

# Intramolecular proton transfer from one ether oxygen to another



Jos Oomens<sup>a,b</sup>, Giel Berden<sup>a</sup>, Jonathan Martens<sup>a</sup>, Thomas Hellman Morton<sup>c,\*</sup>

<sup>a</sup> Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, NL-6525ED Nijmegen, The Netherlands

<sup>b</sup> van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, NL-1098XH Amsterdam, The Netherlands

<sup>c</sup> Department of Chemistry, University of California, Riverside 501 Big Springs Rd., Riverside, CA 92521-0403 USA

## ARTICLE INFO

### Article history:

Received 29 June 2016

Received in revised form 29 August 2016

Accepted 30 August 2016

Available online 1 September 2016

Dedicated to José Manuel Riveros Nigra.

### Keywords:

Infrared

Ether

Cation

Conjugate acid

Action spectroscopy

## ABSTRACT

Proton transfer in the conjugate acid cation of a symmetric diether, 1,5-dimethoxy-3,3-dimethylpentane (**1**), is explored both theoretically and experimentally via IRMPD spectroscopy. The optimized geometry of the cation has one oxygen pyramidalized (sum of the three angles  $\Sigma = 345^\circ$ ), while the other oxygen has a virtually planar geometry (if one includes the strongly hydrogen bonded O...H, the three bond angles sum to  $\Sigma' = 357^\circ$ ). Assuming that this geometry is not preserved upon intramolecular proton transfer from one oxygen to the other, two alternatives remain: either the two oxygens trade geometries ( $\Sigma$  and  $\Sigma'$  change places via a transition state that has a mirror plane of symmetry) or else both oxygens become pyramidalized. Because the asymmetric stretch couples with other vibrational modes of the cation, special attention is paid to the classical turning points at the zero point level corresponding to the lowest frequency vibration that shows a deuterium isotope effect, which occurs experimentally around  $895\text{ cm}^{-1}$ . This stretching vibration has a lower frequency than the bands assigned to O...H–O bends, and it shifts to still lower frequency in the deuterated ion. Because a normal modes calculation matches this vibration, we conclude that the potential energy surface matches a single-well and does not correspond to a double-well minimum.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Intramolecular proton transfer may appear simple, but it can display complexities upon closer scrutiny. For example, proton transit between two amine groups would seem to behave in a relatively straightforward fashion: trivalent nitrogen has only one lone pair, so the  $\text{H}^+$  in a monoprotonated diamine moves from one lone pair to the other. Complications arise even in a symmetric case, however, because situating the proton midway between the two basic atoms often corresponds to a local maximum. As a consequence, the potential energy surface for the  $\text{N–H}\cdots\text{N}$  asymmetric stretch constitutes a double-well minimum, for which the harmonic (normal modes) approximation predicts an asymmetric stretching frequency much higher than experiment reveals [1]. Moreover, the asymmetric  $\text{N–H}\cdots\text{N}$  stretch has a frequency lower than the two  $\text{N–H}\cdots\text{N}$  bending vibrations, which also represents unusual behavior.

Intramolecular proton transfer between two ether groups looks even more complex than intramolecular transfer between amines, because each oxygen has two lone pairs. Intermolecular  $\text{H}^+$  trans-

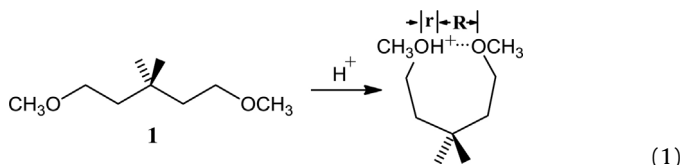
fer between two separate ethers has been studied extensively by experiment and theory [2–4], and the predicted IR spectra match the experimentally observed IRMPD spectra in the gas phase quite well. O...H–O bends appear at higher frequencies than do O...H–O asymmetric stretches, which seems to be characteristic of many proton-bound dimers. DFT calculations on the proton-bound dimer of dimethyl ether using the 6–31G\* basis set [2] (or MP2 calculations using a larger basis set [4]) predict that both oxygens are pyramidalized. In the proton-bound dimer of dimethyl ether at these computational levels the bridging proton turns out to be virtually equidistant from both oxygens, which calculations at higher levels confirm. Among the protonated species previously examined is the conjugate acid of diglyme,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ , [3] which has an intramolecular ionic hydrogen bond, but it remains unclear (as of this writing) which oxygen bears the proton and which is the bonding partner.

