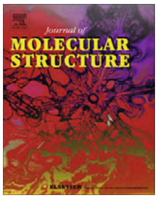
Journal of Molecular Structure 933 (2009) 46–52

Contents lists available at ScienceDirect

Journal of Molecular Structure

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



DABCO mono-betaine hydrate studied by X-ray diffraction, DFT calculations and spectroscopic methods

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A R T I C L E I N F O

Article history:
Received 11 May 2009
Accepted 28 May 2009
Available online 6 June 2009

Keywords:
1.4-Diazabicyclo[2.2.2]octane
Betaines
O–H···O and O–H···N hydrogen bonds
X-ray diffraction
DFT calculations
Spectroscopic methods

A B S T R A C T

A new DABCO mono-betaine (1-carboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt) has been synthesized. It crystallizes as monohydrate in orthorhombic space group *P*mn2$_1$. The DABCO mono-betaine and water molecules are located on a mirror plane. The water molecules link DABCO mono-betaine into linear chains through the H–O–H···OOC and H–O–H···N hydrogen bonds of 2.709(2) and 2.875(2) Å. The structure of the title compound optimized at B3LYP/6-31G(d,p) level of theory is consistent with X-ray diffraction. The absorption bands in the FTIR spectrum have been assigned. The calculated magnetic isotropic shielding tensors confirm the assignments of the ^{13}C NMR resonance signals.

1. Introduction

1,4-Diazabicyclo[2.2.2]octane (triethylenediamine, $N(CH_2CH_2)_3N$), abbreviated as DABCO, is a globular molecule of high symmetry. It crystallizes in a hexagonal space group *P*6$_3$/m [1]. The crystal undergoes a structural phase transition to a plastic phase at 351 K and it melts at 433 K [2,3]. DABCO is a strong base, its pK_a = 8.84 and PA = 230.2 kcal/mol [4], and it is used as a deprotonation agent to yield an ylide from *N*-phenacyl- and *N*-acetonyl-4-cyanopyridinium halides [5]. The protonation of DABCO by inorganic acids (e.g. HBr, $HClO_4$, HBF_4 and $HReO_4$) leads to mono-salts in which the $N(CH_2CH_2)_3N^+$–H cations are linked by the N–H···N hydrogen bond with lengths from 2.787(8) to 2.841(5) Å into linear chains, which is responsible for the polarization of the chain. The mono-salts of DABCO display ferroelectric and ferroelastic phase transitions [6–10].

The Meschutkin reaction with the primary alkyl halides results in the formation of a variety of 1,4-dialkyl-1,4-diazabicyclo[2.2.2]octane dihalides, however, that with the secondary alkyl bromides, leads to both substitution and elimination reactions and only 1-alkyl-1,4-diazabicyclo[2.2.2]octane halides are formed [11]. Wu and Mak [12] have synthesized and solved crystal structures of 1,4-dicarboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt (DABCO di-betaine) and its hydrochloride. DABCO di-betaine crystallized as a trihydrate in space group *P*2$_1$/*n*. Water molecules interact with both carboxylate groups through the O–H···O hydrogen bonds of 2.655(4), 2.687(4) and 2.758(4) Å, forming a five-membered ring.

The aim of this work is the synthesis of 1-carboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt (DABCO mono-betaine) (Fig. 1) and its characterization by the spectroscopic methods, X-ray diffraction and DFT calculations.

2. Experimental

To 13.1 g of 1,4-diazabicyclo[2.2.2]octane (DABCO) dissolved in 50 dm^3 of acetonitrile, 26.2 g ethyl chloroacetate dissolved in 50 dm^3 of diethyl ether was slowly dropped on cooling and stirring. The reaction mixture was kept in the refrigerator for 14 days. The precipitate was filtered off (30.1 g) and washed with diethyl ether. The melting point between 131 and 143 °C suggests the mixture of 1-carbethoxymethyl-1,4-diazabicyclo[2.2.2]octane chloride and 1,4-dicarbethoxymethyl-1,4-diazabicyclo[2.2.2]octane dichloride. The ^{1}H NMR spectrum confirms this suggestion. This mixture (10 g) was dissolved in water (100 cm^3) and treated with an anion-exchange resin in its basic form (150 g, Amberlite IRA 400). After 1 h, when the Beilstein test for halide of the water layer was negative, the resin was eluted with water. Removal of water by a rotary evaporator gave a white precipitate (8.8 g). The mixture of DABCO mono-betaine and DABCO di-betaine was separated by the crystallization from methanol. DABCO mono-betaine is easily soluble in acetonitrile and methanol (m.p. 264–266 °C), while DABCO di-betaine is insoluble in organic solvents (m.p. > 360 °C). The deuterated complex was prepared by exchange with D_2O, followed by removal of excess of D_2O in vacuum.

