# Crystal structure of *bis*(1,3-diaminoimidazolium) 5,5'-azotetrazolate, $(C_3H_7N_4)_2$ $(C_2N_{10})$, $C_8H_{14}N_{18}$

Gerhard Laus*, Klaus Wurst and Herwig Schottenberger

University of Innsbruck, Faculty of Chemistry and Pharmacy, Innrain 52a, 6020 Innsbruck, Austria

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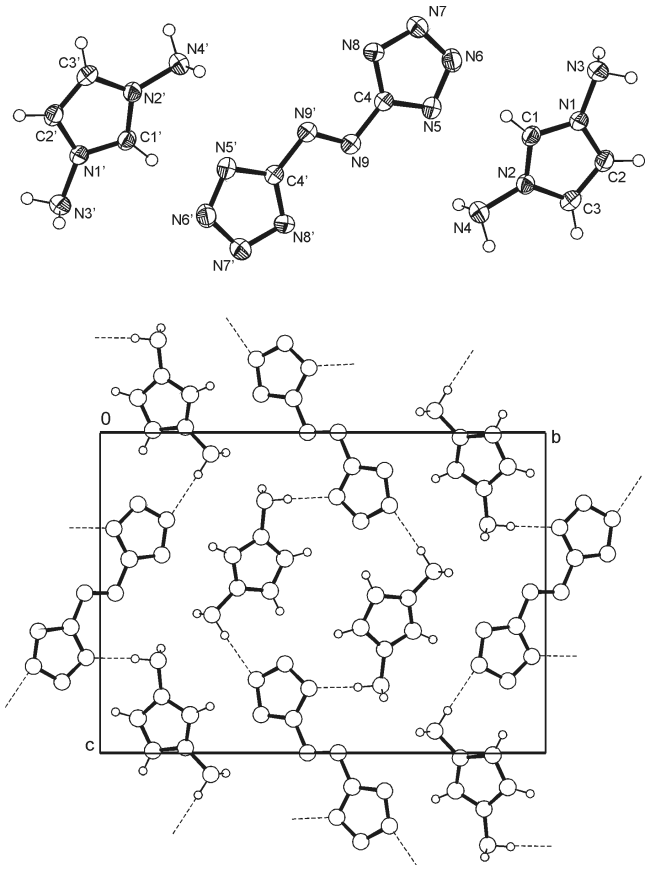
**Abstract**




$C_8H_{14}N_{18}$, monoclinic, $P2_1/n$ (no. 14), $a$ = 3.6429(2) Å, $b$ = 16.883(1) Å, $c$ = 12.150(1) Å, $\beta$ = 90.651(4)°, $V$ = 747.2 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.0332, $wR_{ref}(F^2)$ = 0.0905, $T$ = 233 K.

**Source of material**

The title compound was prepared from barium 5,5'-azotetrazolate pentahydrate [1] and bis (1,3-diaminoimidazolium) sulfate which, in turn, was prepared from the corresponding chloride [2] and silver sulfate in $H_2O$. Precipitates were removed by centrifugation, and supernatant solutions were taken to dryness in vacuum. Single crystals were obtained from MeOH. Decomposition at 115 °C.

IR (neat): 3216, 3120, 3040, 1632, 1430, 1391, 1041, 734 cm$^{-1}$. $^{13}$C NMR ($D_2O$, 75 MHz): 117.3, 130.4, 166.4 ppm.

* Correspondence author (e-mail: gerhard.laus@uibk.ac.at)

**Experimental details**

The asymmetric unit contained one half of the anion which was completed by inversion. Hydrogen atoms at N3 and N4 were found and refined isotropically with bond restraints ($d$ = 0.89 Å).

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | yellow plate, size 0.05×0.15×0.3 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 1.21 cm$^{-1}$ |
| Diffractometer, scan mode: | Nonius Kappa CCD, $\varphi$ and $\omega$ |
| $2\theta_{max}$: | 48° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 3665, 1166 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 1016 |
| $N(param)_{refined}$: | 135 |
| Program: | SHELXS-97 [13] |

**Discussion**

This is the third crystal structure of a 1,3-diaminoimidazolium salt, the chloride [2] and the hexafluorophosphate [3] have been published previously. It is another example of nitrogen-rich 'energetic salts' which have received much attention [4,5]. Crystal structures of other 5,5'-azotetrazolate salts [6-9] including a series of metal salts [10-12] have been reported. The salt consists of two cations and one dianion (Figure, top). All hydrogen atoms of the cation are involved in hydrogen bonds, either via the amino groups or the aromatic ring system. In turn, all nitrogen atoms of the planar dianion serve as acceptors. Thus, strong cation-anion interactions N3–H···N8$^{i}$ ($d$ (H···acceptor) = 2.08 Å and $d$ (donor···acceptor) = 2.994(2) Å, ∠ donor-H···acceptor = 172°) and N4–H···N6$^{ii}$ (2.16 Å and 3.050(2) Å, 166°) create centrosymmetric ring-shaped aggregates (Figure, bottom). The cations are linked to each other into infinite chains by N4–H···N3$^{iii}$ hydrogen bonds between the amino groups (2.48 Å and 3.109(2) Å, 128°). These chains are stacked in the [100] direction by weak N3–H···N$_4^{iv}$ contacts (2.68 Å and 3.409(2) Å, 139°), with an interplanar distance between the imidazole rings of 3.21 Å and a corresponding centroid-centroid distance of 3.64 Å. The three protons of the aromatic ring participate in five C–H···N interactions with three anions, thus establishing a three-dimensional network: C1–H···N5$^{v}$ (2.52 Å and 3.375(2) Å, 151°), C1–H···N6$^{v}$ (2.56 Å and 3.489(2) Å, 170°), C2–H···N7$^{vi}$ (2.48 Å and 3.398(2) Å, 167°), C2–H···N8$^{vi}$ (2.63 Å and 3.382(2) Å, 137°), and C3–H···N7$^{iii}$ (2.52 Å and 3.408(2) Å, 159°). This network is augmented by additional weak interactions of the amino groups and the anion.

