1] Cyclocarbophosphazenes are known since 1975[2] and very recently also its polimerization was investigated[3]. Heterocyclophosphazenes[4] are of interest from the viewpoint of structure and bonding[5] and as precursors for inorganic polymers[6].

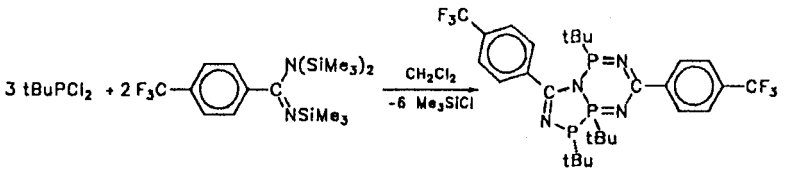
The first structural characterization of a bicyclic carbophosphazene containing two carbon atoms and a P(V)P(III)P(V) unit (1) was obtained by the group of Roesky[7]. We continued to investigate this system in order to understand the influence of substituents on phosphorus. Two different amidines were used: $CF_3C_6H_4$-$CN_2(SiCH_3)_3$ (3) and $CF_3CN_2(SiCH_3)_3$ (4). It was observed that small sized substituents on the phosphorus atom also formed similar bridged compounds.[8] The yield were in the range 20-60 % and depended on the substituent on phosphorus. Figure 1 shows the structure of these compounds.



1

FIGURE 1

With large substituents however we did not obtain these bridged system. The products of the reaction with phosphines containing 2,4,6-$(CH_3)_3C_6H_2$-, 2,4,6-$(CF_3)_3C_6H_2$- and cyclohexyl- organic groups consisted of various mixtures. With the t-butylphosphordichloride ($tBuPCl_2$) the new bicyclic 4[9] was isolated and characterized. Its x-ray crystall structure is shown in Figure 2. The molecule consists of a bicyclic framework with a five and six-membered rings sharing a common P-N bond. It was also characterized by ^1H-, ^{19}F-, ^{31}P-NMR-spectros-copy, massenspectrometry and elementar analysis.



4

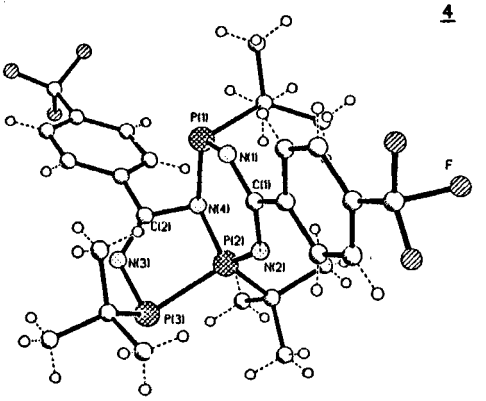
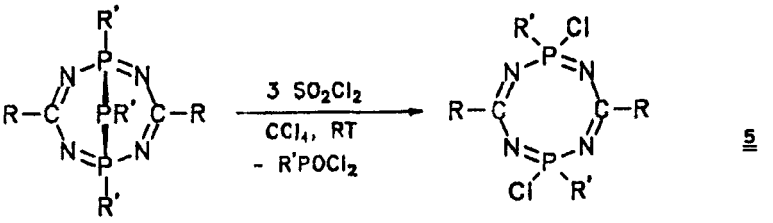


FIGURE 2 X-Ray crystall structure of 4

We have investigated the reactivity of the bridged compounds. Sulfuryl chloride destroys the bridge to give very unique heterocyclic compounds 5. The reaction is shown in Fig. 3.



5

FIGURE 3

The eight membered ring consist of congugated P-N and C-N bonds in alternate positions. 1,5-diphosphatetrazocine 5 are obtained with alkyl- and aryl- substituents on the phosphor atom.[9]

These new P-N and C-N heterocyclic compounds are potential monomers for the ring-opening polymerization to obtain a new class of PN/CN polymers. In order to obtain information on the optimum temperature for the ring opening without decomposing the ring we have studied the thermal properties of these compounds. The thermal stability of 4, 1 and 5 were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). It is observed that 4 and 1 can be heated to 200°C without loss of weight, but in the case of compound 5 thermical decomposition started at about 150°C. 4 and 5 present two exothermal peaks below the thermal decomposition temperature. In 4 the first transition occurs by 153°C and has an enthalpy of 7.12 cal/g and the second occurs by 162°C and has an enthalpy of 3.49 cal/g. In 5 the first transition occurs by 91°C and the second by 106°C, the corresponding changes of enthalpy are 10.18 cal/g and 10.77 cal/g. According with these results, it is suggested that solid state phase changes may be taking place. Figure 3 shows the ATG and DSC graphics of 4. Polimerization studies of 5 are being made.

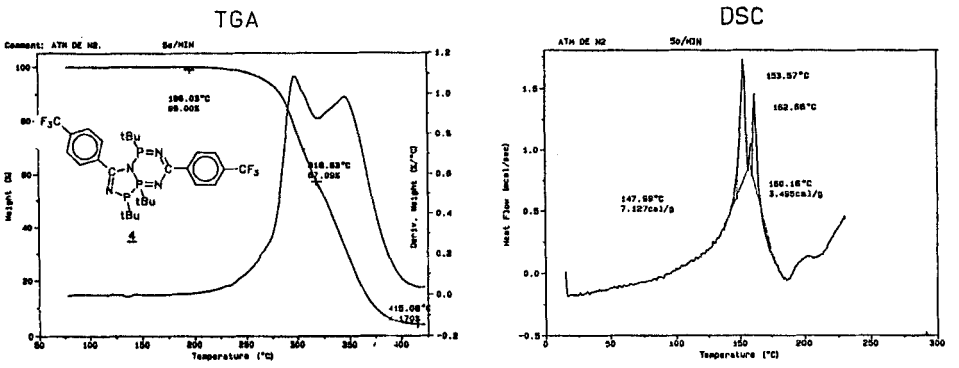


FIGURE 1 ATG and DSC graphics of 4

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