1,4,5,8-Tetraazafulvalene – Darstellung schwefelhaltiger Derivate und Zuordnung des Chromophors*

1,4,5,8-Tetraazafulvalenes – Synthesis of Sulfur-Containing Derivatives and Classification of the Chromophor

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In order to obtain sulfur-containing tetraazafulvalenes the derivatives **1** – **3** were cross-coupled with different types of acetylenes *via* palladium-catalyzed reactions. Starting from the tetrabromoaryl derivative **3a**, four bromine atoms could be replaced by 2-ethynylthiophene. Under analogous conditions, the methylsulfanyl esters **7** – **11** could be obtained by employing 4-ethynylbenzoic acid 4-(methylsulfanyl)butylester **6**. Lipoic acid could be integrated into tetraazafulvalenes successfully in a two step reaction. First, the Sonogashira coupling method yielded the compound **12** possessing two (4-anilino)ethynyl residues which were then condensed with lipoic acid to give derivative **13**.

Whereas the NMR data suggest the predominance of prototropic form **A**, UV/vis spectra of the deeply colored tetraazafulvalenes are in favor with structure **B** rather than with structure **A**. DFT calculations at the B3LYP/6-31G(d) level showed that tautomeric form **B** is about 60 kJ/mol more stable than **A**. In addition, time-dependent density functional theory calculations support the substructure of two crossed diazaheptamethinemerocyanines.

Key words: Tetraazafulvalenes, Cross-Coupling Reactions, Lipoic Acid, Chromophoric System