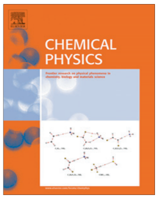
Chemical Physics 427 (2013) 87–94

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys



Short hydrogen bonds in 2,4-dinitrobenzoic acid complexed with pyridine

Monika Hartl [a,*], Luke Daemen [a], Hans Hartl [b], Irene Brüdgam [b], Jürgen Eckert [c]

[a] *Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[b] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany*
[c] *Department of Chemistry, University of South Florida, 4202 East Fowler Ave, Tampa, FL 33620, USA*

ARTICLE INFO

Article history:
Available online 9 November 2013

Keywords:
Short hydrogen bonds
Single crystal XRD
FT-IR
IINS
DFT

ABSTRACT

The aim of this work was to describe the vibrations connected with the short hydrogen bonds of differing geometries in 2,4-dinitrobenzoic acid and in 2,4-dinitrobenzoic acid complexed in two ratios with pyridine. All three compounds contain short hydrogen bonds either between two acid molecules (OH···O bond) or between acid and pyridine (NH···O bonds) or both. We selectively deuterated the proton of the 2,4-dinitrobenzoic acid molecule involved in the proton transfer to aid in the assignment of the H-bond protonic modes. The compounds have been characterized with single crystal X-ray diffraction, CHN elemental analysis, FT-IR and IINS spectroscopy. We show that our combination of analytical methods with DFT calculations represents a fruitful approach to observe the relationship between the geometries of hydrogen bonds and their dynamics.

Published by Elsevier B.V.

1. Introduction

The concept of hydrogen bonding is frequently attributed to Pauling who, in 1931, coined the term 'hydrogen bond' and used it to describe the structure of the $[FHF]^-$ anion. The initial concept can probably be traced back to the Swiss chemist Alfred Werner of transition metal complexes fame, who suggested proton delocalization in acid–base complexes with ammonia to explain the properties of these systems. His concept of Nebenvalenz (secondary valence) was introduced in 1902, which makes the study of hydrogen bonding well over one hundred years old. And yet, hydrogen bonding remains a fascinating topic of chemistry research in 2013.

The properties of low barrier hydrogen bonded acid–base complexes AH···B to $A^- \cdots HB^+$ is a matter of current interest in theoretical chemistry, hydrogen bond research and enzymology [1–5]. Generally, acids are classified according to their pK_a values in water, i.e. the amount of excess protons they produce in aqueous environments. In aprotic environments such as organic liquids, hydrophobic enzymatic environments, surfaces etc. this definition of acidity is not valid. The question then arises as to the variation of the properties of acid–base complexes AH···B as a function of an increasing acidity. It was recently shown in a qualitative way [1] that the geometries of the hydrogen bonded systems change in a characteristic manner when the acidity of AH is increased by a discussion of the H/D isotope effects on chemical shifts. The proton moves more or less in a single well whose minimum is shifted from A towards B. At the same time the A···B distances decrease and increase again when the proton is shifted across the hydrogen bond center. The disadvantage of the liquid state is that it produces a large distribution of proton potentials which renders a theoretical description difficult. Therefore, the study of crystalline model systems is highly desirable and these can be investigated by various techniques including more accurate computational studies. It is well known, however, that it is rather difficult to assign protonic vibrations in low barrier hydrogen bonds by IR spectroscopy [6]. The AH-stretching bands shift to very low frequencies as the A···B distance of the complexes decreases accompanied by a lengthening of the covalent A···H bond, and become very broad. The shift of the stretching mode to low frequencies can result in strong coupling with other molecular modes which makes it difficult to assign soley by spectroscopic means. A detailed knowledge of the vibrational frequencies and their dependence on H-bond geometry is essential for a theoretical description of the hydrogen bond. Inelastic Incoherent Neutron Spectroscopy (IINS) on the other hand can be utilized in cases where it is difficult to assign H-bond vibrations by optical methods particularly when the H-bond proton can selectively be deuterated.

