# Synthesis, physicochemical properties, crystal molecular structure and DFT investigation of an organobismuth(III) bis(dimethyldithiocarbamate)

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## 1. Introduction

Metal dithiocarbamates were reported to exhibit a wide range of applications, e.g. potential biological activity and uses in medicine or single source precursors for metal sulfides.

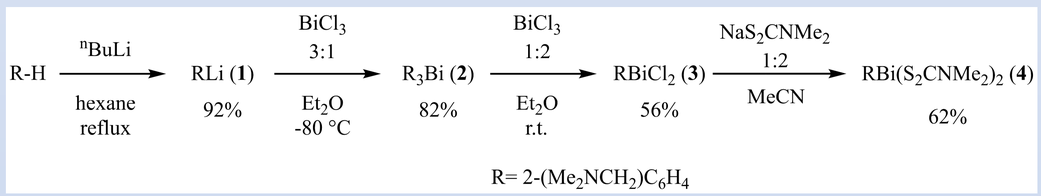
Organobismuth(III) dithiocarbamates could be used as single source precursors for obtaining $Bi_2S_3$, an *n*-type semiconductor material containing environmentally benign elements.

With a bandgap of 1.3-1.7 eV, which can be adjusted depending on the size and shape of particles, $Bi_2S_3$ has found applications in thermoelectrics, photodetectors, photosensitizers, solar cells and supercapacitors.

In this work we report the synthesis and characterization of a new organobismuth(III) dithiocarbamate, $[2\text{-}(Me_2NCH_2)C_6H_4]Bi(S_2CNMe_2)_2$ and we investigate its potential as single source precursors for obtaining $Bi_2S_3$. To better understand the nature of the intramolecular bonds as well as intermolecular interactions DFT, NBO and Hirshfeld surface analyses were carried out.

## 2. Results and discussions

### *Synthetic route*




### *TG-DSC analysis*

**Table 1.** Weight loss steps involved in the TGA of compound **4**

| Process | Temperature (°C) | Theoretical weight loss (%) | Experimental weight loss (%) |
|---|---|---|---|
| 2 $C_{15}H_{24}BiN_3S_4$ (**5**) ⟶ $Bi_2S_3$ + $C_{30}H_{48}N_6S_5$ | 220-320 | 55.95 | 55.61 |
| $Bi_2S_3$ + 9/2 $O_2$ ⟶ $Bi_2O_3$ + 3 $SO_2$ | 450-1000 | 3x1.376 = 4.13 | 5.37 |
| **Total** | | **60.08** | **60.98** |

**Table 2.** Experimental specific enthalpies for compound **4** from DSC curve

| No. | Nature | On set (°C) | Maximum (°C) | ΔH (J/g) |
|---|---|---|---|---|
| 1 | exothermic | 299.21 | 311.26 | 205.0 |
| 2 | exothermic | 443.18 | 443.18 | 341.7 |
| 3 | exothermic | 513.91 | 534,88 | 268.7 |

### *Crystal structure determination*

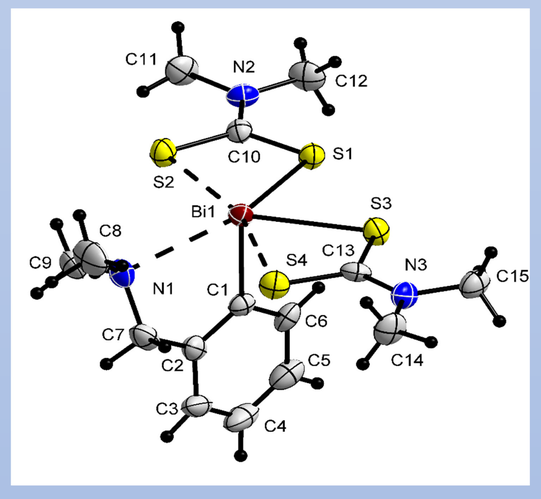



**Figure 1.** The molecular structure of the $pS_N$ isomer of **4** in the asymmetric unit, shown with 30% probability ellipsoids.

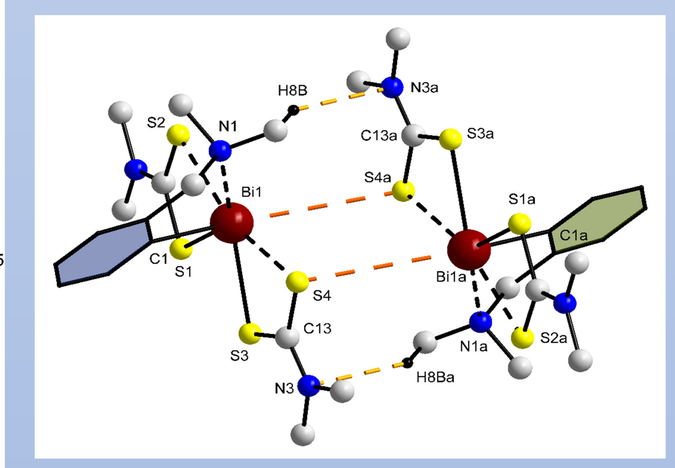



**Figure 2.** Dimeric units formed through weak Bi···S and N···H interactions between the $pR_N$ isomer (*green* aromatic ring) and $pS_N$ isomer (*blue* aromatic ring) of **4** (hydrogen atoms not involved in interactions are omitted for clarity).

