CRYSTAL AND MOLECULAR STRUCTURE OF N,N,N',N'-TETRA(2-NITRILETHYL) ETHANE-1,2-DIAMINE AND N-(2-NITRILETHYL)BENZYLAMINE HYDROBROMIDE

J. Gao,^{1,2} X.-Y. Xu,² T.-T. Xu,² J. Ni,³ and Q.-L. Liu¹

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N,N,N',N'-tetra(2-nitrilethyl) ethane-1,2-diamine and N-(2-nitrilethyl)benzylamine hydrobromide were prepared by the addition reaction of acrylonitrile with corresponding amines, and the two structures were determined by X-ray single crystal diffraction. The two compounds crystallize in monoclinic system, and almost no classical hydrogen bond exists in the two crystal structures.

Keywords: N,N,N',N'-tetra(2-nitrilethyl) ethane-1,2-diamine, N-(2-nitrilethyl)benzylamine hydrobromide, structure of molecular crystals.

Nitriles are of particular interest due to their extensive applications. In organic synthesis they can convert into amides, carboxylic acids, amines and ketones [1]; in chemical industry they are important intermediates for fine chemicals such as medicines, agricultural chemicals and dyes; in coordination chemistry they are ideal ligands for constructing supramolecular architectures [2, 3]. As an interest to nitriles, described herein is the synthesis and crystal structure of two new organic nitriles N,N,N',N'-tetra(2-nitrilethyl) ethane-1,2-diamine (1) and N-(2-nitrilethyl)benzylamine hydrobromide (2).



Experimental. Synthesis of N,N,N',N'-tetra(2-nitrilethyl)ethane-1,2-diamine (1). To ethane-1,2-diamine aqueous solution was added an excess solution of acrylonitrile dropwise. The solution was refluxed for 45 hr. Then excess acrylonitrile and water were distilled out under vacuum. The colorless crystals were obtained. Yield 93%. M. p.: 60°C. IR (cm⁻¹, KBr): 2865, 2838 (m, v_{as} , $v_{s (CH_2)}$), 2243 (s, $v_{(CN)}$). ¹H NMR (CD₃OD, δ) 2.64 ~ 2.68 (t, 8H, -CH₂CH₂CN), 2.76 (s, 4H, -NCH₂CH₂N–), 2.92 ~ 2.96 (t, 8H, -CH₂CH₂CN).

Synthesis of N-(2-nitrilethyl)benzylamine hydrobromide (2). N-(2-nitrilethyl)benzylamine was prepared by addition reaction of benzylamine with acrylonitrile. To benzylamine aqueous solution was added an excess solution of acrylonitrile dropwise. The solution was refluxed for 75 hr. Then excess acrylonitrile and water were distilled out under vacuum. The colorless oil product was obtained. Yield 72%. B. p.: 178-179°C (0.098 MPa). IR (cm⁻¹, KBr): 3338 (m, $v_{(NH)}$), 2926, 2845 (m, v_{as} , $v_{s (CH_2)}$), 2247 (s, $v_{(CN)}$), 1495–1454 (benzene ring). ¹H NMR (CDCl₃, δ) 7.24 ~ 7.30 (t, 5H, Ar—H), 3.78 (s, 2H, Ar–CH₂–), 2.83-2.88 (t, 2H, –CH₂CH₂CN), 2.42-2.46 (t, 2H, –CH₂CH₂CN), 1.69 (s, H, –NH–). N-(2-nitrilethyl)benzylamine hydrobromide (2) was obtained by the addition of 48% HBr to the methanol solution of N-(2-nitrilethyl)benzylamine gradually. Slow evaporation of the above mixed solution produced colorless blocks in a yield of 95%.

¹Department of Chemistry, University of Science and Technology of China, P.R. China; gaojian553@163.com. ²Department of Chemical Engineering, Lianyungang Technical College, P.R. China. ³Central Laboratory of Shantou University, P.R. China. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 47, No. 2, pp. 388-391, March-April, 2006. Original article submitted September 9, 2005.

IR (cm⁻¹, KBr): 3165 (*m*, $v_{(NH)}$), 2915, 2833 (*m*, v_{as} , $v_{s (CH_2)}$), 2756 (*s*, $v_{(HBr)}$), 2243 (*m*, $v_{(CN)}$), 1491-1441 (benzene ring). ¹H NMR (DMSO, δ) 7.44-7.53 (*t*, 5H, Ar–H), 4.21 (*s*, 2H, Ar–CH₂–), 3.36-3.38 (*t*, 2H, –CH₂CH₂CN), 3.28-3.33 (*t*, 2H, –CH₂CH₂CN), 2.99-3.04 (*t*, 2H, –NH₂–).

