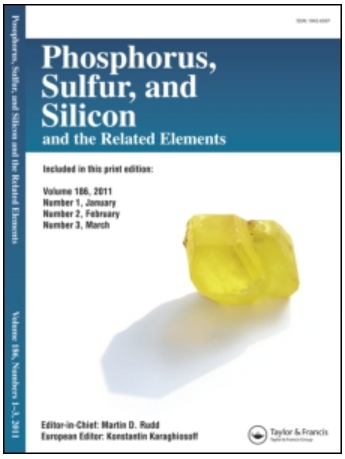

Phosphorus, Sulfur, and Silicon and the Related Elements

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Heterocycles and Polymers Containing Group 15 and 16 Elements from the 1,3-Dipolar Cycloaddition Reaction

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HETEROCYCLES AND POLYMERS CONTAINING GROUP 15 AND 16 ELEMENTS FROM THE 1,3-DIPOLAR CYCLOADDITION REACTION

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Abstract The potential of the nitrile sulphides [R-C≡N-S] in the synthesis of different types of linear polymers is discussed. The generation and cycloaddition chemistry of the first bis(nitrile) sulphide is described. Routes to poly-(isothiazole) are presented and the preparation of the first isothiazole-oxathiazolone compound is reported.

The nitrile sulphides [R-C≡N-S] are a family of 1,3-dipoles that have been known since 1970[1]. They are usually generated *in situ* by the thermal elimination of CO_2 from an oxathiazolone derivative. The nitrile sulphides are unstable with respect to decomposition to a nitrile and elemental sulphur and therefore are usually trapped by cycloaddition to a dipolarophile. Our interest in this system is to use the generation and chemistry of this 1,3-dipole as a model for the future generation of related 1,3-dipoles that are inorganic π systems [thiazyl sulphides: R-S≡N-S] or that contain π bonds to the heavier elements of Groups 15 or 16 [phosphaalkyne sulphides: R-C≡P-S]. We have reported the first systematic structural study by X-ray crystallography of the nitrile sulphide system using the adamantyl derivative of the oxathiazolone precursor.[2] We were able to resolve a mixture of the adamantane derivatives of the nitrile and oxathiazolone by selective complexation of the nitrile with $W(CO)_5$.

Linear polymers with extensively delocalised π systems can be "tuned" by the incorporation of heterocycles such as thiophene or thiazole.[3] The bis(oxathiazolone) I was prepared and its chemistry was evaluated with respect to the alkyne, thiazyl and

phosphaalkyne triple bonds. In these reactions the second cycloaddition fails to prevent decomposition of most of the nitrile sulphide to a nitrile which would severely limit any bis(1,3-dipole) / bis(dipolarophile) polymerisation reactions.

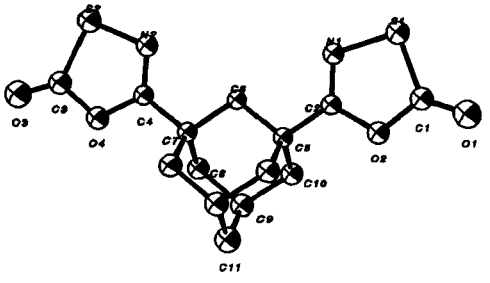

FIGURE 1 ORTEP view of 1,3-bis(1,3,4-oxathiazol-2-one)-adamantane I

To approach the eventual preparation of the poly(isothiazole) polymer we prepared the first isothiazole-oxathiazolone derivative (II) via a four step synthetic procedure from the isothiazole-ester. In this manner we propose to forge a short $(isothiazole)_n$ chain, link by link to develop procedures for the eventual generation of the first alkynyl-nitrile sulphide [R-C≡C-C≡N-S], which may give the polymer directly.

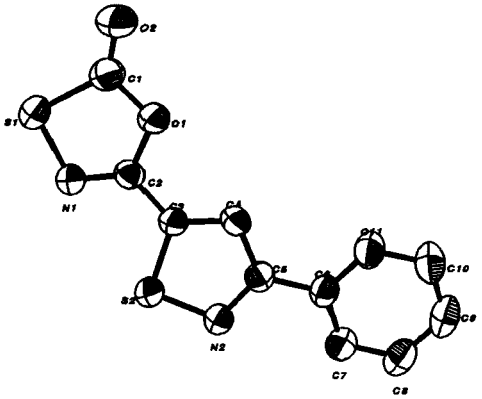

FIGURE 2 ORTEP view of 5-(3-phenylisothiazol-5-yl)-1,3,4-oxathiazol-2-one II

REFERENCES

1. R.M. Paton, Chem. Soc. Rev., 18, 33 (1989).
2. J.N. Bridson, S.B. Copp, M.J. Schriver, S. Zhu and M.J. Zaworotko, Can. J. Chem., 72, 1143 (1994).
3. K.F. Fox, New Scientist, 5 March 1994, p. 33.