

## **ABSTRACT**

**THESIS:** Synthesis of a series of aryl tetrazolethiones and investigation of their anion-binding abilities

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Anions play a critical role in influencing our life. In biology, chloride ions play an important role in metabolism and regulate acid-base balance in the cells. The transportation of chloride ions across cell membrane occurs through the chloride ion channels. When these channels malfunction, chloride binding molecules are needed to restore the transportation of  $\text{Cl}^-$  across the cell membrane. Similarly, nitrate is a common anion used in fertilizers, and cyanide is employed in polymer production. However, their excessive release in the environment can have dangerous consequences on our health. Thus, anion-binding molecules are needed for monitoring and removal of these harmful anions from our environment.

In this thesis, the potential of tetrazolethiones as novel anion binding agents has been investigated. Several tetrazolethione derivatives were synthesized by reacting aryl isothiocyanates

with sodium azide under reflux conditions. Some of the required isothiocyanates were commercially obtained, while others were synthesized in our laboratory due to their high cost. To obtain isothiocyanates, substituted anilines were first reacted with *N,N*-dimethylcarbonyl chloride, however, this method produced low yields. Alternatively, isothiocyanates were synthesized in good to excellent yields by reacting anilines with carbon disulfide *via* the formation of thiocarbamates, followed by desulfurylation with di-*tert*-butyl dicarbonate in the presence of a catalytic amount of DMAP. With aryl isothiocyanates in hand, the phenyl-, -3,5-dimethoxyphenyl-, 4-chlorophenyl-, 4-methoxyphenyl-, and 4-iodophenyl tetrazolethiones as well as the 1,1'-(4-methyl-1,3-phenylene)bistetrazolethione were synthesized by reaction with sodium azide.

Next, the ability of two tetrazolethiones (4-chlorophenyl- and 3,5-dimethoxyphenyl tetrazolethiones) to bind to anions, *e.g.* acetate, bromide, chloride, and nitrate was investigated by using UV and NMR spectroscopy. The results show that tetrazolethiones undergo proton transfer with acetate anion, while form hydrogen bonded interaction with weakly basic chloride, bromide, nitrate and hydrogen sulfate anions. Among the various anions investigated, tetrazolethiones show selective binding to the chloride anion. Density functional methods were employed to support experimentally calculated association constants.