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doi:10.1016/j.molstruc.2009.05.050

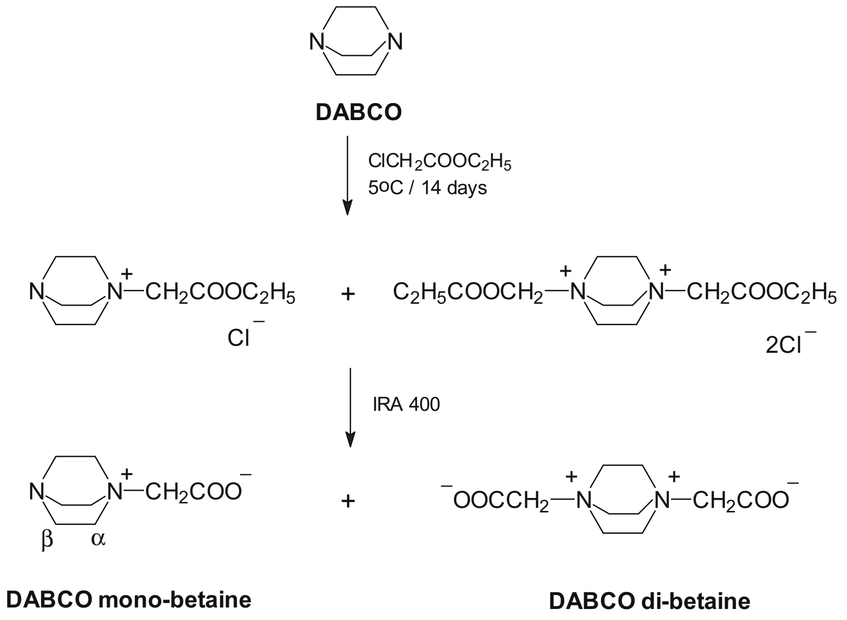

Fig. 1. Scheme of the synthesis.

The crystals for X-ray measurements were grown by slow evaporation of methanol. The crystal structure of DABCO mono-betaine was determined by X-ray diffraction, measured with a KUMA KM-4 CCD diffractometer [13,14]. The structure was solved by direct methods using SHELXS-97 [15] and refined on F^2 by full-matrix least-squares with SHELXL-97 [16]. The crystal data, details of data collection and structure refinement are given in Table 1, and the final atomic coordinates are listed in Table 2. The complete set of structural parameters in CIF format is available as an Electronic Supplementary Publication from the Cambridge Crystallographic Data Centre (CCDC 731399).

The DFT calculations were performed with the GAUSSIAN-03 program package [17]. The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke [18,19] with the gradient-correlation functional of Lee et al. [20] and the split-valence polarized 6-31G(d,p) basis set [21]. The magnetic isotropic shielding tensors were calculated with the standard GIAO/B3LYP/6-31G(d,p) (Gauge-Independent Atomic Orbital) approach using the conductor-like screening continuum solvation model (COSMO) [22] and geometries listed in Table 2.

Table 1
Crystal data and structure refinement for DABCO mono-betaine hydrate.

Empirical formula	$C_8H_{16}N_2O_3$
Formula weight	188.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pmn2_1$
Unit cell dimensions	a = 6.7870(6) Å
	b = 11.1058(5) Å
	c = 6.1202(4) Å
Volume	461.31(5) Å^3
Z	2
Calculated density	1.355 g/cm^3
Absorption coefficient	0.103 mm^{-1}
F(0 0 0)	204
Crystal size	0.32 × 0.23 × 0.05 mm
θ range for data collection (°)	3.52–29.51
Max/min indices h, k, l	−9/9, −14/13, −8/7
Reflections collected/unique	4559/1199 [R_{int} = 0.0413]
θ_{max} (°)/completeness (%)	29.51/94.6
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1199/1/101
Goodness-of-fit on F^2	1.175
Final R indices [$I > 2\sigma_I$]	R_1 = 0.0318, wR_2 = 0.0310
R indices (all data)	R_1 = 0.0879, wR_2 = 0.0337
Absolute structure parameter	0.0(13)
Largest diff. peak and hole	0.162 and −0.127 e.Å^{-3}

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for DABCO mono-betaine hydrate.

Atom[a]	x	y	z	U(eq)
N(1)	0	6691(2)	487(3)	35(1)
C(2)	1818(3)	6990(1)	−842(3)	48(1)
C(3)	1761(3)	8354(2)	−1397(3)	56(1)
N(4)	0	8932(2)	−484(4)	55(1)
C(5)	0	8779(2)	1900(5)	56(1)
C(6)	0	7442(2)	2542(5)	50(1)
C(9)	0	5385(2)	1168(4)	43(1)
C(10)	0	4406(2)	−628(5)	51(1)
O(1)	0	3379(1)	248(3)	75(1)
O(2)	0	4673(1)	−2564(3)	56(1)
O(1W)	0	11344(2)	−2191(4)	83(1)
H(2A)	3010(20)	6765(11)	140(20)	57
H(2B)	1871(19)	6466(10)	−2240(20)	57
H(3A)	1890(20)	8454(14)	−3060(20)	67
H(3B)	3030(20)	8756(12)	−730(30)	67
H(5A)	1310(19)	7231(11)	3380(30)	60
H(6A)	1180(20)	9243(12)	2400(20)	67
H(9A)	1199(17)	5246(11)	2130(30)	51
H(1W)	0	11910(30)	−1200(70)	170(20)
H(2W)	0	10720(20)	−1510(60)	93(13)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

[a] Only the symmetry-independent atoms have been listed; the remaining can be generated by the symmetry code: $-x, y, z$.

FTIR spectrum was measured on a Bruker IFS 66v/S instrument, evacuated to avoid water and CO_2 absorptions, with the resolution of 2 cm^{-1}. The FTIR solid state spectrum was recorded in Nujol and Fluorolube suspensions using KBr plates. Each spectrum consisted of 64 scans.

The NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for ^1H and ^{13}C, respectively. The spectra were measured in D_2O relative to internal standard of 3-(trimethylsilyl)propionic-d$_4$ acid sodium salt.