

Why are rhodanines less efficient reagents in Diels–Alder reactions than isorhodanines? A quantum chemical study.

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Streszczenie

The reactivity of the 5-arylidenerhodanine and 5-arylideneisorhodanine derivatives in reactions with dimethyl maleate was computationally studied at the DFT(M06-2X)/6-311+G(d,p) theory level. Eight stereoisomers of the reaction products were considered. The effect of the solvent was taken into account by means of the continuous and discrete models for acetic acid (PCM and three CH₃COOH molecules). Aromatic stabilization of the transition states was documented by the values of HOMA, NICS(0), and NICS(1) indices. The higher reactivity of the isorhodanine derivative was associated with a relatively low activation energy, ΔE_a (15.2–22.3 kcal mol⁻¹), which is needed to cross the TS. For the rhodanine derivative, higher values of ΔE_a (34.1–36.1 kcal mol⁻¹) were obtained. The reactivity was also studied from the perspective of the frontier molecular orbitals, the energy gaps between the HOMO and LUMO, the flux of electron density, the Fukui functions, $f^+(r)$, $f^-(r)$, and $f^0(r)$, and the global indexes defined in the conceptual DFT, i.e., the electronic chemical potential, chemical hardness, global electrophilicity, and empirical nucleophilicity index.

Słowa kluczowe

Diels-Alder, Rhodanine, isorhodanine, dimethyl maleate

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