A comparison of INS spectra of both isotopomers will in general readily reveal the H-bond vibrations as the scattering from one deuterium atom in the presence of many hydrogen atoms makes it essentially invisible. We have synthesized two acid–base complexes with different ratios of 2,4-dinitrobenzoic acid (2,4-DNBA) and pyridine (PYR) and compared their vibrational spectra with

---

* Corresponding author. Tel.: +1 5056652375.
E-mail address: hartl@lanl.gov (M. Hartl).

0301-0104/$ - see front matter Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.chemphys.2013.10.016

that of the pure acid, 2,4-DNBA, which contain both short OH$\cdots$O and NH$\cdots$O bonds. We selectively deuterated the proton of the 2,4-DNBA molecule involved in the proton transfer to aid in the assignmen of the H-bond protonic modes. The aim of this work was to describe the vibrations connected with the short hydrogen bonds of differing geometries in 2,4-dinitrobenzoic acid (2,4-DNBA) and in 2,4-dinitrobenzoic acid complexed in two ratios with pyridine (PYR). Previously published work by Sobczyk et al. [7] on 2,4-DNBA-PYR used single crystal X-ray diffraction and IR for characterization. We show that our combination of single crystal X-ray diffraction, IR-spectroscopy, CHN-analysis with IINS spectroscopy and DFT calculations, represents a fruitful approach on the interaction between the geometries of hydrogen bonds and their dynamics.

2. Materials and methods

2.1. Synthesis

2,4-dinitrobenzoic acid was used as received (Aldrich, 96%).

2.1.1. Pyridinium-2,4-dinitrobenzoate (2,4-DNBA)(PYR-d_5) and (2,4-DNBA-d_1)(PYR-d_5)

4.42 g 2,4-DNBA (20 mmol) was dissolved in 15 ml methanol (CH_3OH). 1.67 g pyridine-d_5 (20 mmol) was added and the solution was stirred for 30 min. A crystalline precipitate formed upon cooling. In order to obtain the deuterated complex (2,4-DNBA-d_1-PYR-d_5), the same procedure was performed using 20 mmol of 2,4-DNBA-d_1 instead of the protonated acid.

2,5-DNBA-d_1 can be synthesized by exchanging the acidic proton with deuterium: 10.06 g 2,4-DNBA (Aldrich, 96%), and 25 ml methanol-d_1 (CH_3OD) were mixed in a 100 ml glass flask and heated to the boiling point. The solvent was removed using a solvent evaporator. This procedure was repeated three times until IR spectroscopy showed a complete H-D exchange.

2.1.2. Pyridinium-bis (2,4-dinitrobenzoate) (2,4-DNBA)$_2$(PYR-d_5) and (2,4-DNBA-d_1)$_2$(PYR-d_5)

4.42 g 2,4-DNBA (20 mmol) was dissolved in 15 ml ethanol (CH_3CH_2OH). 1.67 g pyridine-d_5 (20 mmol) was added and the mixture stirred for 30 min. Crystals formed upon slow cooling (refrigerator). The deuterated complex was made by deuterating the acid (see above) and then repeating the synthesis as described here.

2.2. Characterization

Elemental analysis of the complexes was done in CHNS modus on a VarioEL (Elementaranalysensysteme GmbH). Fourier Transform Infrared Spectroscopy (FT-IR) was performed on a Nicolet 670 with ATR attachment at room temperature.

Single crystal X-ray data was collected at 173 K and 293 K, respectively, on a Bruker-XPS-diffractometer (CCD area detector, Mo-Kα-radiation, $\lambda = 0.71073$, graphite monochromator). Empirical absorption corrections was applied on the data using symmetry-equivalent reflections (SADABS) [10]. The structures were solved by direct methods and refinement based on F^2 data with a least squares procedure being carried out using SHELXS-97 and SHELXL-97 [11] in the WINGX system [12]. C, N, and O atoms were refined anisotropic. Hydrogen atoms were located in difference Fourier maps and refined for (2,5-DNBA)(PYR). For (2,5-DNBA)$_2$ (PYR) the hydrogen atoms in the NHO and OHO hydrogen bond were located and refined while the positions of the remaining hydrogen atoms were calculated with the standard bond lengths. A list of structure factors, anisotropic displacement parameters and complete geometry has been deposited with the IUCr. CCDC 940341 and CCDC 940342 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Details for the single crystal X-ray diffraction are given in Table 1.

