Crystal structure of *N*-[amino-(3-methylpyrazol-1-yl)methylene]guanidine, C₆H₁₀N₆ and its hydrochloride hydrate, C₆H₁₁N₆Cl · H₂O

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1. *N*-[Amino-(3-methylpyrazol-1-yl)methylene]guanidine hydrochloride hydrate, C₆H₁₁N₆Cl · H₂O

Source of material: 82 g 3-Methylpyrazole and 84 g dicyanamide were dissolved in 160.6 g aqueous HCl (25%) and heated under reflux for two hours at 378 K. After cooling down to room temperature the excess of H₂O and HCl was rectified in vacuum (297 K – 313 K, 13mbar). The precipitate was filtered, washed with 50 ml acetone and dried for two hours at 333 K. The melting point of the impure product was 383 K. It was suspended to a 15% aqueous solution which was centrifuged. After separation of the cloudy matter the clear solution was evaporated in a rotary vaporizer. The crystallized product was again filtered, washed with acetone and dried (see above, mp 392 K – 394 K). Elemental analysis (expected values): C 32.6 (32.65), H 6.0 (5.90), N 38.2 (38.09), Cl 15.9 (16.10), O 7.3 (7.26).

C₆H₁₁ClN₆O, triclinic, *P* $\bar{1}$ (No. 2), *a* = 7.006(2) Å, *b* = 7.279(2) Å, *c* = 10.660(3) Å, α = 107.95(2)°, β = 98.70(2)°, γ = 89.52(2)°, *V* = 510.8 Å³, *Z* = 2, *R*(*F*) = 0.031, *R*_w(*F*²) = 0.082.

Table 1. Parameters used for the X-ray data collection

Crystal:	white, plate shape, size 0.12 x 0.13 x 0.25 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	32.57 cm ⁻¹
Diffractometer:	Nicolet P2 ₁
Scan mode:	$\theta/2\theta$
<i>T</i> measurement:	133 K
$2\theta_{\max}$:	113.24°
<i>N</i> (<i>hkl</i>) _{unique} :	1357
Criterion for <i>I</i> _o :	<i>I</i> _o > 2 σ (<i>I</i> _o)
<i>N</i> (<i>param</i>) _{refined} :	160
Programs:	SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	2i	0.2528(3)	0.3112(3)	−0.0871(2)	0.015(6)
H(2)	2i	0.4874(3)	0.1981(3)	−0.2464(2)	0.015(6)
H(6A)	2i	0.901(1)	0.195(2)	−0.179(1)	0.042(5)
H(6B)	2i	0.8580(8)	−0.0180(6)	−0.174(1)	0.042(5)
H(6C)	2i	0.9710(6)	0.141(2)	−0.0454(2)	0.042(5)
H(8A)	2i	0.614(2)	0.223(3)	0.267(2)	0.017(4)
H(8B)	2i	0.453(3)	0.297(4)	0.349(1)	0.017(4)
H(11A)	2i	0.205(3)	0.691(3)	0.451(2)	0.017(4)
H(11B)	2i	0.3853(7)	0.632(3)	0.381(2)	0.017(4)
H(12A)	2i	−0.108(3)	0.390(3)	0.207(2)	0.020(5)
H(12B)	2i	−0.093(3)	0.549(3)	0.342(2)	0.020(5)
H(20A)	2i	0.0259(5)	0.874(4)	0.602(3)	0.041(6)
H(20B)	2i	0.182(4)	0.995(3)	0.596(3)	0.041(6)

