

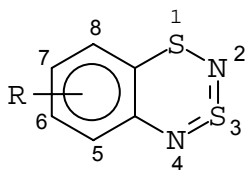
The Structural Dichotomy of Substituted 1,3 $\lambda^4\sigma^2$,2,4-Benzodithiadiazines

Irina Yu. Bagryanskaya, Alexander Yu. Makarov, Yuri V. Gatilov

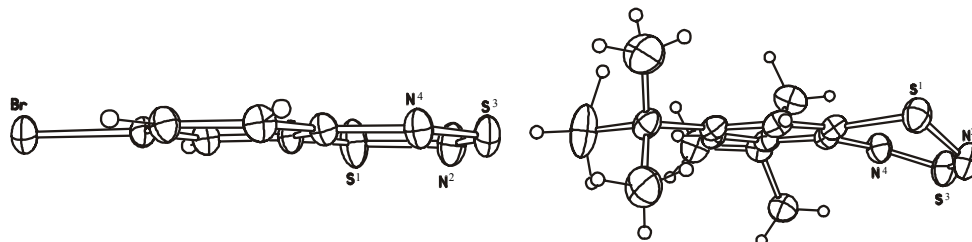
*N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch
Russian, 630090, Novosibirsk, Russia*

Fax: +7 (383 2) 34 4752. E-mail: bagryan@nioch.nsc.ru

1,3 $\lambda^4\sigma^2$,2,4-Benzodithiadiazines, hyperelectronic (π - and σ -excessive) and antiaromatic (12 π -electron) heterocycles, reveal high and varied heteroatom reactivity along with interesting structural dichotomy. According to X-ray crystallography and gas electron diffraction, as well as post-HF and DFT calculations, these compounds are structurally non-rigid because they possess a low-energy vibrational mode that allows the molecule to be deformed easily upon going from the gas phase to the solid. As a consequence, two types of molecular geometry, one perfectly planar and another significantly bent along the S¹...N⁴ line, are observed both for free molecules and those packed in the crystal.



This work presents X-ray molecular geometries for a number of variously substituted 1,3 $\lambda^4\sigma^2$,2,4-benzodithiadiazines. For the parent compound [1] and its substituted derivatives with R = 7-OCH₃, 5-CF₃, 6-F, 7-Br, 5,6,8-F₃ and 5,6,7-F₃ the molecules are planar in the solid state, whilst in the case of R = 6,8-F₂, 6-CH₃, 5-OCH₃, 5-Br, 8-Br, 5,6,7,8-F₄ and 5,7-t-Bu₂ they are bent along the S¹...N⁴ line by up to 25.2° (for 5,7-t-Bu₂ derivative). Of the two crystallographically independent molecules of the 6-Br derivative, one is perfectly planar whereas the other is bent by 3.1°, which directly indicates the importance of packing effects of the crystal lattice.



The bond lengths in studied compounds are typical. In the N² = S³ = N⁴ fragment, the bond lengths are nearly identical for R = 7-OCH₃, 5-CF₃, 6-F, 8-Br and 5,6,7-F₃, whilst for R = 6,8-F₂, 6-CH₃, 5-OCH₃, 5-Br, 6-Br, 7-Br, 5,6,8-F₃ and 5,7-t-Bu₂ they are markedly different. Thus, the S=N double bonds' length position does not depend on the type of molecular geometry - planar or bent.

The X-ray solid-state geometries of 1,3 $\lambda^4\sigma^2$,2,4-benzodithiadiazines are also compared with those from gas electron diffraction experiments and non-empirical quantum chemical calculations.

[1] A.W. Cordes, M. Hojo, H. Koenig, M.C. Noble, R.T. Oakley, W.T. Pennington, *Inorg. Chem.*, 1986, 25, p.1137.