Geometrical isomerism in ?-nitrostyrenes: Preferred conformations of (E)- and (E)-1-(4-methylthiophenyl)-2-nitrobutenes

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Condensation of 4-methylthiobenzaldehyde with 1-nitropropane unexpectedly afforded separable amounts of both (E)- and (Z)-1-(4-methylthiophenyl)-2- nitrobutene. The 1H and 13C NMR spectra allowed the unequivocal assignment of all signals and their correlation with the preferred conformations adopted by these compounds as determined by NOESY experiments. Hartree Fock theory optimizations at the 6-311G(d,p) level were carried out for the stereoisomeric 4-methylthionitroethene, -nitropropene, and -nitrobutene pairs, and the relative energy differences between isomers were calculated in order to estimate approximate E/Z equilibrium constants. These energy differences decrease with the increasing number of side chain carbon atoms, explaining the possibility of separating (E)- and (Z)-nitrobutenes and the failure to isolate the (Z) isomers of the lower homologues under the usual thermodynamically controlled reaction conditions.