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Synthesis, Structure, and One-electron Redox Reactions of Novel Benzodithiolium Salts

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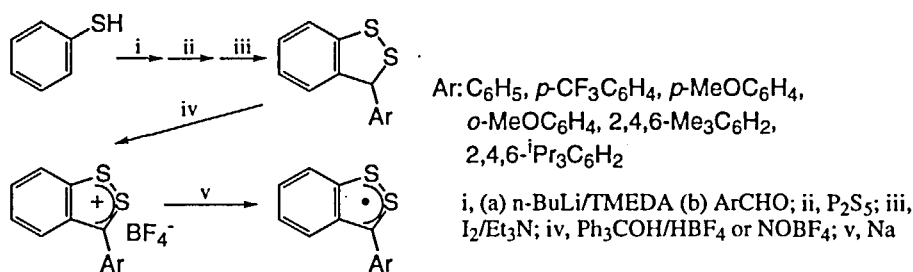
Abstract Novel stable benzodithiolium salts have been synthesized and characterized by X-ray crystallographic analysis, which have been readily converted to the first isolable dithioly radicals by one-electron reduction.

INTRODUCTION

Considerable current interest has been focused on 5-membered heterocycles containing sulfur atoms because of their chemical reactivities and electrical conductivity. Our interest in the design of reversible one-electron redox systems¹ by using unusual 7π electron frameworks has prompted us to synthesize novel benzodithiolium salts. We report here the synthesis of stable benzodithiolium salts by a new synthetic strategy, characterization of the crystal structure by X-ray analysis, and their one-electron redox reactions.

RESULTS AND DISCUSSION

The dithiolium salts were synthesized as follows (Scheme 1). Thiophenol reacted with *n*-BuLi/TMEDA and then with aryl aldehydes to give desired ortho-substituted benzenethiols in moderate yields, which were easily converted to the corresponding 3-aryl-3H-1,2-benzodithiols by the sequential treatment with P_2S_5 and I_2/Et_3N . When the dithiols were allowed to react with trityl cation or NOBF₄, corresponding oxidized products, 3-aryl-1,2-benzodithiolium salts, were obtained in moderate yields.



Scheme 1

The crystal structure of the dithiolium salt containing 2,4,6-triisopropylphenyl substituent at the 3-position was confirmed by X-ray analysis (Figure 1). Cyclic voltammetry of the dithiolium salt in MeCN at 20 °C under Ar exhibited a well-defined reversible reduction wave.

The corresponding novel dithiolyl radical was isolated as green crystals in the reduction by metal sodium in THF. The structure of the radical was analyzed by high resolution Mass and ESR spectroscopy (Scheme 2).

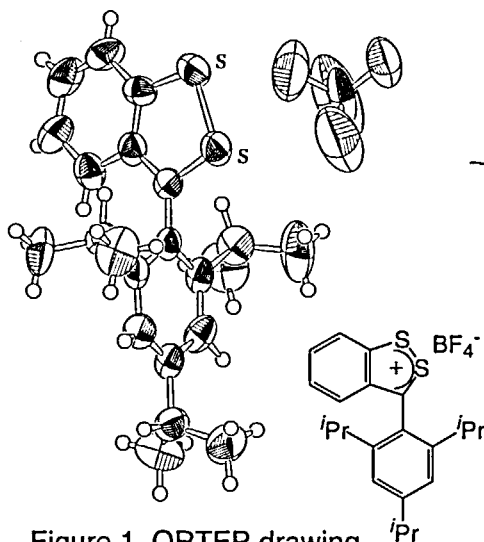
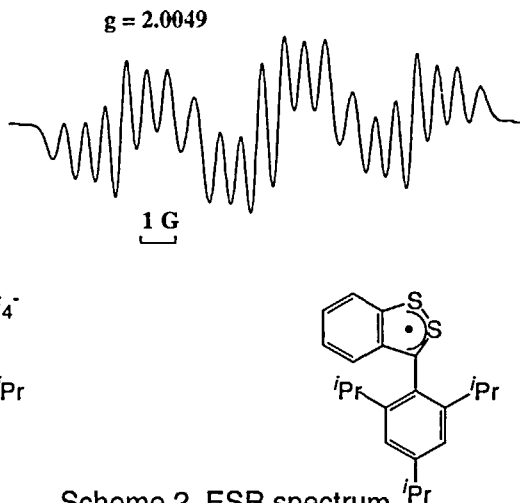


Figure 1. ORTEP drawing



Scheme 2. ESR spectrum

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