



Synthetic Exploration making Aryl-Dithiocarboxylate Salts

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Introduction

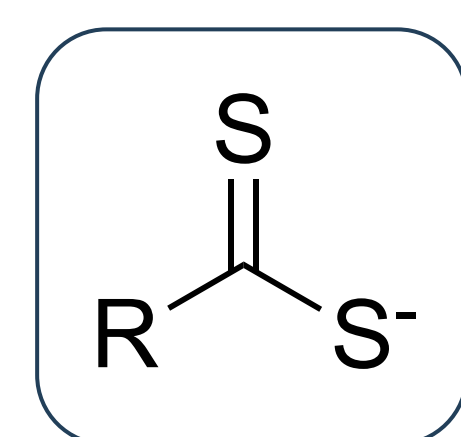


Figure 1: Structure of the $-CS_2^-$ functional group

Dithiocarboxylates (**dtc**) are a class of compound that contains the dithiocarboxylate functional group ($-CS_2^-$)

- Absorb light throughout the UV and visible regions of the spectrum due to $-CS_2^-$ localized transitions
- Are isolable as organic soluble salts

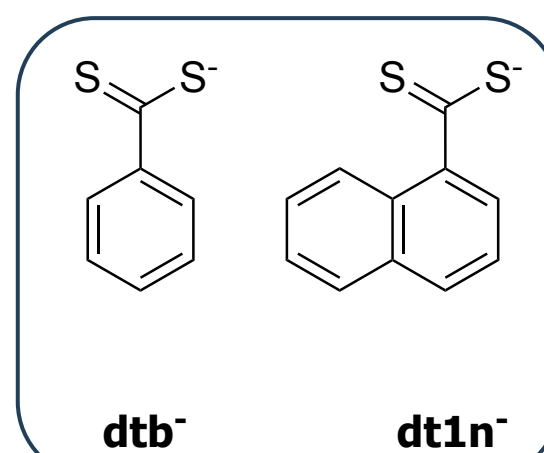


Figure 2: Example aryl-dithiocarboxylates

Aryl-dithiocarboxylates like dithiobenzoate (**dtb⁻**) and 1-dithionaphthoate (**dt1n⁻**) have additional electronic states due to electronic coupling of the aryl and $-CS_2^-$ π -systems