1,5-Dimethoxy-3,3-dimethylpentane, **1**, having two oxygens equivalent by symmetry, removes this ambiguity. The bridging proton in the conjugate acid of **1**, however, does not lie equidistant between the two oxygens. This paper addresses the question as to what the asymmetric stretch potential looks like when symmetry is broken in this manner. It makes use of IR Multiple Photon Dissociation (IRMPD) spectroscopy of gaseous positive ions to assess whether the potential surface for the fundamental O...H–O stretch

\* Corresponding author.

E-mail address: [morton@citrus.ucr.edu](mailto:morton@citrus.ucr.edu) (T.H. Morton).

is symmetrical or unsymmetrical. As in the case of intermolecular proton-bound dimers [2–4], a match between experiment and theory demonstrates a single-well potential minimum, whereas a severe mismatch suggests a double-well minimum.

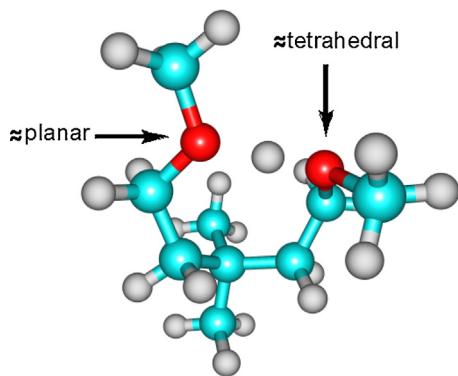


In general, protonation of an ether results in a pyramidalized oxygen. For example, the three bond angles around  $\text{Me}_2\text{OH}^+$  sum to  $\Sigma = 339^\circ$  [5]. In other words, the lone pair coplanar with the two C–O bonds has lower basicity than one out of the plane. For  $\alpha,\omega$ -dimethoxyalkanes, an unsymmetrical, strong hydrogen bond prevails in the conjugate acid ions. The protonated  $\alpha,\omega$ -dimethoxyalkane oxygen having the shorter O–H distance again has a pyramidal geometry, while (in the optimized structure) the longer O...H distance (corresponding to the strong hydrogen bond) has a very nearly planar orientation of the O...H relative to the two C–O bonds. This structural feature suggests that the potential surface for proton motion might correspond to transit from the more basic lone pair of one oxygen to the less basic lone pair of the other. Eq (1) depicts a typical case for a protonated, symmetrical diether, the conjugate acid of **1**. DFT predicts for the optimized geometry that the three angles around the protonated oxygen sum to roughly  $\Sigma = 345^\circ$ , while the three angles around the other oxygen (including the O...H) sum to nearly  $\Sigma' = 357^\circ$ .

This report focuses on 1,5-dimethoxy-3,3-dimethylpentane, **1**, an aliphatic diether whose conjugate acid gives one of the closest approaches between the two oxygen atoms. The first objective has been computationally to seek out the most basic  $\alpha,\omega$ -dimethoxyalkane having chemically equivalent oxygens, so that its conjugate acid ion can form in sufficient abundance via electrospray mass spectrometry (ESI). The second objective compares computation with experiment to explore the vibrational spectrum of the conjugate acid (as well as its deuterated analogue) in the gas phase by means of IRMPD spectroscopy (which leads to methanol expulsion) to decide between alternative potential surfaces.

The geometries at the classical turning points of the zero point level of the asymmetric stretch vibration have much more chemical relevance than the computationally optimized geometry. Three limiting cases for proton transfer can be imagined:

1. The geometry at the zero point level might transform such that the oxygens are pyramidalized at one (or both) of the classical turning points.



