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Preparation and Recognition Ability of Cyclic Anion Receptors Having Two Phosphorus Triamides

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Summary

Halogen ions have been widely applied in industrial and environmental chemistry. For recognition of anions, in particular halides, receptors bearing phosphorus triamides as a novel functional group were studied in this work. Acyclic bis(phosphorous triamide)-based receptors **6** and **7** were successfully prepared from the corresponding phosphorus diamide intermediate. Preparation of cyclic bis(phosphorus triamides) receptors were also attempted, however, the product was hardly obtained may due to low reactivity of phosphorus bisamide with amines as observed for the preparation of **6** and **7**. The recognition abilities of the receptors were measured by means of UV-vis spectroscopic and ^{1}H NMR titrations in acetonitrile. Slight bathochromic shifts were observed on UV-vis spectra of receptors **6** and **7** upon the addition of AcO^-. The peaks of amide N-H groups of **6** by ^{1}H NMR in acetonitrile-d_3 showed clear downfield shift upon the addition of Cl^- indicating hydrogen bonding of the groups to the anion. The recognition abilities of receptors **6** and **7** for AcO^- and Cl^- were greater than that of the corresponding mono(phosphorus triamide) **3b** implying multiple hydrogen bonding to the guest anion. The optimized structure of **6** with AcO^- and Cl^-, respectively, were calculated by DFT method (B3LYP/6-31+G(d) level of theory) revealed that all six N-H groups cooperatively hydrogen-bonded to one anion. These results might give significant information on the design of new phosphorus triamide-based receptors. These results are the first examples of anion receptors bearing two phosphorus triamide.