The Incoherent Inelastic Neutron Scattering (IINS) spectra were collected with the samples at 10 K on the Filter Difference Spectrometer (FDS) at the Manuel Lujan, Jr. Neutron Scattering Center at Los Alamos National Laboratory. The instrument is used for vibrational spectroscopy with neutrons and is designed for high count rates thanks to a large solid-angle detector. The samples were sealed under helium atmosphere and loaded into cylindrical annular aluminum sample holders mounted in a closed-cycle refrigerator. The background for the samples was approximated by the scattering from a vanadium rod.

2.3. Computing

The Gaussian 03 suite was used throughout the article for DFT calculations [13]. Structural optimization and frequency calculations were performed using the Density Functional Theory (DFT) method with the hybrid B3LYP density functional (Becke 3-parameter and Lee–Yang–Parr correlation functional) and the 6–31 g basis set. The software aCLIMAX [14] generated the simulated IINS spectra from the output of the DFT calculations.

Table 1
Crystal data and structure refinement for pyridinium 2,4-dinitrobenzoate (2,4-DNBA)(PYR) and pyridinium-bis (2,4-dinitrobenzoate) (2,4-DNBA)$_2$(PYR) at 173 K.

Sample	(2,4-DNBA)(PYR)	(2,4-DNBA)$_2$(PYR)
Empirical formula	$C_{12}H_9N_3O_6$	$C_{19}H_{13}N_5O_{12}$
Formula weight	291.29	503.34
Temperature (K)	173(2)	293(2)
Wavelength (Å)	0.71073	0.71069
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C1c1
Unit cell dimensions		
a (Å)	7.454(2)	19.172(5)
b (Å)	7.960(2)	9.902(5)
c (Å)	11.330(3)	11.565(5)
Alpha (°)	92.669(5)	90.000(5)
Beta (°)	103.423(5)	108.364(5)
Gamma (°)	110.627(5)	90.000(5)
Volume (Å^3)	605.9(2)	2083.7(2)
Z	2	4
Calculated density (mg/m^3)	1.596	1.604
Absorption coefficient (mm^{-1})	0.13	0.14
F (000)	236	516
Crystal size (mm)	0.3 × 0.18 × 0.05	0.4 × 0.3 × 0.05
Crystal shape, color	plate, colorless	plate, colorless
Theta range for data collection (°)	1.87 to 30.02	2.2 to 25.4
Limiting indices	$-8 \leqslant h \leqslant 10$ $-11 \leqslant k \leqslant 11$ $-15 \leqslant l \leqslant 15$	$-23 \leqslant h \leqslant 23$ $-11 \leqslant k \leqslant 11$ $-13 \leqslant l \leqslant 13$
Reflections collected/unique	7225/3432 [R (int) = 0.0464]	8668/3288 [R (int) = 0.0749]
Reflections [I>2σ(I$_{obs}$)]	2635	1691
Completeness to	θ=30.02° 96.9%	θ= 25.34° 100%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3432/0/227	3288/2/333
Goodness-of-fit on F^2	1.057	1.068
Final R indices $[I > 2\sigma(Iobs)]$	R1 = 0.0400 wR2 = 0.1072	R1 = 0.0470 wR2 = 0.0983
R indices (all data)	R1 = 0.0538, wR2 = 0.1141	R1 = 0.1420, wR2 = 0.1378
Largest diff. peak and hole (e.Å^{-3})	0.415 and −0.214	0.267 and −0.280