**Fig. 1.** 3-Dimensional representation of the DFT equilibrium geometry of the conjugate acid of **1** (B3LYP/AUG-cc-pVTZ). The predicted dihedral angle between the methoxy groups is  $102^\circ$ .

2. Alternatively, the oxygens might exchange geometries; *i.e.* the planar oxygen at one classical turning point becomes pyramidalized at the other classical turning point, while the pyramidal oxygen becomes planar in turn.
3. The optimized geometry described above at the bottom of the potential well (one oxygen virtually planar while the other oxygen is pyramidalized) might describe the geometry at both classical turning points of the zero point level.

The last choice appears chemically unreasonable, for it predicts that intramolecular  $\text{H}^+$ -transfer yields a protonated oxygen that remains planar. We discard this last option without further discussion, since calculations do not justify it. This paper will treat only the first two cases.

## 2. Experimental

Ions were generated in an electrospray ionization (ESI) source. For the FTICR experiments, [6] solutions containing mM concentrations of **1** were introduced at 10–50  $\mu\text{L}/\text{min}$  flow rates, while for the quadrupole ion trap experiments [7] (owing to increased sensitivity), 1  $\mu\text{M}$  solutions of **1** were introduced at a flow rate of 120  $\mu\text{L}/\text{h}$ . In both cases, the ions were guided to an ion trap (ICR cell or quadrupole ion trap) where protonated **1** ( $m/z = 161$  or 162 for the deuterated species) was mass isolated and irradiated by the tunable infrared beam from the FELIX free electron laser. In the experiments reported here, FELIX was set to produce 6  $\mu\text{s}$  long pulses in the 300–1800  $\text{cm}^{-1}$  frequency range with an energy up to 40 mJ/pulse at a repetition rate of 5 Hz and a bandwidth of 0.4% of the center frequency. The wavelength is calibrated using a grating spectrometer. Resonant absorption of the infrared radiation leads to an increase of the internal energy of the ion which results in dissociation. An infrared spectrum is obtained by monitoring the dissociation yield as function of the laser frequency. The yield at each infrared point is obtained from averaged mass spectra and is linearly corrected for the frequency dependent laser power.

The diol corresponding to compound **1** was prepared by reduction of 3,3-dimethylglutaric anhydride (Aldrich) with an excess of lithium aluminum hydride. This diol was dissolved in dry THF, doubly deprotonated with an excess of pentane-washed sodium hydride, then treated with an excess of iodomethane, refluxed, followed by aqueous workup, removal of solvent, and two successive distillations. Unless otherwise stated, DFT calculations were optimized using the B3LYP/AUG-cc-pVTZ basis set. Normal mode calculations on optimized geometries were performed at that level and vibrational frequencies above 800  $\text{cm}^{-1}$  are scaled by 0.97 [8]. Comparison with MP2/6-311++G\*\* optimizations shows that the difference between the minimum and the  $\text{C}_s$  geometry is 7.5 kJ/mol, versus 2.2 kJ/mol at the DFT level.

## 3. Results

Previous investigations have portrayed proton-bound homodimers of ethers as having two nearly equivalent O–H bond distances [2–4], which our B3LYP/AUG-cc-pVTZ calculations corroborate. For the intramolecular hydrogen bond in protonated **1**, however, the O–H and H...O bond lengths differ by about 0.177 Å. We ascribe this variation to constraints upon the rotations of the methoxy groups.

DFT modelling indicates that 1,5-dimethoxy-pentane is the most basic of the  $\alpha,\omega$ -dimethoxy-*n*-alkanes, consistent with previously published experimental data [9]. Based on the Thorpe-Ingold effect [10], one would expect dimethyl substitution of one of the carbons in the methylene chain to favor further cyclization of the conjugate acid. Whereas the fully extended conformation is calculated to have the lowest energy for neutral **1**, protonation on

Download English Version:

<https://daneshyari.com/en/article/5134233>

Download Persian Version:

<https://daneshyari.com/article/5134233>

[Daneshyari.com](https://daneshyari.com)