No. 1904

Construction of Novel Halogen Receptor with Phosphorus Triamides

Shin-ichi Kondo

Faculty of Science, Yamagata University

Summary

Halogen ions have been widely applied in industrial and environmental chemistry. For recognition of anions, in particular halides, anion recognition by phosphorus triamide as a novel functional group was studied in this work. Phosphorus triamide-based receptors 3a ((PhNH)3P=O), 3b ((PhNH)2(BuNH)P=O), and 3c ((PhNH)(BuNH)2P=O) were successfully prepared. The recognition abilities of the receptors were measured by means of UV-vis spectroscopic titrations in acetonitrile, however, small spectral changes due to the low association ability for anions and less effective electronic perturbation on □-electron of phenyl group(s) prevent the determination of the association constants. The peaks of amide N-H groups of the receptors by 1H NMR in acetonitrile-d3 showed clear downfield shift upon the addition of anions such as AcO− and Cl− indicating hydrogen bonding of the groups to the anions. The association constants of all receptors for AcO− were greater than those for Cl−. In addition, the order of the association constants was found to be 3a > 3b > 3c. This result clearly indicates that the hydrogen bond ability of aryl N-H is more effective than that of alkyl N-H. The observed results are quite important for the design of receptors based on phosphorus triamides. DFT calculations (B3LYP/6-31+G(d) level of theory) of 3a and a 3b analog in acetonitrile revealed the structures of free receptors and the anion complexes, in which three N-H groups cooperatively hydrogen-bonded to anions. Energetic evaluation of the complexation also suggested that the effective binding properties of aryl N-H comparing to alkyl N-H. Receptor 4b having two phosphorus triamides bearing 2,2’-binaphthalene as a spacer was prepared from the corresponding diamine and mono-chlorophosphorus diamide in low yield.