X-ray diffraction study. The intensity data were collected on a SMART APEX CCD diffractometer at room temperature (ω -2 θ scan mode, graphite monochromated Mo K_{α} radiation, $\lambda = 0.71073$ Å). The unit cell parameters and details of experiment are given in Table 1. The structures were solved by direct methods and refined anisotropically using the least-squares technique implemented in the SHELX-97 package [4, 5]. All hydrogen atoms were added according to theoretical models.

Results and discussion. The atomic coordinates and thermal parameters of atoms for 1 and 2 are given in Table 2; the bond lengths and angles are presented in Table 3. The molecular and crystal structures of compounds 1 and 2 are shown in Fig. 1, and Fig. 2, respectively.

Compound	1	2
Formula	$C_{14}H_{20}N_6$	$C_{10}H_{13}N_2Br$
Molecular weight	272.36	241.13
Crystal size, mm	0.30×0.30×0.28	0.3×0.2×0.14
Space group, Z	<i>P</i> 2(1)/ <i>n</i> , 2	P2(1)/c, 4
<i>a</i> , <i>b</i> , <i>c</i> , Å	5.4702(7), 11.2192(14), 13.0369(16)	6.4596(9), 15.072(2), 12.2635(18)
β, deg	92.670(2)	101.807(2)
<i>V</i> , Å ³	799.22(17)	1168.7(3)
ρ_{calc} , g/cm ³	1.132	1.370
μ , mm ⁻¹	0.073	3.478
No. of reflections	4651	6711
Independent reflections	1791	2401
No. of refined parameters	91	118
No. of reflections with $I > 2\sigma(I)$	1402	1691
<i>R</i> 1, <i>wR</i> 2 for $I > 2\sigma(I)$	0.0537, 0.1349	0.0309, 0.0669
wR2 for all Independent reflections	0.1443	0.0764
GOOF	0.988	0.993
CCDC	282984	257996

TABLE 1. Crystal Data and Details of Experiment for 1 and 2

TABLE 2. Atomic Coordinates (×10⁴) and Thermal Parameters ($Å^2 \times 10^3$) for 1 and 2

Atom	x	У	Z	$U_{ m eq}$	Atom	x	У	Z	$U_{ m eq}$
					1				
C(1)	-154(3)	6559(2)	270(2)	68(1)	C(6)	-591(3)	9228(1)	2745(1)	58(1)
C(2)	2220(3)	6860(1)	753(1)	60(1)	C(7)	-1810(3)	8083(2)	2756(1)	60(1)
C(3)	2885(3)	8161(1)	582(1)	51(1)	N(1)	-1986(3)	6321(2)	-111(2)	103(1)
C(4)	811(3)	10082(1)	483(1)	48(1)	N(2)	1147(2)	8958(1)	1047(1)	44(1)
C(5)	1716(3)	9157(1)	2139(1)	53(1)	N(3)	-2719(3)	7178(2)	2764(1)	90(1)
				, í	2				
Br(1)	2711(1)	4096(1)	9637(1)	58(1)	C(5)	10821(5)	3155(2)	2294(2)	66(1)
N(1)	7916(3)	3754(1)	-205(1)	38(1)	C(6)	8763(4)	3296(2)	1762(2)	49(1)
N(2)	5514(7)	3926(2)	-4172(2)	119(1)	C(7)	7977(5)	2993(2)	580(2)	54(1)
C(1)	7420(5)	3729(2)	2326(2)	66(1)	C(8)	7206(4)	3497(2)	-1393(2)	46(1)
C(2)	8150(7)	4023(2)	3405(3)	85(1)	C(9)	7063(5)	4318(2)	-2116(2)	63(1)
C(3)	10215(8)	3886(2)	3917(3)	88(1)	C(10)	6194(6)	4100(2)	-3279(3)	76(1)
C(4)	11538(6)	3446(3)	3374(3)	85(1)					