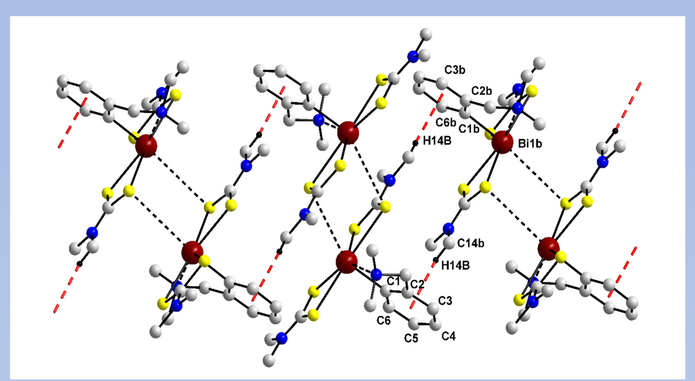



**Figure 3.** Intermolecular associations between dimeric units through C–H···π contacts (*red* fragmented lines) in the crystal of **4** (hydrogen atoms not involved in interactions are omitted for clarity).

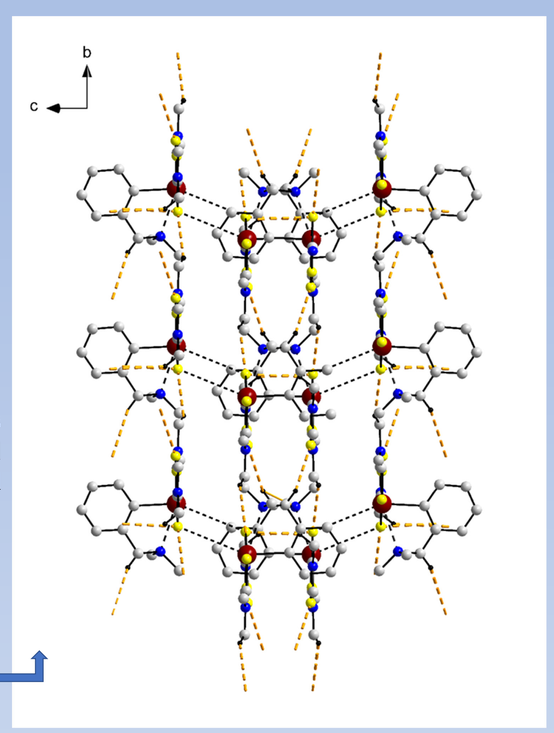



**Figure 4.** View along the *a* axis of the unit cell showing the supramolecular network arising from weak C–H···S interactions (*orange* fragmented line) in the crystal of **4**. Dimeric units are between the *black* fragmented lines

***Hirshfeld surface analysis***

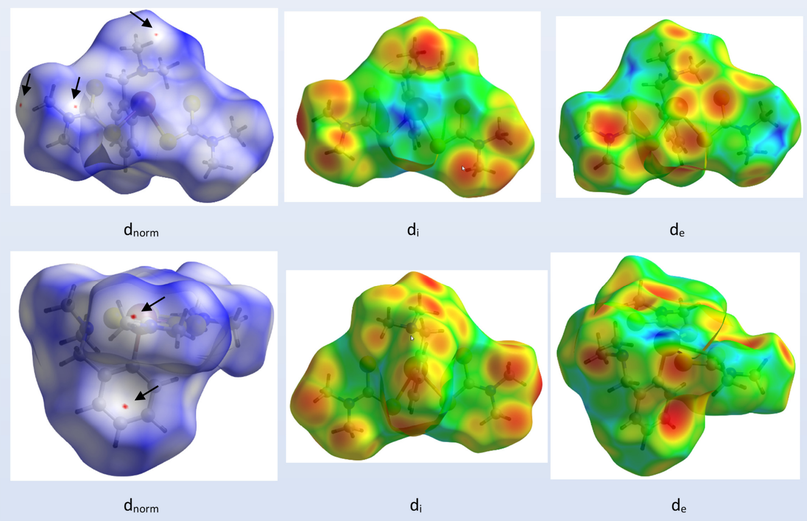



**Figure 5.** Hirshfeld surface for **4**, mapped over $d_{norm}$ over the range -0.010 to +1.367 arbitrary units (a. u.), $d_i$ over the range 1.053 to +2.943 a. u., and $d_e$ over the range 1.053 to +2.752.

