

# Symmetry of Halonium Complexes in Solution

ANNA-CARIN CARLSSON



UNIVERSITY OF GOTHENBURG

Department of Chemistry and Molecular Biology

University of Gothenburg

2012

AKADEMISK AVHANDLING

För avläggande av filosofie doktorsexamen i kemi som, med medgivande av Institutionen för kemi, Göteborgs Universitet, kommer att försvaras offentligt fredagen den 3 februari 2012, kl 9.15 i sal KB, Kemigården 4, Göteborgs Universitet och Chalmers Tekniska Högskola. Fakultetsopponent är Professor Pierangelo Metrangolo, Politecnico di Milano, NFMLab-DCMIC  $\zeta$ Giulio Natta $\zeta$ , Milano, Italien. Avhandlingen kommer att försvaras på engelska.

## ABSTRACT

In this thesis the symmetry of two interaction types involving electropositive halogens have been studied in solution; the  $N-X^+-N$  halogen bond ( $X = Br$  or  $I$ ), and the  $C-X^+-C$  interaction of previously characterised, cyclic, 1,2-bridged halonium ions ( $X = Cl$  or  $Br$ ), respectively. The three  $N-X^+-N$  model structures included are bispyridine, 1,2-bis(pyridine-2-ylethynyl)benzene and 1,2-bis((4-methylpyridin-2-yl)ethynyl)benzene halonium triflate complexes. Model structures representing the  $C-X^+-C$  interaction are the dimethylethylene- and ethylenehalonium ions.

All structures included in this thesis are comprised of symmetrically arranged atoms, but have the possibility to exist as either a static, symmetric structure, or as two asymmetric, fast equilibrating tautomers. For a symmetric structure, the positive halogen is positioned with equal distances to the electron donor nitrogens/carbons. In asymmetric structures, the halogen is always closer to one of the nitrogens/carbons, and is consistently jumping between the two nitrogens/carbons. In this investigation the NMR spectroscopic method Isotopic Perturbation of Equilibrium (IPE) has been applied for distinguishing a single symmetric structure from rapidly, interconverting tautomers. The technique measures  $^{13}C$  NMR isotope shifts,  $^n\Delta_{obs}$ , resulting from unsymmetrical introduction of deuterium isotopes in the molecule for which the symmetry is in doubt. Based on the magnitudes, signs, and temperature-dependency of  $^n\Delta_{obs}$  obtained from  $^{13}C$  NMR spectra of a mixture of non-labelled and deuterium labelled molecules, the symmetry of the molecule being considered can be determined.

The IPE NMR experiments revealed that all bis(pyridine)based halonium complexes were best represented as static, symmetric structures in dichloromethane. The symmetric  $N-X^+-N$  arrangement was also shown to be independent of environmental factors, such as increased solvent polarity and tight binding of the counter ion. Thus, these observations indicated that the formation of a symmetric  $N-X^+-N$  halogen bond is energetically favourable. The  $^{15}N$  and  $^{13}C$  chemical shifts of the pyridine rings revealed significantly stronger  $N-X^+-N$  interaction for the iodonium complexes than for the corresponding bromonium complexes, suggesting a covalent character of the  $N-I^+-N$  interaction and an ionic character of the  $N-Br^+-N$  interaction. Strongest interaction was observed for the bispyridine halonium complexes, in which the  $N-N$  distances are freely adjustable to provide the most favourable interaction.

Ionisation of 2,3-dihalobutane or 1,2-dihaloethane precursors in  $SbF_5-SO_2$  at  $-80$  °C were attempted for generation of the desired ethylenehalonium ions. Both bromonium ions were characterised as asymmetric, equilibrating structures; the dimethylethylenebromonium ions from their  $^n\Delta_{obs}$  values, and the ethylenebromonium ion from the dynamic behaviour, typical for asymmetric structures in a slow equilibrium, of the signals shown in its  $^1H$  and  $^{13}C$  NMR spectra. The  $^1H$  NMR spectral pattern of the ethylenechloronium ion was also consistent with asymmetric structures in a slow equilibrium. The symmetry of the dimethylethylenechloronium ions could not be determined, as they, if formed at all, immediately rearranged.  $SO_2$  was revealed to be sufficiently nucleophilic to add to the cations formed. Hence, the source of the asymmetry observed is ascribed the labile addition of  $SO_2$  to either cyclic halonium ions or open  $\beta$ -halocarbenium ions.

---

**Keywords:** bis(pyridine)-based halonium complexes, ethylenehalonium ions, structure symmetry, isotopic perturbation of equilibrium, solution NMR spectroscopy, isotope effects,  $N-X^+-N$  halogen bond,  $C-X^+-C$  interaction

**ISBN:** 978-91-628-8407-9