



## Deep eutectic melt of betaine and trichloroacetic acid; its anomalous thermal behavior and green promotion effect in selective synthesis of benzimidazoles

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### ABSTRACT

Trichloroacetic acid and betaine form glassy liquids on melting together in some molar ratios, of which the melt with mole fraction of trichloroacetic acid about 0.83 displayed the lowest freezing point, so was detected as their deep eutectic mixture. It showed two reversible DSC effects on cooling from 70 °C to -70 °C; a normal exotherm on freezing followed by an abnormal endotherm on melting. Electric conductance of the melt against temperature exhibited two regions of deviation from a perfect exponential curve. These regions correspond to the temperatures of the two reversible phase transitions detected by DSC analysis. As another evidence in support of its freezing on heating, the kinematic viscosity of the melt is increased within the temperature range of 40-50 °C. Moreover, the FT-IR spectrum and TGA analysis of the eutectic mixture point to its exceptional nature in comparison to other mixtures of the two components. The melt proved to be an efficient promoter for selective synthesis of benzimidazoles from *o*-phenylenediamine and arylaldehydes at room temperature. No *N*-substituted derivatives of the products were resolved from the reaction mixtures.

### 1. Introduction

Solvents and catalysts are two indispensable elements of most organic productions, being annually used in large scales by the chemical plants. Commonly used solvents are toxic volatile liquids that inevitably emit into environment during chemical processes and may find their way to our aquatic ecosystem or breathing air [1]. On the other hand, catalysts have a limited durability and should be either refreshed or discarded into environment after expiration of their performance lifetime [2]. In response to these environmental concerns, chemists have turned their attention to application of ionic liquids (ILs) as solvents and catalysts [3]. Because, these non-volatile liquids are known for their low vapor pressures, convenient separation from mixtures, great solubility for both organic and inorganic compounds, significant electric conductivity, and low flammability [4]. Since their emergence as valuable solvents, ILs rapidly evolved to found key roles as reaction promoters [5], reaction substrates [6], and supports of catalysts [7]. Although of these excellent properties, ILs are harmful for aquatic organisms [8], since their preparation is limited to using salts of bulky organic ions. In contrast to ILs, their congeners, the so-called deep eutectic solvents (DESs) are usually composed of at least a molecular component in

addition to a salt [9]. This potential of formulation manifests itself in a great compositional diversity of DESs [10]. To date, many DESs of four types have been discovered and proved to be significant elements in development of green chemistry [11], covering the area from organic reactions catalysis [12-16] to electro-chemistry [17], absorption of organic impurities [18], preparation of Nofidesols [19], bio-transformations [20], polymerization processes [21] and in production of nano-materials [22]. A large number of organic reactions, such as Knoevenagel condensation and Michael addition [23], oxidations [24], Suzuki-Miyaura cross-coupling [25], Friedel-Crafts [26-28], Paul-Knorr [29], and Diels-Alder [30] reactions are reportedly promoted in DESs. There are also some reports on utility of DESs as green solvent or promoter in organic reactions [31].

DESs are indeed simple mixtures of two or three different compounds, melting at temperatures far below the melting points of their individual components. Effective non-covalent halogen-bonding or H-bonding between the components is the main event underlying the remarkable melting point depression [32]. Upon formation of the H-bonds, the local negative charge on the anionic component is partially dispersed over the H-donating component and thereby the electrostatic attraction forces between the ionic species are softened. In the case of

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