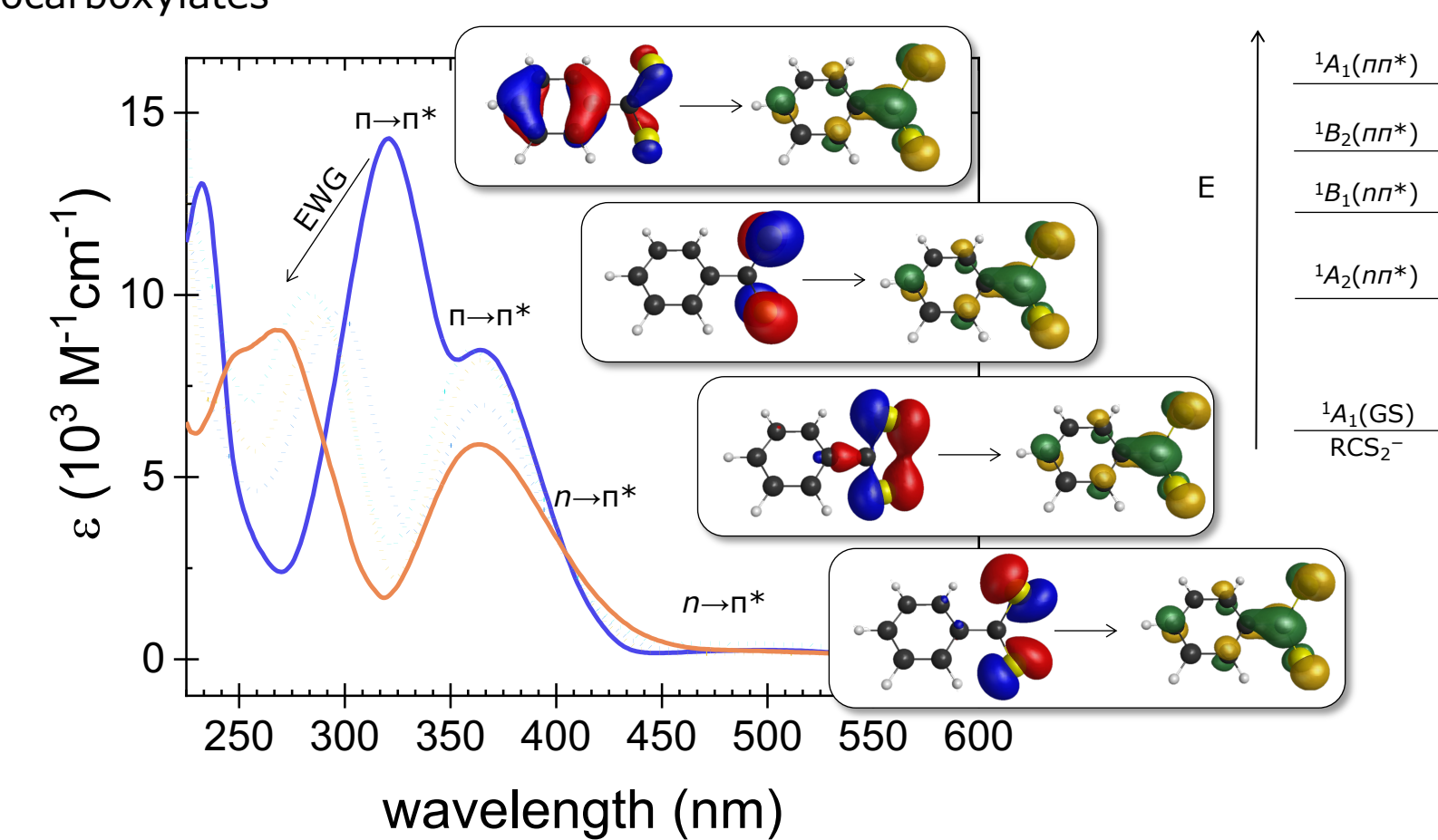


Figure 3: Experimental electronic absorption spectra for various substituted aryl dithiocarboxylates. Natural transition orbital isosurfaces are plotted for the 4 lowest excited electronic states, from TD-CAM-B3LYP/def2-TZVPD/CPCM(EtOH). The Jablonski diagram illustrates the relative state energies identified with their molecular terms (using C_{2v} point group)

- The energy of the 3 lowest electronic transitions is insensitive to the substituents *para*- to the dithiocarboxylate group

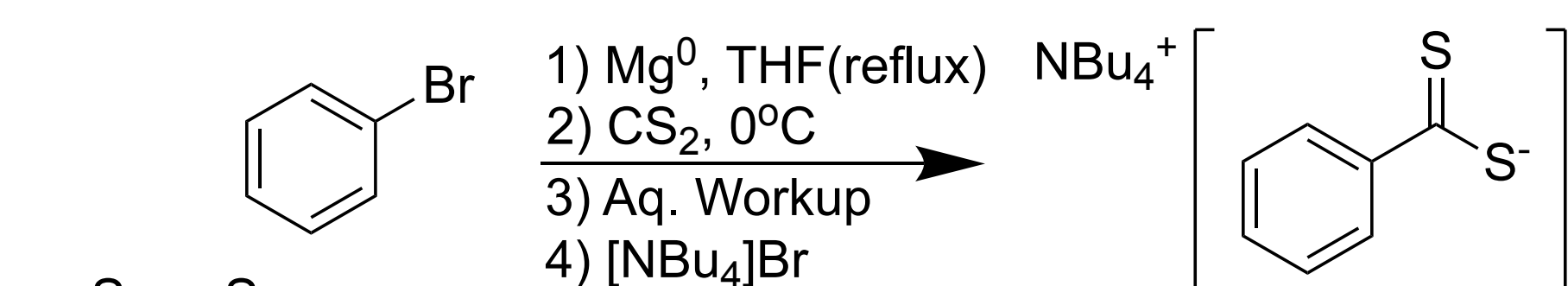
The synthesis of dithiocarboxylates aims to support:

- Developing methods for creating new aryl- CS_2^- compounds
- Characterization of new aryl dithiocarboxylates via NMR, UV-Visible spectrophotometry, IR spectroscopy and ESI mass spectrometry
- Provide experimental data for benchmarking computational methods used to simulate spectra

General Synthetic Procedures

- Synthesis for dithiocarboxylates uses a nucleophilic addition to CS_2 by a Grignard reagent
- Organic soluble salts were obtained and isolated by the addition of NBu_4^+ or $PbZPPH_3^+$

Scheme 1. General synthetic procedure utilized in formation of aryl-DTC compounds.



