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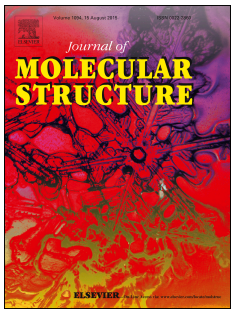

Synthesis, conformation, and photochemistry of difluoroacetyl isocyanate $CF_2HC(O)NCO$ and isothiocyanate $CF_2HC(O)NCS$

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Synthesis, Conformation, and Photochemistry of Difluoroacetyl Isocyanate $CF_2HC(O)NCO$ and Isothiocyanate $CF_2HC(O)NCS$

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ABSTRACT. Two carbonyl pseudohalogen compounds $CF_2HC(O)NCO$ and $CF_2HC(O)NCS$ have been synthesized and fully characterized by IR (gas-phase, matrix-isolation), Raman (liquid), UV−vis (gas-phase), and NMR (^{19}F, ^{13}C, ^{1}H) spectroscopy. The conformational properties and photochemistry of both species have been studied by combining matrix-isolation IR spectroscopy and quantum chemical calculations with the B3LYP, MPW1PW91, CBS-QB3 methods. Two conformers (*syn* and *anti*), depending on the configuration between the C=O and pseudohalogen ligands (NCO and NCS), have been unambiguously identified in both gas phase and solid noble gas matrices (Ar and Ne). Consistent with the theoretical calculations, the *syn* conformation is energetically more favorable. Upon irradiation with an ArF excimer laser (193 nm), $CF_2HC(O)NCO$ and $CF_2HC(O)NCS$ in cryogenic matrices eliminate CO and yield CF_2HNCO and CF_2HNCS, respectively. The underlying mechanism for the photochemistry of $CF_2HC(O)NCO$ is rationalized by the elimination of the carbonyl rather than the isocyanato C=O moiety.

Keywords: Isocyanates, isothiocyanates, conformation, photochemistry, matrix-isolation, quantum chemical calculations.