Experimental and quantum chemical studies on the molecular structure of 3,3,3-trifluoropropane-1-sulfonyl chloride: CF3CH2CH2SO2Cl

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ABSTRACT

The experimental and theoretical study on the molecular and vibrational analysis of $CF_3CH_2CH_2SO_2Cl$, 3,3,3-trifluoropropane-1-sulfonyl chloride is presented. The IR and Raman spectra were recorded in liquid state and compared with the spectral data obtained by the DFT/B3LYP method usingthe6-311G(3df) basis set. The influence of hyperconjugation effects of the lone pairs (LP) chlorine atom on the vibrational behavior of the group SO_2 was determined. The TD-DFT approach was applied to assign the electronic transitions observed in the UV—visible spectrum.

1. Introduction

The sulfonyl group has many important applications in organic and medicinal chemistry. As a solid group, it is used for the protection of amines and sulfones [1,2].

Sulfonyl chlorides are often chosen as building blocks in medicinal chemistry for their ability to easily react with heterocyclic amines to create complex sulfonamides [3,4] like 3,3,3-trifluoropropane-1-sulfonyl chloride. Cyclopropanesulfonyl chloride and cyclopentanesulfonyl chloride are reported in detail as building blocks in the synthesis of TNF- converting enzyme (TACE) inhibitors [3].

Structural and conformational properties of several compounds of the YSO_2R type with $Y = CF_3, CH_3$, CCl_3 and $R = F$, OH, NH_2, CH_3, CF_3, Cl, O^-, Na^+ [5—8] were previously studied in this laboratory. The electronic properties and vibrational spectra of 3,3,3-trifluoropropane-1-sulfonyl chloride were not studied previously.

Because of the extensive and varied field of application of this compound, we have extended our investigation to the $CF_3CH_2CH_2SO_2Cl$ molecule, to obtain information about the conformational and vibrational properties. The transferability concept is very useful to predict the structure and conformational preference of the compounds of the YSO_2R type by means of quantum mechanical calculations and vibrational analysis. In this paper we present a complete analysis of vibrational spectra (infrared and Raman) obtained from experimental and theoreticalparametersoptimized with different combinations of basis sets.

Besides, the energy of the system in relation to the internal rotation around the CC-SCl dihedral angle was calculated using several computational approaches and fitted to the six-fold Fourier-type expansion. The conformational preference of the molecule can be explained using this methodology.

The UV—visible spectrum of the $CF_3CH_2CH_2SO_2Cl$ in methanol solution was also recorded and electronic property (Frontier orbitals) and band gap energy were calculated by the TD-DFT approach. The influence of hyperconjugation effects of the lone pairs (LP) chlorine atom on the vibrational behavior of the group SO_2 was studied in the two conformers. The lpCl → $\sigma^*S=O$ interaction incrementis correlated with a decrease of the S=O antisymmetric stretching in all conformers.

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2. Materials and methods

2.1. Experimental

The $CF_3CH_2CH_2SO_2Cl$ compound was purchased from Sigma-Aldrich Chemical Company with a stated purity greater than 97% and was used without further purification. The FTIR spectrum was recorded in the $4000-400$ cm^{-1} region with a spectral resolution of 2 cm^{-1} using a Perkin-Elmer GX1 FTIR spectrometer. The Raman spectrum of the liquid at RT was measured in the $4000-100$ cm^{-1} interval with a Thermoscientific DXR Raman microscope. The Raman data were collected using a diode-pump, solidstate laser of 532 nm.

The UV−visible absorption spectrum of the $CF_3CH_2CH_2SO_2Cl$ in methanol solution was examined in the $200-400$ nm range using a Beckman DU 7500 diode array spectrophotometer.

2.2. Computational details

Quantum-chemical calculations were performed using the Gaussian 03 program package [9]. Geometry optimisations were performed using DFT functionals. Pople's 6-31G(d), 6-311G(d,p), 6-311G(3df), 6-311++G(d,p) [10–12] and Dunning correlation consistent cc-pVDZ [13] basis sets were used throughout. DFT calculations were performed using Becke's three-parameter hybrid exchange functional(B3) combined with the Lee-Yang-Parr gradient-corrected correlation functional(LYP) [14–17]. The second DFT method used, mPW1PW91 [18], applies a modified Perdew-Wang exchange functional and Perdew-Wang 91 correlation functional. The gradient-corrected correlation functional of Perdew, Burke and Ernzerhof (PBEPBE) was also used in the geometry optimisations [19,20]. All calculations were performed with standard gradient techniques and default convergence criteria. The nature of stationary points was checked through the vibrational wavenumbers calculated from the analytical second derivatives of the energies, with zero-point energy corrections neglected.

