Journal of Molecular Structure 994 (2011) 144–149

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Molecular structure of the 1:2 complex of 2-quinuclidinium-butyrate with *p*-hydroxybenzoic acid

Z. Dega-Szafran *, A. Katrusiak, M. Szafran

Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland

ARTICLE INFO

Article history:
Received 1 February 2011
Received in revised form 4 March 2011
Accepted 4 March 2011
Available online 9 March 2011

Keywords:
Quinuclidinium-butyrate inner salt
p-Hydroxybenzoic acid
X-ray diffraction
DFT calculations
FTIR and NMR spectroscopy
Hydrogen bonds

ABSTRACT

The structure of the 1:2 complex of 2-quinuclidinium-butyrate, QNBu, with *p*-hydroxybenzoic acid, HBA, (**1**) has been determined by X-ray diffraction, DFT calculations, and the complex was characterized by FTIR and NMR spectroscopy. The crystals are triclinic, space group $P\bar{1}$. The QNBu and HBA molecules are linked by medium-strong O—H···O hydrogen bonds into a double strand related by two types of inversion centers, each inside different H-bonded rings. The O···O distances vary between 2.652(3) and 2.720(2) Å. The FTIR spectrum of the solid complex is consistent with the X-ray results. The second-derivative IR spectrum and calculated frequencies for the optimized structure of QNBu·2HBA were used to explain the FTIR spectrum in the carbonyl-carboxylate region. The interpretation of ^{1}H and ^{13}C NMR spectra has been based on 2D experiments and calculated GIAO/B3LYP/6-31G(*d*, *p*) magnetic isotropic shielding constants.

1. Introduction

Quinuclidine (1-azabicyclo[2.2.2]octane) as a very strong base, pK_a = 11.15 [1], reacts with alkyl halides to give a variety of quaternary quinuclidinium salts. Recently, we studied molecular structures and spectroscopic properties of quinuclidinium-acetate (quinuclidine-betaine, QNB) [2,3], 2-quinuclidinium-propionate (QNPr) [4], 2-quinuclidinium-butyrate (QNBu) [5] inner salts and their hydrohalides, and complex of QNB with *p*-hydroxybenzoic acid (HBA) [6]. Although QNBu is a weaker base, pK_a = 0.92, than QNB, pK_a = 1.59 [5] it also forms a crystalline complex with *p*-hydroxybenzoic acid, HBA (Scheme 1). HBA has two proton-donor groups, COOH (pK_{a1} = 4.67) and OH (pK_{a2} = 9.37) [7].

The aim of this work is to establish the effect of the ethyl group at a chiral CH carbon atom in the N^+—CH(C_2H_5)COO^- substituent on the structure of QNBu·2HBA, and to compare the results with those obtained for the 1:1 complex of QNB·HBA [6].

2. Experimental

2.1. Synthesis

2-Quinuclidinium-butyrate inner salts, QNBu, was prepared as described previously in Ref. [5]. The 1:2 complex of QNBu with *p*-hydroxybenzoic acid was obtained by mixing the substrates dissolved in methanol. The solvent was evaporated and the residue was dried over P_2O_5. The QNBu·2HBA complex (**1**) was recrystallized from the mixture of acetonitrile–methanol (10:1), m.p. 151–152 °C.

2.2. Measurements

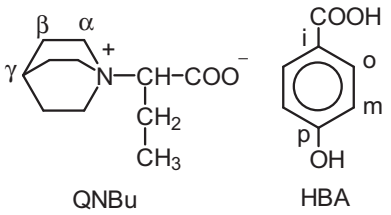
Single crystals of QNBu·2HBA (**1**) were grown from acetonitrile. The crystal structure of (**1**) was determined by X-ray diffraction, measured with a KUMA KM-4 CCD diffractometer [8,9]. The structure was solved by direct methods using SHELXS-97 and refined on F^2 by full-matrix least-squares with SHELXL-97 [10]. Most of atoms were located from the molecular geometry with U_{iso} = 1.2 U_{eq} of their carriers, and acidic H(3) and H(7) and hydroxyl, H(5) and H(8) atoms were located from difference Fourier maps and their U_{iso} refined. The numbering of atoms is shown in Fig. 1. The crystal data, details of data collection and structure refinement are given in Table 1. The final atomic coordinates listed in Table A and the bond lengths, bond and torsion angles given in Table B are included in the Supplementary Material. The complete set of structural parameters in the CIF format is available as an Electronic Supplementary Publication from the Cambridge Crystallographic Data Centre (CCDC 809281).

FTIR spectra were measured on a Bruker IFS 66v/S instrument, with the resolution of 2 cm^{-1}. The FTIR solid-state spectra were recorded in Nujol and Fluorolube suspensions using KBr plates.

NMR spectra were recorded on a Bruker Advance DRX spectrometer operating at 600.31 and 150.75 MHz for ^{1}H and ^{13}C,

* Corresponding author. Tel.: +48 61 8291216; fax: +48 61 8291505.
E-mail address: degasz@amu.edu.pl (Z. Dega-Szafran).

0022-2860/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2011.03.008



Scheme 1. The structural formulas of 2-quinuclidinium-butyrate inner salt (QNBu) and *p*-hydroxybenzoic acid (HBA).

respectively. The spectra were measured in D_2O relative to internal standard of 3-(trimethylsilyl)propionic-d_4 acid sodium salt. The concentration of sample was 0.2 mol dm^{-3}. The 2D ^1H-^1H (COSY), ^1H-^{13}C (HETCOR) and HMBC (Heteronuclear Multiple-Bond Connectivity) spectra were obtained with the standard Bruker software.

