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THE STUDY OF STRUCTURE OF 3-METHYL-2,2,4-TRINITRO-3-THIOLEN-1,1-DIOXIDE

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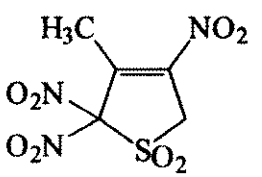
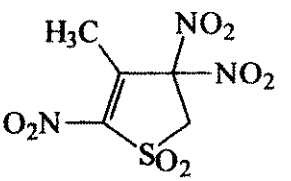
3-Methyl-2,2,4-trinitro-3-thiolen-1,1-dioxide (I) is a representative of a new type of polynitroheterocyclic compounds. This compound combines typical properties of trinitromethyl compounds with reactivity of thiolen-1,1-dioxides. The unusual combination of functional groups in the molecule of this compound causes a great variety of ways of reactions and results in a wide range of forming compounds[1-3]. Besides that the results of the study of chemical behavior and spectra of 3-methyl-2,2,4-trinitro-3-thiolen-1,1-dioxide (I) (IR, UV, NMR H^1, C^{13} spectroscopy methods) haven't excepted the possibility of exsistence of this compound as two isomeric forms (I) and (II).



I



II

To determine which isomer is more thermodynamically stable we performed DFT geometry optimization on the B3PW91/6-311+G* level of theory using G98 computer program. The calculated results revealed that isomer II is only 0.3 kcal/mole more than I. Theoretical ^{13}C NMR shifts and IR frequencies agree better with observed counterparts for the solid compound of the form I. The results of the study of its molecular crystal structure by powder diffraction data have turned out to be the basic experimental proof of existence of studied compound as structure I in solid phase. X-ray powder diffraction pattern for indexing, structure solution and refinement was measured in transmission mode with Stadi-P laboratory powder diffractometer in 8 – 80° 2θ region, CuK_{a1} radiation. The orthorhombic crystal structure - a= 13.999(3) Å, b= 11.806(3) Å, c= 5.979(2) Å, sp. gr. $Pna2_1$ - was solved with the grid search procedure[4] and refined by the Rietveld method.

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(4) Chernyshev V.V., Schenk H. *Z. Kristallogr.* **1998**, *213*, 1.