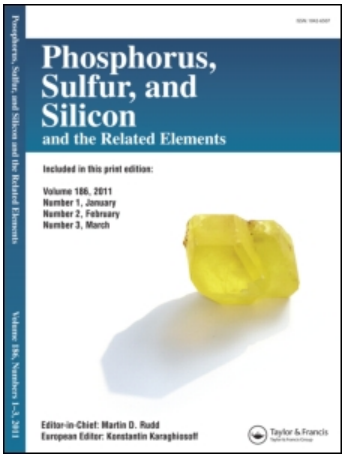

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The cycloaddition chemistry of the dithionitronium cation (SNS^+) has led to the synthesis of dithiadiazolyl ($\overline{CNSNS}$, $\overline{CNSSN}$) and dithiazolyl ($\overline{CSNSC}$) ring systems from the corresponding nitriles and alkynes respectively.[1] Olefins are isolobal with both alkynes and nitriles and can undergo cycloaddition with one or two stoichiometric aliquots of olefin because of the two mutually perpendicular π-manifolds of SNS^+. The chemistry of SNS^+ with extended π-systems has not yet been investigated beyond the case of benzene, where an electrophilic substitution results in the sulfur protonated substitution product, likely $C_6H_5SNSH^+$.[4] Wolmershauer first described the synthesis of benzo-fused 1,3,2-dithiazolylium chloride salt on a preparative scale,[2] which was characterized by x-ray crystallography.[3]

Preliminary investigations of the extended π-systems of 1,4-benzoquinone and 1,4-naphthoquinone with SNS^+ have been shown by x-ray crystallography to be 2,5-dihydroxybenzo-1,3,2-dithiazolylium ($\mathbf{1}^+$ $\mathbf{AsF_6^-}$) and 2,7-dicarbonylnaphtha-1,3,2-dithiazolylium ($\mathbf{2}^+$ $\mathbf{AsF_6^-}$) salts (Figure 1). The salt (**1**) has been characterized by multinuclear NMR {^{1}H, ^{13}C, ^{14}N, ^{19}F, HMQC, COSY}, infrared spectroscopy, and supported by DFT calculations (B3LYP/6-311++G**). The intermediate (**3**) was found to be thermodynamically unfavorable in the gas phase and suggests that it will not be observed in solution or solid state. Both salts (**1**) and (**2**) show a similar layered motif, forming columns in the solid state, and few contacts between the anion and the $C_2S_2N^+$ ring are observed in the case of (**1**).

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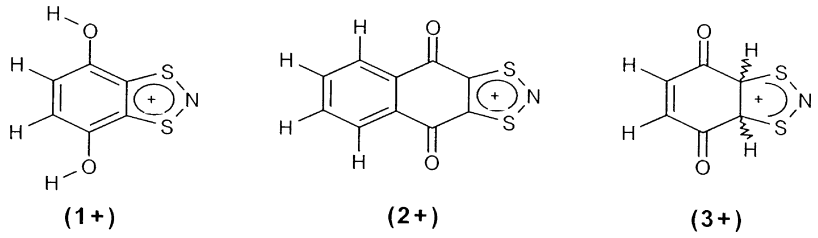

FIGURE 1 Dithiazolylium salts.

The simplicity of these reactions allows easy access to new derivatives of benzo-fused 1,3,2-dithiazolylium cations and subsequent reduction may yield potentially new, useful synthetic materials with interesting magnetic properties.

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