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Publisher Taylor & Francis

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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

Azaphosphabenzenes and their Classical Valency Isomers

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To cite this Article Regitz, M., Haber, S. and Hees, U.(1990) 'Azaphosphabenzenes and their Classical Valency Isomers', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 324

To link to this Article: DOI: 10.1080/10426509008040855 URL: http://dx.doi.org/10.1080/10426509008040855

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AZAPHOSPHABENZENES AND THEIR CLASSICAL VALENCY ISOMERS

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In contrast to phosphabenzenes so far no valency isomers of azaphosphabenzenes have been described in literature. They can be synthesized-starting with the azacyclobutadiene $\frac{1}{2}$ and the phosphaalkyne $\frac{2}{2}$ by a sequence of thermal and photochemical transformations.

The dewar azaphosphabenzene $\frac{3}{2}$ (accessible from $\frac{1}{2}$ and $\frac{2}{2}$ in a regiospecific cycloaddition reaction) can be isomerised by irradiation into the prismane $\frac{4}{2}$, which at 25°C slowly yields the heteroaromatic compound $\frac{7}{2}$. Photochemical excitation of $\frac{7}{2}$ leads to the azaphosphabenzvalene $\frac{6}{2}$. Both, the bicyclic $\frac{3}{2}$ and the tricyclic $\frac{6}{2}$ are extremely stable in the thermal sense: Isomerization into the 1,3-azaphosphabenzene $\frac{4}{2}$ only occurs at 140°C.