Convenient synthesis of bis(benzo)-fused BEDT-TTF and higher homologues — New electron donor molecules for organic charge transfer salts and “molecular rulers”

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Abstract

A convenient synthesis of bis(benzo)- and bis(naphtho)-fused bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) derivatives, employing the [4+2] cycloaddition reaction of oligo(1,3-dithiole-2,4,5-trithione) with appropriate alkenes as a key step, is presented.

Keywords: Organic superconductors, molecular rulers, BEDT-TTF or ET derivatives, heterocycle synthesis, coupling reactions.

1. Introduction

Among the number of tetrachalcogenafulvalenes employed as \( \pi \) donors for organic superconducting salts, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) 1 has been, by far, the most promising. A substantial number of cation-radical salts of ET have exhibited superconductivity, which to a large measure is due to the ability of ET molecules to engage in intermolecular inter-stack and intra-stack \( \pi-\pi \) interactions leading to quasi-two-dimensional band electronic structures [1,2]. Enlargement of the unit cell of isostructural ET salts, achieved by use of large charge-compensating anions, has been the most successful guiding principle to achieve higher superconducting transition temperatures (\( T_c \)) [2,3]. Alternatively, lengthening the ET donor molecule could also lead to a larger unit cell volume, and in salts with proper packing motifs and quasi-two-dimensionality, higher \( T_c \)s might be realized. Replacement of the terminal 1,2-ethanediyl groups in ET with fused aromatic rings is expected to enlarge the unit cell volume, in addition to the attendant possibility of aromatic \( \pi-\pi \) interactions leading to new molecular packing motifs. To this end, the synthesis of dibenzo-ET 2 and dinaphtho-ET 3 derivatives was accomplished. The preparation of the dibenzo-ET derivative has been reported recently starting from 1,2-dimercapto benzene in five steps, involving a low yielding cyclization step, with an overall yield of less than 4\% [4]. A convenient and more general synthetic methodology was thus needed for the preparation of 2 and the hitherto unknown dinaphtho-ET 3 for our studies as potential donors molecules for superconducting salts and for their possible applications in the design of “molecular rulers” [5].

2. Results and Discussion

The synthesis of the target molecules 2 and 3 was achieved by use of the trithione oligomer, oligo(1,3-dithiole-2,4,5-trithione) 4 [6] as the common starting material. Oligomer 4 is known to undergo thermal depolymerization at ca. 100°C and present itself as an effective 4\( \pi \) component in pericyclic Diels-Alder reactions [6,7]. Scheme I outlines the synthesis of the dibenzo-ET derivative 2 wherein the key step is the [4+2] cycloaddition of 1,3-cyclohexadiene with the trithione derived from oligomer 4. Aromatization of the resulting adduct 5 with DDQ in boiling toluene yielded the 4,5-benzenedithio-1,3-dithiole-2-thione 6. Oxidation of thione 6 to the carbonyl...
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derivative 7, employing mercuric acetate in chloroform/acetic acid at room temperature, followed by phosphite coupling afforded 2. Our route to the preparation of dibenzo-ET is a far more convenient and efficient method (overall yield of ca. 30%) than the recently reported synthesis [4]. Furthermore, the Diels-Alder protocol provides a general methodology for the preparation of a variety of ET derivatives [6].

The Diels-Alder reaction of the oligomeric trithione was further exploited in the synthesis of the higher homologue, viz. the dinaphtho-ET 3 (Scheme II). Cycloaddition reaction of 4 with 1,4-dihyronaphthalene-1,4-endoxide (as a 2π component) in refluxing toluene resulted in the formation of the endoxide adduct 8. Subsequent aromatization of 8 with polyphosphoric acid gave the thione 9. Conversion of thione 9 to the carbonyl derivative 10, employing mercuric acetate in chloroform/acetic acid, followed by triethylphosphite-mediated coupling of 10 yielded the dinaphtho-ET 3. The overall yield of 3 from the above four steps was ca. 10%. Studies on the electronic behavior of the aromatic ring-annulated ET derivatives are in progress.

3. Conclusions

The synthesis of two examples of bis(aren0)-fused ET derivatives, viz. dibenzo-ET 3 and dinaphtho-ET 4 has been accomplished by a general and convenient method taking advantage of the facile [4+2] cycloaddition reaction of the known oligo(1,3-dithiole-2,4,5-trithione) 4 with appropriate dienophiles.

References