

The conformational analysis of push-pull enamines using FTIR and NMR spectroscopy, and quantum chemical calculations. VI. β -*N*-Methyl-aminovinyl trifluoromethyl ketone and α -methyl- β -*N*-methylaminovinyl trifluoromethyl ketone.

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Artykuł

X-Ray analysis, NMR and IR Fourier spectra of two enaminoketones 4-(N-methylamino)-1,1,1-trifluorobut-3-en-2-one $\text{F}_3\text{Csbnd COsbnd CHdbnd CHsbnd NH(CH}_3\text{)}$ (1) 4-(N-methylamino)-1,1,1-trifluoro-3-methylbut-3-en-2-one $\text{F}_3\text{Csbnd COsbnd C(CH}_3\text{)dbnd CHsbnd NH(CH}_3\text{)}$ (2) were studied in solid state and solutions. It was shown that the substitution of proton at α -position of vinyl moiety with methyl group changes significantly electronic and spatial structure of enaminoketone. In solid state enaminoketone 1 is found to be exclusively as Z-s-Z-ap isomer with intramolecular hydrogen bond. At the same time molecules of enaminoketone 2 have E-s-E-ap stereoisomeric structure forming dimers due to intermolecular $\text{Nsbnd HctdotOdbnd C}$ hydrogen bonds. Exposure of Ar-matrix isolated 1 to UV-radiation results in appearance of various E forms with free methylamino- and hydroxy groups. The same effect was observed for 2 in solutions in CCl_4 under addition of polar HMPA or DMSO during spontaneous $\text{E} \rightleftharpoons \text{Z}$ isomerization. For enaminoketone 1 under similar conditions we observed

reverse process of $\text{Z} \rightleftharpoons \text{E}$ isomerization, E stereoisomeric forms with hydroxy group being trace quantity only. Study of solvent influence on FTIR spectra revealed that introduction of methyl group as substituent at α -position of vinyl moiety increases electron population of Cdbnd O double bond. Consequently, in contrast with enaminoketone 1 where the main contribution to the $\tilde{\nu}(\text{Cdbnd O})$ band shift to lower wavenumbers in all three stereoisomeric structures makes solvent polarity/polarizability term (π^*), influence of solvent's hydrogen bond acceptor (HBA) basicity (β) on $\tilde{\nu}(\text{Cdbnd O})$ band shift of 2 predominates in the E-s-Z-ap and Z-s-Z-ap isomers. Similarly to enaminoketone 1, negative shift of the $\tilde{\nu}(\text{Cdbnd C})$ band to lower wavenumbers occurs due to hydrogen bond formation between π system of vinyl moiety and hydrogen bond donor solvents in all stereoisomeric forms of enaminoketone 2.

Słowa kluczowe

NMR and IR-spectra, conformational analysis, enaminoketones, density functional calculations

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