Abstract

The objective of this thesis is to study the effect of non-covalent interactions in chemical reactions, with a major focus on π–π interactions. The important role of π–π interactions in geometrical organisation of macromolecules and materials are well known, however, its effect in chemical reactions are little explored. In this thesis, I discuss explorative studies on various manifestations of non–covalent interactions on thermal cyclisation reactions – Bergman cyclisation (BC) and Garratt–Braverman cyclisation (GBC).

The thesis is organised as follows. **Chapter 1** provides a brief overview of the non-covalent interactions and current status of research in the area of cyclisation reactions. In **Chapter 2**, a brief description on the theoretical background of the methods relevant to the thesis are described. In **Chapter 3**, the effect of π–π interactions on Bergman cyclisation is discussed. This chapter provides the basis for understanding the effects of π-π interactions in chemical reactions, the changes in the interaction energy (IE) along the reaction coordinate, the effects on the activation energies, and the effect of substitution on the IE. In the remaining chapters, I discuss the studies on GB cyclisation reactions. The **Chapter 4** is dedicated to the discussion of the mechanism of GBC – a base catalysed cyclisation reaction of bispropargyl systems. I also introduce an approximate method involving the calculation of pK_a for predicting the relative rates of isomerisation steps in the reactions. Using the rates predicted from pK_a calculations and from the activation energies, we have reproduced the experimentally observed chemoselectivity in the unsymmetrical bisapropargyl ethers, and made predictions on other bispropargyl systems. **Chapter 5** deals with the competitive reaction pathways of the bispropargyl substrates that contain two vinyl groups invoking the possibility of GB cyclisation and 6π–electrocyclisation. I have discussed two kinds of substrates for this study - conformationally unconstrained and constrained systems. The selectivity obtained from the calculations match the experimental results – unconstrained substrates favour GBC and constrained ones favour 6π–EC. **Chapter 6** describes the systems where amino or keto groups close to the allene centre, which can undergo competing cyclisations – GBC and intramolecular nucleophitic addition or 6π–EC. Here also we were able to reach good agreement with the experimentall observed selectivities.

Keywords: π–π interactions, density functional theory, computational chemistry, reaction mechanism, cyclisation, isomerisation and chemoselectivity.