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cl	2i	−0.27979(7)	0.77273(7)	0.48973(5)	0.0100(3)	0.0127(3)	0.0106(3)	−0.0003(2)	0.0016(2)	0.0042(2)
C(1)	2i	0.3816(3)	0.2751(3)	−0.0668(2)	0.012(1)	0.009(1)	0.010(1)	−0.0017(9)	−0.0024(9)	0.0042(9)
C(2)	2i	0.5091(3)	0.2147(3)	−0.1533(2)	0.015(1)	0.011(1)	0.006(1)	−0.0045(9)	0.0008(9)	0.0029(9)
C(3)	2i	0.6819(3)	0.1813(3)	−0.0763(2)	0.015(1)	0.001(1)	0.010(1)	−0.0026(8)	0.0024(9)	−0.0004(8)
N(4)	2i	0.6611(2)	0.2161(2)	0.0507(2)	0.0082(9)	0.0061(9)	0.009(1)	0.0020(7)	0.0030(7)	0.0018(7)
N(5)	2i	0.4741(2)	0.2739(2)	0.0554(2)	0.0084(9)	0.0054(9)	0.009(1)	0.0008(7)	0.0019(7)	0.0012(7)
C(6)	2i	0.8689(3)	0.1196(3)	−0.1228(2)	0.015(1)	0.012(1)	0.013(1)	0.0019(9)	0.0067(9)	0.0027(9)
C(7)	2i	0.3983(3)	0.3233(3)	0.1748(2)	0.010(1)	0.001(1)	0.009(1)	−0.0029(8)	0.0010(9)	−0.0004(8)
N(8)	2i	0.5073(2)	0.2897(2)	0.2775(2)	0.012(1)	0.011(1)	0.007(1)	0.0039(7)	0.0035(8)	0.0031(8)
N(9)	2i	0.2246(2)	0.3908(2)	0.1686(2)	0.0086(9)	0.0095(9)	0.0087(9)	0.0015(7)	0.0017(7)	0.0016(7)
C(10)	2i	0.1523(3)	0.4944(3)	0.2790(2)	0.012(1)	0.005(1)	0.010(1)	0.0024(8)	0.0018(9)	0.0058(9)
N(11)	2i	0.2592(2)	0.6204(2)	0.3822(2)	0.0089(9)	0.0091(9)	0.010(1)	0.0007(8)	0.0033(8)	−0.0002(8)
N(12)	2i	−0.0365(2)	0.4778(3)	0.2754(2)	0.009(1)	0.012(1)	0.011(1)	0.0006(7)	0.0029(8)	−0.0011(8)
O(20)	2i	0.1566(2)	0.8918(2)	0.6232(1)	0.0112(8)	0.0125(8)	0.0167(8)	0.0015(6)	0.0011(7)	0.0055(7)

2. *N*-[Amino-(3-methylpyrazol-1-yl)methylene]guanidine, C₆H₁₀N₆

Source of material: 11.5 g Ethyldiisopropylamine was dropped to a saturated aqueous solution (298 K) of 22g *N*-[amino-(3-methylpyrazole-1-yl)-methylene]guanidinehydrochloride hydrate. The solution was stirred for one hour and shaken with 20 ml isopropanol. The isopropanol was separated and evaporated in a desiccator. The precipitate of the title compound was filtered, washed with isopropanol and dried in vacuum by 308 K. It was free of chloride (mp 401 K). The solid product was dissolved at 303 K in an aqueous solution and recrystallized at room temperature forming the crystals with up to 0.5 mm length.

The NMR and IR spectra correspond well with the refined structures of the compound. Elemental analysis (expected values): C 43.4 (43.37), H 6.1 (6.06), N 50.5 (50.57).

C₆H₁₀N₆, monoclinic, *P*12₁/*c*1 (No. 14), *a* = 5.974 Å, *b* = 8.883(1) Å, *c* = 14.975(1) Å, β = 95.02°, *V* = 791.6 Å³, *Z* = 4, *R*(*F*) = 0.038, *R*_w(*F*²) = 0.098.

