

Experimental Structure of $\text{CF}_3\text{CO}_2\text{CH}_2\text{CF}_3$ from Electron Diffraction Data, Infrared Spectra and Quantum Chemical Calculation of Vibrational Properties

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The molecular structure of 2,2,2-trifluoroethyl trifluoroacetate, $\text{CF}_3\text{CO}_2\text{CH}_2\text{CF}_3$, was determined in the gas phase from electron-diffraction data supplemented by ab initio (HF, MP2) and DFT calculations using 6-31G(d), 6-311++G(d,p) and 6-311G(3df,3pd) basis sets¹. The experimental and theoretical data indicate that, although both *trans* and *gauche* conformers are possible by rotation about the O-CH₂ bond, the preferred conformation is *trans*. To explain this fact, the total energy of each conformation and the natural bond orbital (NBO) partition schemes were considered. In addition, the total potential energy was deconvoluted using a Fourier-type expansion with six terms. The infrared spectra of the substance in the gaseous, liquid and solid states as well as the Raman spectrum of the liquid were also obtained. These spectra show the presence of both *trans* and *gauche* conformers by the components of some fundamental mode bands. The harmonic vibrational frequencies and the force field were calculated² using the above-mentioned techniques. The force constants were adjusted by scaling to achieve a final root-mean-square deviation of 10 cm⁻¹ between calculated and experimental frequencies.

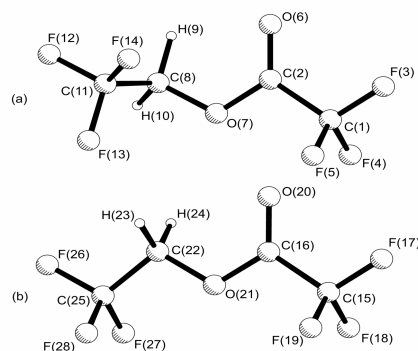


Figure 1: Molecular structure, including numbering scheme, for (a) *gauche* conformer, and (b) *trans* conformer of $\text{CF}_3\text{CO}_2\text{CH}_2\text{CF}_3$.

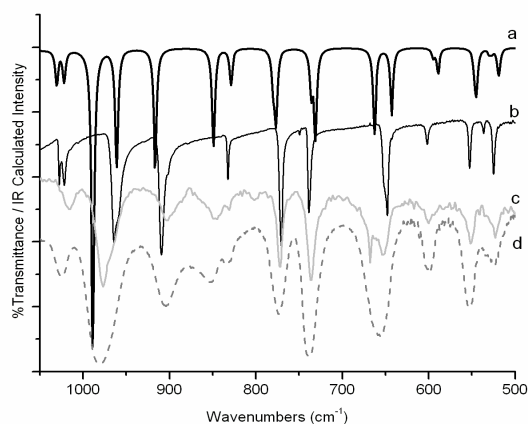


Figure 2: Infrared spectra of $\text{CF}_3\text{CO}_2\text{CH}_2\text{CF}_3$. a) calculated with B3LYP/6-311++G** for the mixture of conformers; b) solid (-160°C); c) liquid (room T); d) gas.

[1] *Gaussian 03*, Revision B.02, Gaussian, Inc., Pittsburgh PA, 2003.

[2] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, *J. Am. Chem. Soc.* 105 (1983) 7037.