Symmetry codes **i**: -½-x, ½+y, ½-z; **ii**: -½+x, 2.5-y, ½+z; **iii**: ½+x, 2.5-y, ½+z; **iv**: ½+x, 2.5-y, -½+z; **v**: -1+x,y,z; **vi**: ½-x, ½+y, ½-z.

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(31) | 4*e* | 0.019(5) | 1.363(1) | 0.174(2) | 0.064(7) |
| H(32) | 4*e* | –0.272(6) | 1.421(1) | 0.206(2) | 0.060(7) |
| H(41) | 4*e* | 0.065(6) | 1.218(1) | 0.564(2) | 0.081(9) |
| H(42) | 4*e* | –0.118(6) | 1.280(1) | 0.631(2) | 0.056(6) |
| H(1) | 4*e* | –0.316 | 1.2531 | 0.3543 | 0.032 |
| H(2) | 4*e* | 0.1648 | 1.4652 | 0.3731 | 0.036 |
| H(3) | 4*e* | 0.2 | 1.4034 | 0.557 | 0.035 |

**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| N(1) | 4*e* | –0.0978(4) | 1.36165(7) | 0.3244(1) | 0.0316(8) | 0.0237(7) | 0.0256(8) | 0.0042(6) | 0.0007(6) | –0.0012(6) |
| N(2) | 4*e* | –0.0715(4) | 1.30848(8) | 0.4838(1) | 0.0300(8) | 0.0228(7) | 0.0279(8) | 0.0026(6) | 0.0029(6) | 0.0007(6) |
| N(3) | 4*e* | –0.1892(5) | 1.36982(9) | 0.2115(1) | 0.050(1) | 0.0326(9) | 0.0267(9) | 0.0050(7) | –0.0047(7) | 0.0013(7) |
| N(4) | 4*e* | –0.1210(5) | 1.25134(9) | 0.5673(1) | 0.053(1) | 0.0300(9) | 0.0303(9) | 0.0002(7) | 0.0052(8) | 0.0043(7) |
| N(5) | 4*e* | 0.2494(4) | 1.13853(8) | 0.3817(1) | 0.0413(9) | 0.0246(8) | 0.0336(9) | –0.0025(6) | 0.0011(7) | 0.0002(6) |
| N(6) | 4*e* | 0.2470(4) | 1.14928(8) | 0.2727(1) | 0.0425(9) | 0.0284(8) | 0.037(1) | 0.0014(6) | 0.0064(7) | 0.0048(7) |
| N(7) | 4*e* | 0.1154(4) | 1.08518(9) | 0.2231(1) | 0.0459(9) | 0.0337(9) | 0.0304(9) | 0.0010(7) | 0.0051(7) | 0.0035(7) |
| N(8) | 4*e* | 0.0282(4) | 1.03126(8) | 0.2990(1) | 0.0416(9) | 0.0297(8) | 0.0238(8) | –0.0034(6) | 0.0024(6) | –0.0011(6) |
| N(9) | 4*e* | 0.0684(4) | 1.03436(8) | 0.5004(1) | 0.0338(8) | 0.0260(7) | 0.0281(8) | –0.0017(6) | 0.0003(6) | –0.0015(6) |
| C(1) | 4*e* | –0.1900(4) | 1.29771(9) | 0.3815(1) | 0.0300(9) | 0.0217(9) | 0.030(1) | 0.0024(7) | –0.0005(7) | –0.0026(7) |
| C(2) | 4*e* | 0.0759(5) | 1.41492(9) | 0.3927(1) | 0.0328(9) | 0.0227(9) | 0.034(1) | –0.0016(7) | 0.0036(7) | –0.0025(7) |
| C(3) | 4*e* | 0.0944(4) | 1.3814(1) | 0.4931(1) | 0.0303(9) | 0.0268(9) | 0.031(1) | –0.0012(7) | 0.0010(7) | –0.0062(7) |
| C(4) | 4*e* | 0.1118(4) | 1.06581(9) | 0.3943(1) | 0.0290(9) | 0.0243(9) | 0.0263(9) | 0.0011(7) | 0.0008(7) | –0.0010(7) |

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