Spectrochimica Acta Part A 81 (2011) 99–103

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Spectroscopic and structural properties of *N*-(acetamide) morpholinium bromide

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ARTICLE INFO

Article history:
Received 27 October 2010
Received in revised form 13 May 2011
Accepted 19 May 2011

Keywords:
Morpholine derivative
Spectroscopy
Structure
X-ray
NMR
HETCOR

ABSTRACT

A new crystal of *N*-(acetamide) morpholinium (NAM) bromide has been prepared in methanol at room temperature and characterized by single crystal X-ray analysis, elemental analysis, GS-MS, FTIR, NMR(^{1}H,^{13}C, DEPTH and HETCOR). The *N*-(acetamide) morpholinium crystallizes in the orthorhombic crystal system, Pnma with unit cell a = 12.798(9) Å, b = 7.222(5) Å, c = 9.244(5) Å, β = 90.00, V = 854.4(9) Å^3, Z = 4. The X-ray structure determination revealed that there are strong inner and intermolecular hydrogen bonds in the crystal.

1. Introduction

Morpholine and its derivatives are used extensively in many chemical reactions. The alkyl and aryl derivatives of morpholine occupy a pivotal place in chemical and pharmaceutical industries. The *N*-alkyl and *N*-aryl derivatives of morpholine are important precursors in the pharmaceutical preparations of analgesics, local anesthetics, antibiotics, antimycotics and also in the production of antiplaques. 4-methylmorpholine-*N*-oxide is used as one of the oxidants in the oxidation of fullerenes. Morpholine/morpholinium buffer was used in the cleavage uridyluridine [1]. Methyl phenylmorpholinyl phenol derivatives have been used as ligands in zinc complexes [2] and some of them show gastro kinetic activity [3] and also act as antiviral agents [4], antimalarial agents [5], spermicides [6] and anti arrhythmic agents [7]. Besides, these amides are well known for their therapeutic values. Some important drugs contain the morpholine moiety in addition to *N*-heterocycles which are separated by one or higher number of carbon atoms. Drugs derived from morpholine incorporated compounds include dextromoramide, a narcotic analgesic and doxapram HCl, a respiratory stimulant.

2. Experimental

N-(acetamide) morpholinium (NAM) bromide was prepared in methanol. NMR spectra (^{1}H, ^{13}C, DEPTH and 2D HETCOR) were recorded using a Varian Gemini 300 MHz spectrometer. FT-IR spectra were recorded as KBr pallet using a Perkin Elmer, spectrum 100 spectrometer over the wave number range 4000–450 cm^{-1}. Elemental analyses were performed on a LECO, CHNO organic element analyzer. Mass spectra were measured with a GC-MS, Thermo Finnigan Trace DSQ. X-Ray diffraction data were collected on a Rigaku, Mercury CCD area detector with graphite monochromated Mo-Kα (λ = 0.7107 Å)

2.1. *N-(acetamide) morpholinium bromide*

A solution of morpholine (4.356 g, 50 mmol) and 2-bromoacetamide (6.85 g, 50 mmol) in methanol (100 mL) was stirred at room temperature for 20 h. The reaction was monitored by TLC analysis. On completion, the solid was filtered with a sintered glass funnel. The filtrate was evaporated on a rotary evaporator and the residue was washed twice with cold ethanol. The solid was dissolved in hot methanol–water mixture and left for crystallization. M.p. 116 °C, analysis for $C_6H_{13}N_2O_2$: cald. C, 49.64%; H, 9.03%; N, 19.30%, found: C, 49.22%; H, 8.96%; and N, 19.44%. FTIR (KBr): υ = 3369, 3243, 3154(N—H), 2993(C—H aliph.), 1691 (C=O). ^{1}H NMR (300 MHz, D_2O): δ = 3.28 (2 H_{ax}), 3.80 (2 H_{eq}), 3.73 (2 H_{eq}), 3.95 (2 H), 4.45 (2 H_{ax}), ^{13}C (D_2O): 52.64 (1C, C—N), 55.96 (2C, C—O), 63.63 (2C, C—O morp), 166.95 (1C, C=O). MS (70 eV, EI) *m/z* (%): 145.12 (calc. 145.12) for $C_6H_{13}N_2O_2$.

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doi:10.1016/j.saa.2011.05.055

Table 1
Crystal data and refinement for NAM bromide.

