

Article

Effect of Aromatic System Expansion on Crystal Structures of 1,2,5-Thia- and 1,2,5-Selenadiazoles and Their Quaternary Salts: Synthesis, Structure, and Spectroscopic Properties

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Abstract: Rational manipulation of secondary bonding interactions is a crucial factor in the construction of new chalcogenadiazole-based materials. This article reports detailed experimental studies on phenanthro[9,10-*c*][1,2,5]chalcogenadiazolium and 2,1,3-benzochalcogenadiazolium salts and their precursors. The compounds were synthesized, characterized employing NMR and UV-Vis spectroscopy. TD-DFT calculations were also performed. The influence of the size of the aromatic system on the molecular motifs formed by the compounds in the solid state has been studied by means of single-crystal X-ray diffraction. In case of the salts, the nature of an anion was also taken into consideration. The results show that cyclic [E⋯N]₂ supramolecular synthon connects neighboring molecules of phenanthro[9,10-*c*][1,2,5]chalcogenadiazoles, with a relatively large aromatic system, in dimers regardless of the chalcogen atom in the molecule. Both *N*-methyl-2,1,3-benzothiadiazolium and *N*-methylphenanthro[9,10-*c*][1,2,5]chalcogenadiazolium cations have a strong affinity for triflate and iodide anions, therefore the formation of S⋯N or Se⋯N secondary bonding interactions is observed only in two out of the eight quaternary salts. Less coordinating anions must be used to enable the building blocks studied to form cyclic [E⋯N]₂ synthons. Moreover, for two of the triflate salts, which are isostructural, a new supramolecular motif has been observed.

Keywords: chalcogenadiazoles; chalcogen bonds; crystal engineering; spectral properties

1. Introduction

Due to their unique physical and chemical characteristics, molecules containing the 2,1,3-benzothiadiazole and/or 2,1,3-benzoselenadiazole unit are mainly known as components used in construction of optoelectronic devices, including organic light-emitting diodes (OLEDs), solar cells, and liquid crystals [1–7]. Apart from that, these systems are also building blocks in crystal engineering [8], self-assembly of supramolecular capsules [9,10], macrocycles, and polymers [11].

The presence of two nitrogen atoms separated by a heavy p-block element (sulfur or selenium) in their structures enables these molecules to aggregate through chalcogen bonding [12–15], which is a subgroup of non-covalent interactions which has received growing attention in the last two