2.3. DFT calculations

The DFT calculations were performed with the GAUSSIAN-03 program package [11]. The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke [12,13] with the gradient-correlation functional of Lee, Yang and Parr [14] and the split-valence polarized 6-31G(*d*, *p*) basis set [15]. The magnetic isotropic shielding constants were calculated with the standard GIAO/B3LYP/6-31G(*d*, *p*) (Gauge-Independent Atomic Orbital) approach with the GAUSSIAN-03 program package using the conductor-like screening solvating model (COSMO) [16]. The calculated IR frequencies for complex **2** were positive and confirmed that the optimized structure was in the state of minimum energy.

3. Results and discussion

3.1. Crystal structure

2-Quinuclidinium-butyrate inner salt, QNBu, forms with *p*-hydroxybenzoic acid, HBA, a complex of the 1:2 stoichiometry. The crystals are triclinic, space group $P\bar{1}$. Molecular structure of QNBu·2HBA (**1**) with the anisotropic displacement ellipsoids and atom labeling scheme is shown in Fig. 1. Selected bond lengths, bond and torsion angles are given in Table 2. QNBu exists in a zwiterionic form, the bond lengths C(10)—O(1) and C(10)—O(2) are 1.262(2) and 1.238(2), respectively (Table 2). QNBu is linked to two HBA molecules. One HBA molecule interacts with QNBu through the O(3)—H(3)···O(2) hydrogen bond of 2.652(3) Å, formed between the carboxylic group of HBA and carboxylate group of QNBu. The other HBA molecule is linked by the O(8)—H(8)···O(1) hydrogen bond of 2.680(3) Å between the hydroxyl group of HBA and the carboxylate oxygen atom of QNBu (Fig. 1, Table 3). The QNBu·2HBA units are further hydrogen-bonded into a double strand along the [0 0 1] direction (Fig. 2). Symmetry of the strands include translation *a* and two types of inversion centers, each inside different H-bonded rings. The rings can be described by graph descriptors $R_6^4(24)$ and $R_4^4(24)$ [17,18]. First of the rings comprises two 4-hydroxybenzoic acid molecules, hydroxyl groups of two other 4-hydroxybenzoic acid molecules and one oxygen atom of the carboxylate group of two QNBu units; the second ring likewise comprises two 4-hydroxybenzoic acid molecules and both oxygen atom of the carboxylate group of two 2-quinuclidinium-butyrate zwitterions. The carboxyl group of two symmetry-independent HBA molecules are twisted by ca. 5° of the benzene rings.

The main differences between the crystal structures of QNBu·2HBA and QNB·HBA [6] are the ratios of the components and their arrangements in the crystal units. In the structure of QNB·HBA at the ratio 1:1, two symmetry non-equivalent QNB·HBA complexes are linked by a sequences of four O—H···O hydrogen bond into a zigzag chain, through the COOH···OOC hydrogen bonds of 2.561(2) and 2.556(2) Å, and O—H···OOC hydrogen bonds of 2.609(2) and 2.687(2) Å. Both types of hydrogen bonds are shorter in QNB·HBA then in QNBu·2HBA. A similar centrosymmetric cyclic aggregate is formed in the 1:1 complex of N-methylpiperidine betaine with HBA [19] and trigonelline hydrate with HBA [20].

The piperidinium rings in quinuclidinium moiety of QNBu·2HBA have distorted-boat conformations and the quinuclidinium moiety is in the propeller conformation. All torsion angles of the ethylene bridges, N(1)—C—C—C(4), are of about 14° (Table 2). These torsion angles are greater than those in QNBu·HBr [5] and QNB·HBA [6].

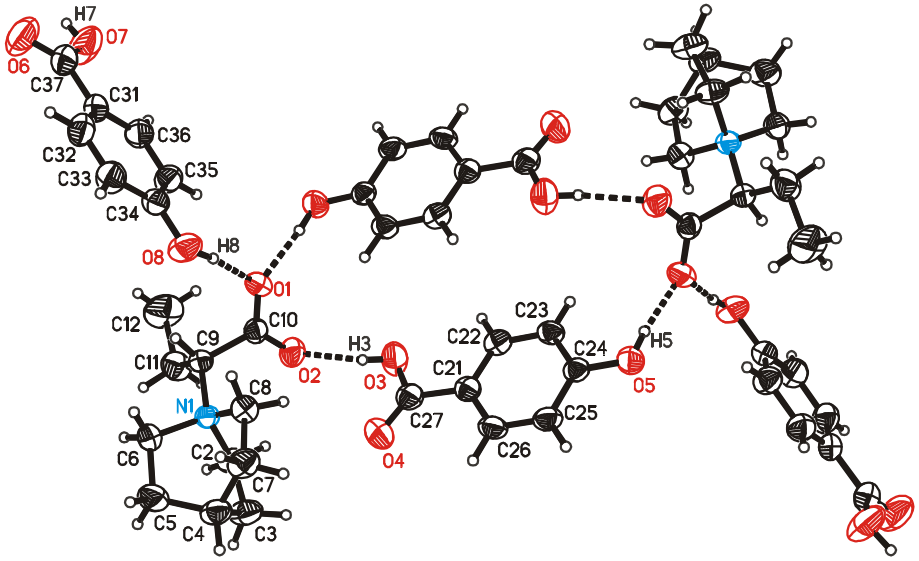


Fig. 1. A centrosymmetric segment of the hydrogen-bonded ring, $R_6^4(24)$, in the crystal of **1**. The atoms of the symmetry-independent part of the unit cell, consisting of one 2-quinuclidinium-butyrate and two *p*-hydroxybenzoic acids, are labeled. The hydrogen bonds are shown as the dashed lines. The thermal ellipsoids have been drawn at the 50% probability level.