Identification code	NAM
Empirical formula	$C_6H_{12}O_2N_2Br$
Formula weight	224.08
Temperature (K)	273
Wavelength (Å)	0.71073
Crystal size	0.60 mm × 0.60 mm × 0.50 mm
Crystal system	Orthorhombic
Space group	Pnma
a, Å	12.798(9)
b, Å	7.222(5)
c, Å	9.244(5)
α, (°)	90.00
β, (°)	90.00
γ, (°)	90.00
V, Å^3	854.4(9)
Z	4
$D_{calcd.}$, g cm^{-3}	1.742
Absorption coefficient, mm^{-1}	0.478
$F(0\,0\,0)$, e	452.00
Limiting indices	$-17 \le h \le +17$ $-10 \le k \le +10$ $-12 \le l \le +12$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.0088
Reflections measured	1415
Reflections unique	191
R_{int}	0.055
Parameters refined	72
$R(F)/wR(F^2)^a$ (all ref.)	0.0476
GoF (F^2)	1.259
Largest diff. peak and hole (e Å^{-3})	0.61–0.46

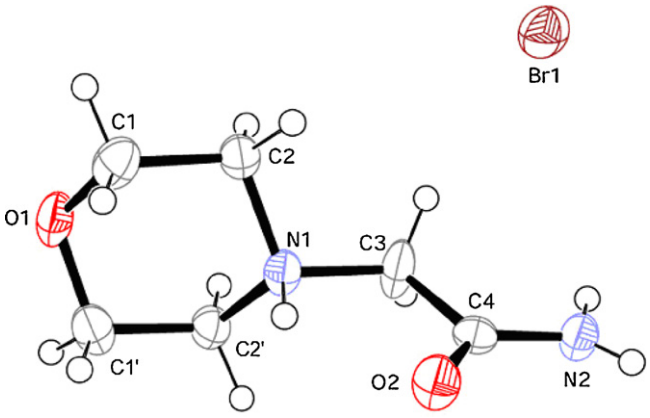

Fig. 1. Crystal structure of the NAM bromide.

2.2. X-ray structure determination

A colorless block crystal of $C_6H_{13}O_2N_2Br$ having approximate dimensions of 0.60 mm × 0.60 mm × 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of 0 ± 1 °C to a maximum 2θ value of 59.1°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at $\chi = 45.0°$ and $\phi = 0.0°$. The structure was solved by direct methods [8] and expanded using Fourier techniques [9]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 1014 observed reflections and 72 variable parameters. All calculations were performed using the crystal structure [10,11] crystallographic software package. The crystal data have been deposited in the Cambridge crystallographic database centre as supplementary publications, no: CCDC 778481.

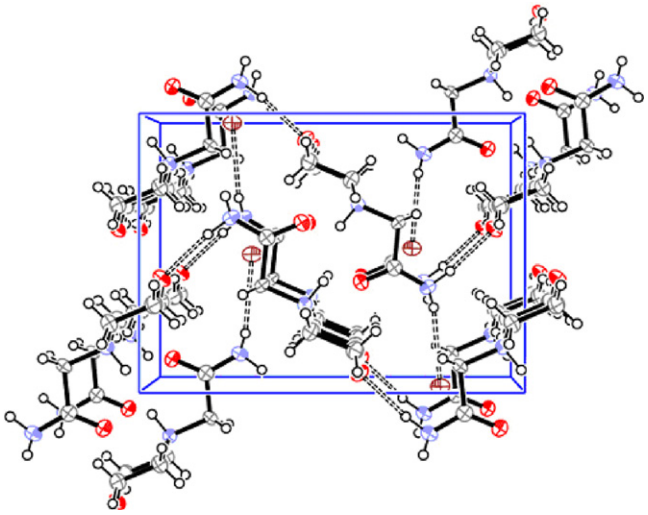

Fig. 2. Crystal packing diagram of NAM with intermolecular and inter ionic contacts of the Br anion.

3. Results and discussion

3.1. Crystal structure of NAM

2-bromoacetamide reacted with morpholine yield *N*-(acetamide) morpholinium bromide salt. The structure of the *N*-(acetamide) morpholinium bromide with the atom numbering is shown in Fig. 1. The IUPAC name of the compound NAM is 2-morpholin-4-ylacetamide. The crystal data and experimental details concerning the X-ray data collection and structure refinement for NAM bromide are given in Table 1. The bond lengths, bond and dihedral angles for the NAM bromide are listed in Table 2. The morpholine ring has a half-chair conformation in the structure. The crystal packing diagram and intermolecular and interionic contacts of the NAM are shown in Figs. 2 and 3.

Table 2
Selected bond distances (Å), angles (degree), and dihedral angles (degree) for NAM bromide with estimated standard deviations in parentheses. The symmetry codes: X, $-Y+1/2$, Z.

Parameter	Distances	Parameter	Angles	Parameter	Dihedral angles
N4—C2	1.507(2)	C3—C4—N2	114.12(1)	O1—C1—C2—N1	58.621(2)
N1—C3	1.505(2)	C1—C2—N1	109.17(1)	N1—C3—C4—N2	179.980(2)
C4—O2	1.235(2)	O2—C4—N2	127.17(2)	C2′—N1—C3—C4	118.312(2)
C4—N2	1.320(1)	N1—C3—C4	108.34(2)	O1—C1′—C2′—N1	58.621(2)

Hydrogen bonds	Distances
N2—H···O2=C	2.007(1)
N2—H···Br	2.684(1)
O1···NH2	2.051(2)