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Bond	d	Bond	Bond d		d			
C(1)–N(1)	1.130(2)	C(4) - N(2)	1.4677(16)	C(5)–C(6)	1.522(2)			
C(1)-C(2) C(2)-C(3)	1.456(2)	C(4) = C(4) = 1 C(5) = N(2)	1.517(3)	C(6)-C(7) C(7)-N(3)	1.448(2)			
Angle	ω	Angle	ω	Angle	ω			
N(1)-C(1)-C(2)	179.4(2)	N(2)-C(5)-C(6)	111.68(11)	C(5)–N(2)–C(3)	112.70(10)			
C(1)–C(2)–C(3)	111.91(13)	C(7)–C(6)–C(5)	110.64(13)	C(5)–N(2)–C(4)	111.98(10)			
N(2)-C(3)-C(2)	111.22(12)	N(3)-C(7)-C(6)	178.66(19)	C(3)-N(2)-C(4)	112.76(11)			
N(2)-C(4)-C(4)#1	111.48(13)							
	2							
Bond	d	Bond	d	Bond	d			
N(1)–C(8)	1.486(3)	C(1)–C(6)	1.379(4)	C(3)–C(4)	1.359(5)			
N(1)–C(7)	1.492(3)	C(1)–C(2)	1.384(4)	C(4)–C(5)	1.382(4)			
N(2)–C(10)	1.124(4)	C(2)–C(3)	1.369(6)	C(5)–C(6)	1.372(4)			
C(6)–C(7)	1.505(3)	C(8)–C(9)	1.515(4)	C(9)–C(10)	1.459(4)			
Angle	ω	Angle	ω	Angle	ω			
C(8)–N(1)–C(7)	113.17(19)	C(6)–C(5)–C(4)	120.6(3)	N(1)–C(7)–C(6)	110.3(2)			
C(6)–C(1)–C(2)	120.3(3)	C(5)-C(6)-C(1)	118.8(3)	N(1)-C(8)-C(9)	109.3(2)			
C(3)–C(2)–C(1)	120.0(4)	C(5)–C(6)–C(7)	121.0(3)	C(10)–C(9)–C(8)	110.7(2)			
C(4)–C(3)–C(2)	120.1(3)	C(1)-C(6)-C(7)	120.2(3)	N(2)-C(10)-C(9)	179.4(5)			
C(3)-C(4)-C(5)	120.2(3)							

TABLE 3. Bond Lengths (Å) and Angles ω (deg) for 1 and 2



Fig. 1. Molecular structure and crystal packing for compound 1.

The structure of molecule 1 has much in common with the structure of bi(2-nitrilethyl)aminoacetonitrile in our previous report [6]. The bond distances of C(1)-N(1) and C(7)-N(3) are all 1.130 Å, belonging to the typical C=N. The bond length of C(6)–C(7) is smaller than that of C(6)–C(5), which can be attributed to the effect of hyperconjugation, so do the other arms. Fig. 1*b* shows that the layer-like structure is formed when every molecule is linked to others by intermolecular van der Waals forces.

In Fig. 2*a*, the phenyl ring together with the adjacent C(7) atom defines a plane: 2.186x + 13.174y - 5.032z = 5.3713,



Fig. 2. Molecular structure and crystal packing for compound 2.

TABLE 4. Hydrogen Bond Geometries (Å, deg)

D–H····A	[ARU]	$d_{ m D-H}$	$d_{\mathrm{H}_{\ldots}\mathrm{A}}$	$d_{\mathrm{D}\mathrm{A}}$	θ_{DHA}
$N(1)-H(1A)\cdots Br(1)$ $N(1)-H(1B)\cdots Br(1)$	[1654.01] [1554.01]	0.9810 0.9347	2.2406 2.7522	3.184(2) 3.368(2)	161.04 124.24
$N(1)-H(1B)\cdots Br(1)$	[3666.01]	0.9347	2.6035	3.356(2)	137.86

with the maximum deviation of 0.0291 Å for H(3), and mean deviation of 0.0106 Å. The distance between Br(1) and the centroid of aromatic ring is 10.198 Å, which is too long to have interaction. Fig. 2*b* shows its layer-like crystal structure, which is formed by intermolecular van der Waals forces and intermolecular hydrogen bonds between Br(1) and N(1) atoms. The bond lengths and bond angles of the hydrogen bonds are listed in Table 4.

From the spectra characterization and crystal structure of **2**, it can be found that monocyanoethylation of benzylamine has occurred, and dicyanoethylation is very difficult without the aid of catalyst. But ethane-1,2-diamine, being primary aliphatic amine, can react completely with acrylonitrile in the absence of catalysts with high yields, and aniline did not react with acrylonitrile in a sealed tube at 200°C in the absence of a catalyst nor did any reaction take place between the two when refluxed [7]. The difference among them could mainly be attributed to the higher steric hindrance of benzylamine compared with ethane-1,2-diamine, and lower steric hindrance compared with aniline.

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