The potential energies associated with dihedral angles were calculated with MP2 [21]. and B3LYP methods using the 6-31G(d), 6-311G(d,p) and 6-311++G(d,p) basis sets where the molecular geometry was optimised for fixed values of the C1-C2-C5-S11 dihedral angle and all other parameters allowed to relax. In a second similar set of calculations, the C2-C5-S11-Cl12 dihedral angle was fixed. The total energy curve was constructed in 10° steps using default convergence criteria as implemented in the Gaussian03 programs.

Vibrational modes were assigned using the GaussView program [22]. The calculated frequencies were scaled using the Yoshida [23] methodology and the potential energy distribution (PED) was calculated using the VEDA program [24].

Electronic transitions within the single-electron approximation and the SCRF, Polarizable Continuum Model (IEF-PCM and C-PCM) approximation in methanol [25–30], were analyzed by the time-dependent DFT (TD-DFT) method. The absorption energies in the UV−visible range with their CI (configuration interaction) description as well as their oscillator strength ($f > 0$) were obtained from vertical electronic excitation energies.

A natural bond orbital (NBO) calculation was performed at the B3LYP/6-311++G(d,p) level using the NBO 3.1 [31–34]program as implemented in the Gaussian 03 package.

The population was calculated according to a Boltzmann distribution:

$$\%pop_i = \frac{e^{-\Delta G_i/RT}}{\sum_{k=1}^{n} e^{-\Delta G_k/RT}} \times 100\% \tag{1}$$

2.3. Prediction of Raman dispersion intensities

The Raman activities (SRa) calculated with Gaussian 03 program were converted to relative Raman intensities (IRa) using the following relationship derived from the theory of Raman scattering intensity [35]:

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[1 - \exp\left(\frac{-hc\,v_i}{k\,T}\right)\right]} \tag{2}$$

where v_0 is frequency of the exciting laser light ($v_0 = 18797$ cm^{-1} corresponding to the wavelength of 532 nm of a diode-pump, solidstate laser a con-focal aperture of 25 lm pinhole and 10 objective), v_i is the frequency of the ith normal mode (cm^{-1}) and S_i is the Raman scattering activity of the ith normal mode. f is a suitably chosen common normalization factor for all peak intensities (equal to 10^{-12}).

3. Results and discussion

3.1. Molecular energy and structural properties

The potential energies surface (PES) (Fig. S1) of the $CF_3CH_2CH_2SO_2Cl$ were calculated with PM6 [36] semiempirical methods, with respect to the CCCS and CCSCl dihedral angles. There were eight minima on the potential surface, four of which were the mirror image of the other four (Fig. 1). Since three of them had a free energy difference lower than 10 kJ mol^{-1} with respect to the most stable form they were chosen to be studied.

In order to make a comprehensive study of the conformations, other calculations of potential energy variation were made with respect to the CCCS and then with respect to the CCSC dihedral angles calculated with MP2 and B3LYP methods using different basis sets (Fig. 2(a) and (b)). There is a good agreement between them in terms of maxima and minima positions, although the B3LYP method gave slightly smaller relative energies. The potential-energy scans of the CCCS dihedral angle showed two minima. One represented the *anti, anti*(a, a) (C_s)form (CCCS and CCSCl = 180°) and the other a *gauche, quasi-anti*, (g, q-a) (C_1) form (g, q-a) (CCCS = 160° and CCSCl = 75.3°). All the groups in both conformers were staggered. The potential-energy scan of the CCSCl dihedral angle identified two minima, the *anti, anti*(a, a) (C_s)form (CCCS and CCSCl = 180°) and the *anti, gauche (a, g)*(C_1)form (CCCS = −176.9 and CCSCl = −69.8°). All groups in both conformers were staggered.

In Table 1 the free energy is shown for the above mentioned conformers and the amounts of each conformer that should be observed in the gas phase at room temperature (using the Boltzman distribution equation). The conformer population ratio was predicted to be 1:29:70 (B3LYP/6-311G(3df)) since the free energy differences were $\Delta G_{(a,g-a,a)} = 9.90$ kJ mol^{-1} and $\Delta G_{(g,q-a-a,a)} = -0.49$ kJ mol^{-1} considering that the a, g and g, q-a conformers have a double degeneracy relative to the a, a conformer. Three conformers are shown in Fig. 1.

3.2. Internal barrier decomposition schemes

The total energy surface for the target torsion angle was