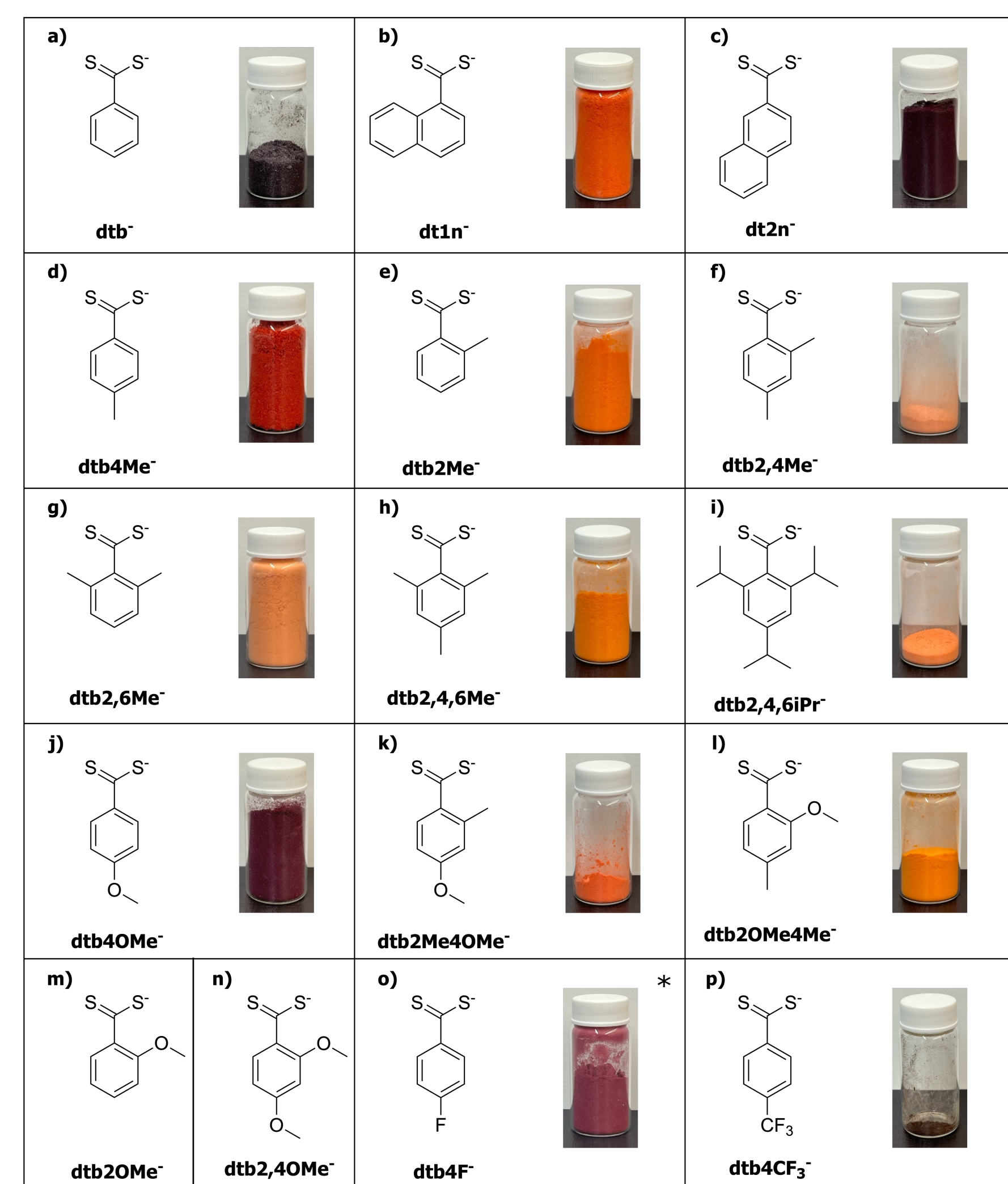
- All syntheses started with commercially available, substituted aryl halides
- Fully characterized compounds include *ortho*- and *para*- substituents have been made, with majority of synthetic procedures following this method.

- The salts of DTCs were purified using recrystallization and/or reprecipitation

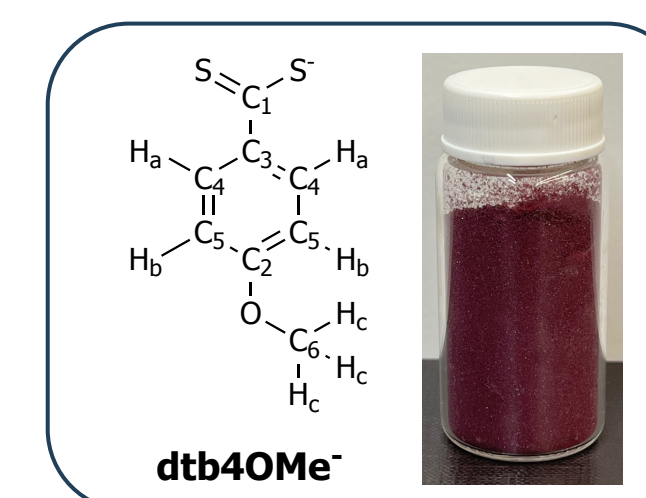
Characterization and Discussion

Synthetic Library of Aryl-DTCs

Chart 1. Series of dithiocarboxylate compounds isolated as NBu_4^+ salts



* Compounds were paired with $BzPPh_3^+$.



- Each compound was characterized using 1H - and ^{13}C -NMR, IR, UV-Visible spectroscopy, and ESI mass spectrometry
- Example spectra of $[NBu_4][dtb4OMe]$ are provided below

