

ABSTRACT

THESIS: Investigating the Interaction of Aryl Tetrazolones with Anions

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Anions play an important role in biology, industry, and environment. Compounds that have the capability of binding anions may find applications in the treatment of various diseases and disorders, in the removal of harmful anions from drinking water and much more. Tetrazolones possess an N-H moiety that offers the potential to interact with negatively charged species through hydrogen bonding, however, the anion-binding ability of tetrazolones remains largely unexplored. In this study, three substituted aryl tetrazolones, namely 1-(4-nitrophenyl)-1,4-dihydro-tetrazol-5-one, 1-(4-trifluoromethylphenyl)-1,4-dihydro-tetrazol-5-one, and 1-(4-methoxyphenyl)-1,4-dihydro-tetrazol-5-one, were synthesized by reacting the isocyanates with trimethylsilyl azide under reflux for 24 hours. The interaction of synthesized tetrazolones with anions of varying basicity *e.g.* acetate, hydrogen sulfate, bromide, nitrate, thiocyanate and chloride was investigated in acetonitrile/DMSO. UV and NMR titrations indicated that tetrazolones interact through hydrogen bonding with Br^- , NO_3^- , NCS^- , HSO_4^- , and Cl^- . The association constants were found to be in the order $\text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{NCS}^- > \text{HSO}_4^-$ which followed the basicity trend of the anions in acetonitrile, except for Br^- . Remarkably, the tetrazolones exhibited 10 times higher selectivity towards Cl^- than Br^- . The affinity of *p*-nitrophenyl tetrazolone towards various anions was higher than that of *p*-trifluoromethylphenyl

tetrazolone (except for HSO_4^-). This was attributed to higher electron withdrawing ability of a $-\text{NO}_2$ group vs. a $-\text{CF}_3$ group. Significant UV changes were observed upon addition of the acetate anion to the solution of tetrazolones in MeCN. NMR titrations further revealed that tetrazolones underwent deprotonation with the acetate anion owing to its higher basicity as peaks corresponding to the formation of acetic acid were observed. To gain further support for deprotonation, UV and NMR titrations of tetrazolones with a strong organic base, triethylamine were carried out which showed similar spectroscopic changes as observed in case of the acetate.