Table 6. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	4e	0.4732(4)	0.7160(2)	0.5236(1)	0.025(1)	0.020(1)	0.025(1)	0.001(1)	−0.0002(9)	−0.001(1)
C(2)	4e	0.5298(4)	0.8127(2)	0.4586(1)	0.030(1)	0.021(1)	0.025(1)	0.0034(9)	−0.003(1)	0.0035(9)
C(3)	4e	0.7639(4)	0.8028(2)	0.4577(1)	0.033(1)	0.019(1)	0.021(1)	0.0003(9)	0.0012(9)	0.0014(9)
N(4)	4e	0.8506(3)	0.7062(2)	0.5188(1)	0.028(1)	0.025(1)	0.027(1)	−0.0009(8)	0.0044(8)	0.0051(8)
N(5)	4e	0.6692(3)	0.6534(2)	0.5596(1)	0.028(1)	0.0148(9)	0.0209(9)	0.0007(8)	0.0028(8)	0.0020(7)
C(6)	4e	0.9096(4)	0.8863(3)	0.3984(2)	0.038(1)	0.033(1)	0.038(1)	0.001(1)	0.004(1)	0.015(1)
C(7)	4e	0.7052(4)	0.5463(2)	0.6307(1)	0.030(1)	0.013(1)	0.020(1)	0.0002(9)	0.0004(9)	−0.0027(8)
N(8)	4e	0.8973(3)	0.4842(2)	0.6474(1)	0.030(1)	0.031(1)	0.031(1)	0.0061(9)	0.0061(9)	0.0091(9)
N(9)	4e	0.5164(3)	0.5301(2)	0.6746(1)	0.029(1)	0.0143(9)	0.0216(9)	0.0011(7)	0.0039(8)	0.0013(7)
C(10)	4e	0.5023(3)	0.4168(2)	0.7326(1)	0.029(1)	0.014(1)	0.019(1)	−0.0025(9)	−0.0017(9)	−0.0032(9)
N(11)	4e	0.6624(3)	0.3170(2)	0.7555(1)	0.032(1)	0.016(1)	0.029(1)	0.0020(9)	0.0027(8)	0.0059(8)
N(12)	4e	0.3090(3)	0.4079(2)	0.7725(1)	0.031(1)	0.025(1)	0.030(1)	0.0027(9)	0.0048(9)	0.0104(9)

References

- Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Large Structures. *Acta Crystallogr. A* **46** (1990) 467–473.
- Sheldrick, G. M.: SHELXL-93, a program for refining crystal structures. University of Göttingen, Germany 1993.

Table 4. Parameters used for the X-ray data collection

Crystal:	white, plate shape, size 0.18 x 0.20 x 0.51 mm
Wavelength:	Cu K _α radiation (1.54178 Å)
μ:	8.00 cm ^{−1}
Diffractometer:	Siemens P4
Scan mode:	θ/2θ
<i>T</i> _{measurement} :	203 K
2θ _{max} :	112.48°
<i>N</i> (<i>hkl</i>) _{unique} :	1039
Criterion for <i>I</i> ₀ :	<i>I</i> ₀ > 2 σ(<i>I</i> ₀)
<i>N</i> (<i>param</i>) _{refined} :	132
Programs:	SHELXS-86, SHELXL-93

Table 5. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.3280(4)	0.6964(2)	0.5403(1)	0.026(6)
H(2)	4e	0.4318(4)	0.8737(2)	0.4218(1)	0.035(7)
H(6A)	4e	0.908(3)	0.9928(4)	0.4128(9)	0.077(6)
H(6B)	4e	0.853(2)	0.872(2)	0.3362(2)	0.077(6)
H(6C)	4e	1.0623(8)	0.849(2)	0.408(1)	0.077(6)
H(8)	4e	0.986(4)	0.512(3)	0.605(1)	0.043(7)
H(11A)	4e	0.786(2)	0.329(3)	0.727(2)	0.041(5)
H(11B)	4e	0.620(4)	0.234(2)	0.783(2)	0.041(5)
H(12A)	4e	0.184(2)	0.447(3)	0.745(2)	0.042(5)
H(12B)	4e	0.296(4)	0.332(2)	0.811(1)	0.042(5)