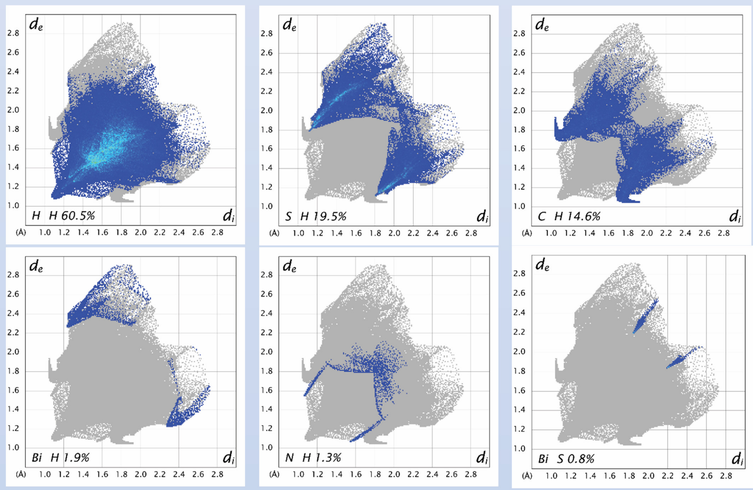



**Figure 6.** Decomposed two-dimensional fingerprint plots for **4** showing the percentage contribution to Hirshfeld $d_{norm}$ mapped surface for each type of interaction.

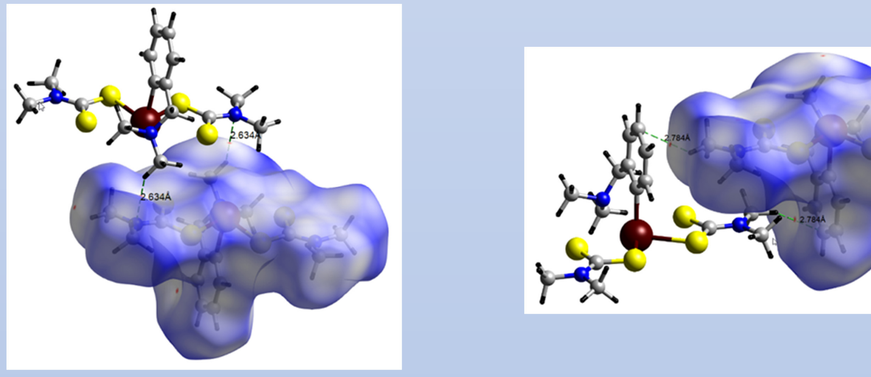



**Figure 7**. Localization of the C–H···π (*left*) and C-H···N (*right*) interactions on the Hirshfeld surface mapped with $d_{norm}$ showing the neighboring molecules involved.

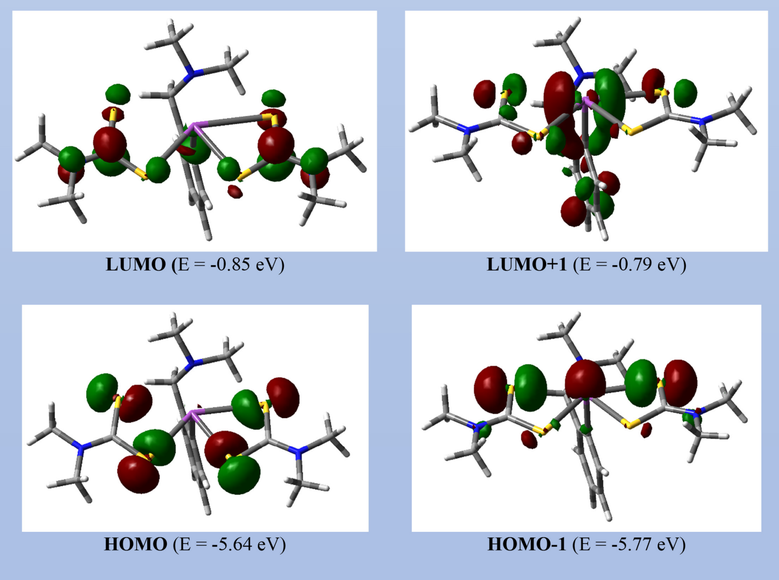



**Figure 8.** Isosurfaces (with 0.05 isovalue) of selected molecular orbitals of **4**.

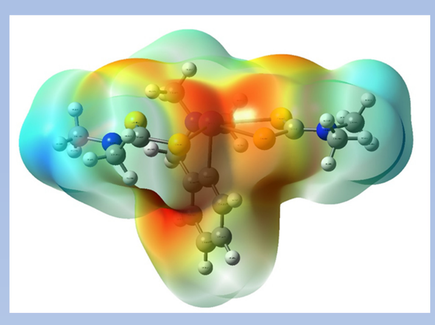


**Figure 9.** Electrostatic surface potential map (higher electron density regions are in *orange-red* and lower electron density regions are in *blue*) in the molecule of **4**.

## Conclusions

Compound **4** shows clean decomposition to $Bi_2S_3$ in the 220-320°C temperature range and could be a good candidate as a single source precursor for $Bi_2S_3$.

In the crystal structure of compound **4** weak Bi···S, C–H···S, C–H···N and C–H···π interactions were identified and also confirmed by analysis of Hirshfeld surface.

The DFT and NBO analysis revealed that Bi participates in bonding with valence *p* orbitals; the *s* valence orbital being mainly nonbonding.

Several stabilizing *3c-4e* interactions involving Bi, N, and S favor coordination of the ligands to the metal center. The charge distribution over the molecule correlates well we the observed interactions in the crystal

**Acknowledgements**

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