

# C-H $\cdots$ N $\equiv$ C hydrogen bonding in cyanobenzeneethylenedithio-tetrathiafulvalene compounds

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The importance of C-H $\cdots$ N $\equiv$ C interactions in the crystal engineering of conducting materials was recently evidenced by a new type of two-dimensional conducting material with the composition of (5-CNB-EDTTTF)<sub>4</sub>A with a variety of anions A, where CNB-EDT-TTF denotes the electron donor cyanobenzeneethylenedithiotetrathiafulvalene, which has been described in the last few years, presenting a new type of bilayer structure.[1-6] The unique bilayer donor structure of these compounds is due to the network of C-H $\cdots$ N $\equiv$ C interactions, which although generally considered weak, are effective in the self-assembly of the crystal structure. The role of these weak interactions is made clear by a comparison of the salts of this donor and the related isomer 4-CNB-EDT-TTF, where no bilayer structure is obtained but a variety of related interactions are observed instead.[7] This comparison allows different patterns of weak C-H $\cdots$ N $\equiv$ C interactions to be identified in these compounds, which can be described as combinations of several different synthons of type R<sup>2</sup><sub>2</sub>(10), R<sup>2</sup><sub>2</sub>(24), R<sup>2</sup><sub>2</sub>(26), R<sup>2</sup><sub>3</sub>(10), R<sup>2</sup><sub>4</sub>(8), R<sup>2</sup><sub>4</sub>(10), R<sup>4</sup><sub>8</sub>(20), and R<sup>3</sup><sub>4</sub>(30) or C(5) and C(6) infinite chains. The different patterns of interactions are comparable with those observed in other cyano compounds, as well as the magnitude of the interaction enthalpy associated with the different synthons, as estimated by means of density functional theory (DFT) calculations.

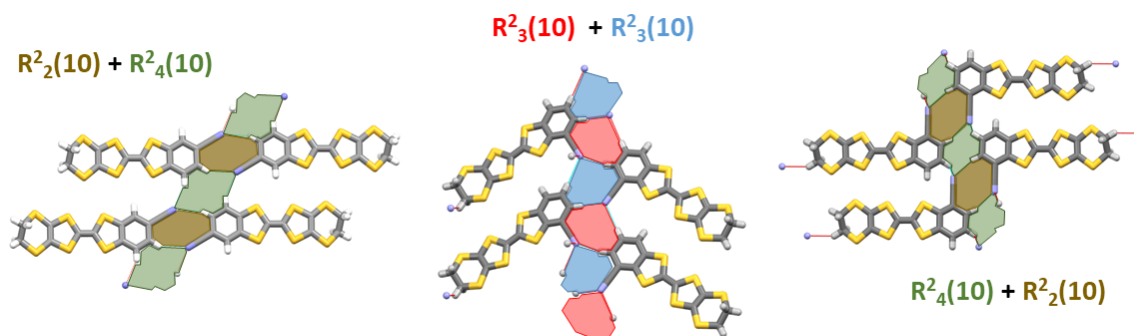


Fig. 1. C-H $\cdots$ N $\equiv$ C Hydrogen bonding in cyanobenzene-ethylenedithio-tetrathiafulvalene compounds.

## References

- [1] S. Oliveira et al., *Inorg. Chem.* **6677–6679**, 54 (2015).
- [2] S. Rabaça et al., *Inorg. Chem.* **10343–10350**, 55 (2016).
- [3] S. Rabaça et al., *Crystals* **142**, 8 (2018).
- [4] S. Oliveira et al., *Crystals* **608** 9 (2019).
- [5] I.C. Santos et al., *CrystEngComm* **8313–8321** 22 (2020).
- [6] I.C. Santos et al., *CrystEngComm* **8313–8321** 22 (2020).
- [7] S. Rabaça et al., *CrystEngComm* **1145–1155** 24 (2022).