

Electron Density Study of 2,5-Dimethyl-3,4-trimethylene-6a-thiathiophthene Using XRD, XAS and DFT Calculations

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Thiathiophthene, a planar molecule with two fused heterocyclic five-membered rings and essentially a linear S-S-S bond, is a molecule of great interest due to the unusual bonding characters and the possible aromatic properties of the two five-membered rings. In order to understand the remarkable bonding properties, the electron density distribution of one of the derivatives, i.e. 2,5-dimethyl-3,4-trimethylene-6a-thiathiophthene ($C_{10}H_{12}S_3$), was investigated both by single crystal X-ray diffraction and by DFT calculations. The X-ray crystal structure of $C_{10}H_{12}S_3$ was studied both at 295 K and at 100 K. The Space group is C2/m at 295 K, which is transformed to P2₁/n at 100 K. The mirror symmetry perpendicular to 2-fold axis disappears at low temperature. Such reduction of symmetry elements was also found in a previous study on the 2,5-dimethyl-6a-thiathiophthene[1]. The bond lengths of two S-S bonds are crystallographically the same [2.3341(8)Å] at 295K, but are significantly different [2.3274(5) and 2.3393(5) Å] at low temperature. The experimental electron density is produced according to multipole model. The theoretical electron density is calculated by DFT calculation, where the basis set of 6-31G** is used for all the atoms but an additional diffuse function is added for S atom. Results on the electron density distribution will be presented in terms of deformation density, Laplacian maps and the topological properties. Sulfur K-edge X-ray absorption spectroscopy (XAS) is also undertaken to further our knowledge on the electronic configuration of S atom.

[1] Wang Y., Wu S. Y., Cheng A. C., *Acta Cryst.* 1990, **B46**, 850.

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