Conformational studies of 2-butanol using temperature-dependent Raman measurements and MM3 calculations

HAGEMANN, Hans-Rudolf, et al.

Abstract

Temperature-dependent Raman measurements between 190 and 358 K yield conformational enthalpy differences between 550 and 690 cal mol$^{-1}$ for racemic liquid 2-butanol. The conformational properties of 2-butanol were also studied using MM2 and MM3 calculations. The conformer 1, where C1 and C4 are in anti position, was found to be the most stable conformer with the MM3 calculations. Conformer 2, which has C1 and O5 in anti arrangement, has ca. 500 cal mol$^{-1}$ higher energy than 1. Comparisons of the calculated MM3 vibrational frequencies with the Raman spectra suggest that the most stable conformer in the liquid phase also adopts a C1,C4 anti conformation.

Reference


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Conformational studies of 2-butanol using temperature-dependent Raman measurements and MM3 calculations

H. Hagemann*, J. Mareda, C. Chiancone, H. Bill

Départements de Chimie Physique et de Chimie Organique, Université de Genève, 30 quai E. Ansermet, CH-1211 Geneva, Switzerland

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Abstract

Temperature-dependent Raman measurements between 190 and 358 K yield conformational enthalpy differences between 5.50 and 690 cal mol⁻¹ for racemic liquid 2-butanol. The conformational properties of 2-butanol were also studied using MM2 and MM3 calculations. The conformer 1, where C1 and C4 are in anti position, was found to be the most stable conformer with the MM3 calculations. Conformer 2, which has C1 and O5 in anti arrangement, has ca. 500 cal mol⁻¹ higher energy than 1. Comparisons of the calculated MM3 vibrational frequencies with the Raman spectra suggest that the most stable conformer in the liquid phase also adopts a C1.C4 anti conformation. © 1997 Elsevier Science B.V.

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1. Introduction

The conformational properties of chiral 2-butanol was recently the subject of an ab initio investigation as a model for the O–C–C–C moiety found in C-glycosides [1]. However, there are only limited experimental data available on the conformation of 2-butanol [2,3]. We have therefore undertaken a temperature-dependent Raman study of this compound. Furthermore, the conformational properties were studied in detail using MM2 and MM3 calculations. The MM3 calculations also provide vibrational frequencies which can be compared with the Raman spectra [4,5]. This comparison allows us, in the present case, to identify the conformation of the stable form in the pure liquid.

* Corresponding author.

2. Experimental

Raman spectra were obtained for racemic 2-butanol (Fluka, nominal purity > 99%) using our laboratory-assembled instrument. This consists of a computer-controlled SPEX 1403 monochromator equipped with a cooled PM detection system. Most of the spectra were obtained using the 488 nm line of the argon ion laser. The spectral resolution was ca. 2.5 cm⁻¹.

Measurements above room temperature were done using a thermostatted metal block built for conventional 1 cm optical quartz cells. An Oxford Instruments helium flow cryostat was used for the low temperature measurements.

The band intensities were estimated from band fitting, using Lorentzian or combined Lorentzian and Gaussian lineshapes to simulate the spectra. The same lineshape was kept over the entire temperature range (190–358 K).
Fig. 1. Two-dimensional MM3 conformation energy map for internal rotation in 2-butanol. The units of the energy contours are [kcal mol$^{-1}$] $\times$ 10.
3. Results and discussion

3.1. MM3 calculations

The MM3 [4] calculated conformational energy map for internal rotations around the dihedral angles $\Psi$ and $\Phi$ for 2-butanol is shown in Fig. 1. The most stable conformer $1$ on this surface has carbons C1 and C4 in anti orientation ($\Psi = 177.6^\circ$). This global minimum is located in the flat region of the energy surface. Indeed, for the rotations of the C2–C3–O5–H dihedral angle $\Phi$ between ca. $70^\circ$ and $170^\circ$, two shallow minima in this flat region have been computed. As the energy barrier between them is very small, it is presumed that at room temperature an averaged conformation for $1$ is observed.

Conformer $3$ ($\Psi = 178.4^\circ$ and $\Phi = 298.6^\circ$) presents an enthalpy difference of 660 cal mol$^{-1}$ with respect to the global minimum $1$.

Conformer $2$, where the O5 atom is in an anti position with respect to the C1 atom ($\Psi = 67.3^\circ$, $\Phi = 163.0^\circ$), is 490 cal mol$^{-1}$ higher in energy than conformer $1$. This value is slightly smaller than the one obtained from the $ab$ initio calculation (800 cal mol$^{-1}$) [1].

3.2. Raman spectra

The Raman spectra agree with previous data [3]. The spectra at 300 and 120 are shown in Fig. 2 for the region between 700 and 1200 cm$^{-1}$. In this spectral region, where C–C and C–O stretching modes are expected, important spectral changes are observed as a function of temperature. The spectrum at 120 K corresponds to some glassy state, as 2-butanol is not easy to crystallize. The melting point of racemic 2-butanol has been observed at 184.7 K [6]. A comparison between the spectra at 300 and 120 K allows the identification of bands at 779, 822 and 915 cm$^{-1}$ as pertaining to the most stable conformer in the condensed phase.

Plots of the relative intensity of several band pairs as a function of reciprocal temperature are given in Fig. 3. The corresponding slopes yield experimental enthalpy differences, with standard deviations in brackets, of 689(27), 556(54) and 550(89) cal mol$^{-1}$ respectively for the band pairs 792/822, 771/822 and 908/915 cm$^{-1}$. Other spectral regions showed too many overlapping lines for reliable fittings to be made.

MM3-computed vibrational frequencies of 785, 844 and 933 cm$^{-1}$ were obtained for the most stable conformer $1$. These values are shifted to 775, 842 and 935 cm$^{-1}$ for conformer $2$, and to 787, 842 and 931 cm$^{-1}$ for conformer $3$.

In the skeletal bending region (between 350 and 550 cm$^{-1}$), the Raman spectra present several overlapping bands. Nevertheless, the low temperature
spectra indicate that the bands for the most stable conformer are located at 383, 474 and 502 cm\(^{-1}\). These values can be compared with the calculated MM3 vibrational frequencies found at 356, 436 and 467 (conf. 1), 381, 406 and 466 (conf. 2) and 354, 443 and 474 cm\(^{-1}\) (conf. 3). Previous MM3 vibrational calculations for various organic molecules showed a tendency to slightly underestimate the skeletal bending frequencies [4,7]. In our case, if one shifts the calculated skeletal bending frequencies upwards by ca. 30 cm\(^{-1}\), one obtains excellent agreement with the different maxima observed in the Raman spectra. The calculated vibrational frequencies of conformers 1 and 3 are very similar, as they have practically the same C1–C2–C3–C4 dihedral angle. Comparison of the MM3 calculated and observed Raman spectra suggests that the stable conformer in the liquid has indeed the C1, C4 anti conformation. The comparison of computed and experimental data does not allow for any conclusion with respect to the C2–C3–O5–H dihedral angle.

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References