N,N,N′,N′-Tetramethyl-N″-[2-(N′,N′,N″,N″-tetramethylguanidino)-ethyl]guanidine

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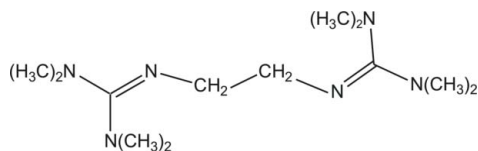Correspondence e-mail: willi.kantlehner@htw-aalen.de

The title compound, $C_{12}H_{28}N_6$, is located about an inversion center situated at the center of the $-CH_2-CH_2-$ bond. The C—N bond lengths are 1.285 (2), 1.384 (2) and 1.395 (1) Å, indicating double- and single-bond character. The N—C—N angles are 114.1 (1), 119.3 (1) and 126.5 (1)°, showing a deviation of both CN_3 planes from an ideal trigonal–planar geometry.

Related literature

For the crystal structure of N,N,N′,N′-tetramethylchloro-formamidinium-chloride, see: Tiritiris & Kantlehner (2008). For the synthesis of N,N,N′,N′-tetramethyl-N″-[2-(N′,N′,N″,N″-tetramethylguanidino)-ethyl]-guanidine and the crystal structure of the corresponding diprotonated bis-guanidinium dichloride salt, see: Wittmann et al. (2000). For the synthesis and characterization of bisguanidine–copper complexes, see: Bienemann et al. (2010).

Experimental

Crystal data

$C_{12}H_{28}N_6$	V = 761.88 (10) Å^3
M_r = 256.40	Z = 2
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 8.4189 (6) Å	μ = 0.07 mm^{-1}
b = 8.5894 (6) Å	T = 293 K
c = 11.0089 (8) Å	0.22 × 0.18 × 0.15 mm
β = 106.858 (5)°	

Data collection

Bruker–Nonius KappaCCD diffractometer	1835 independent reflections
7247 measured reflections	1120 reflections with $I > 2\sigma(I)$
	R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036	87 parameters
$wR(F^2)$ = 0.096	H-atom parameters constrained
S = 0.86	$\Delta\rho_{max}$ = 0.11 e Å^{-3}
1835 reflections	$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Data collection: *COLLECT* (Hooft, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

N,N,N′,N′-Tetramethyl-*N″*-[2-(*N′,N′,N″,N″*-tetramethylguanidino)ethyl]-guanidine

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Comment

The synthesis of *N,N,N′,N′*-tetramethyl-*N″*- [2-(*N′,N′,N″,N″*-tetramethylguanidino)-ethyl]- guanidine is well known in literature (Wittmann *et al.*, 2000). The compound was used as a nitrogen donor ligand in reactions with copper halogenides (CuI or CuCl$_2$), to give mono- or bis-chelate complexes (Bienemann *et al.*, 2010). However, the crystal structure of the free guanidine base was previously unknown. According to the structure analysis, the C1–N3 bond in the bisguanidine is 1.285 (2) Å, indicating double bond character. The bond lengths C1–N2 = 1.384 (2) Å and C1–N1 = 1.395 (1) Å are elongated and characteristic for a C–N imine single bond. The N–C1–N angles are 114.1 (1)° (N1–C1–N2), 126.5 (1)° (N2–C1–N3) and 119.3 (1)° (N1–C1–N3), showing a deviation of both CN$_3$ planes from an ideal trigonal planar geometry (Fig. 1). The dihedral angle N3—C6—C6^i—N3^i is 180.00 (9). The bonds between the N atoms and the terminal *C*-methyl groups, all have values close to a typical single bond (1.442 (2)–1.459 (1) Å). This is completely different compared with the geometrical parameters from the crystal structure analysis of the corresponding diprotonated bisguanidinium dichloride salt (Wittmann *et al.*, 2000). Here, the C–N bond lengths of the CN$_3$ units are in a range between 1.336 (2) and 1.342 (2) Å, the N–C–N angles are 119.5 (1), 120.1 (1) and 120.4 (1)°, indicating also delocalization of the positive charges on both CN$_3$ planes. The crystal packing in the here presented title compound is through van der Waals interactions, only.

Experimental

Two equivalents of *N,N,N′,N′*-tetramethylchloroformamidinium-chloride (Tiritiris & Kantlehner, 2008) were reacted with one equivalent of ethane-1,2-diamine in acetonitrile in the presence of triethylamine at 273 K. The obtained protonated bisguanidinium dichloride salt was reacted in a next step with an aqueous sodium hydroxide solution at 273 K. After extraction of the bisguanidine with diethyl ether from the water phase, the solvent was evaporated and the title compound was isolated in form of a colourless solid. Single crystals have been obtained by recrystallization from a saturated acetonitrile solution.

Refinement

The hydrogen atoms of the methyl groups were allowed to rotate with a fixed angle around the C–N bond to best fit the experimental electron density, with U(H) set to 1.5 U_{eq}(C) and d(C—H) = 0.96 Å. The remaining H atoms were placed in calculated positions with d(C—H) = 0.97 Å. They were included in the refinement in the riding model approximation, with U(H) set to 1.2 U_{eq}(C).

Computing details

Data collection: *COLLECT* (Hooft, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).
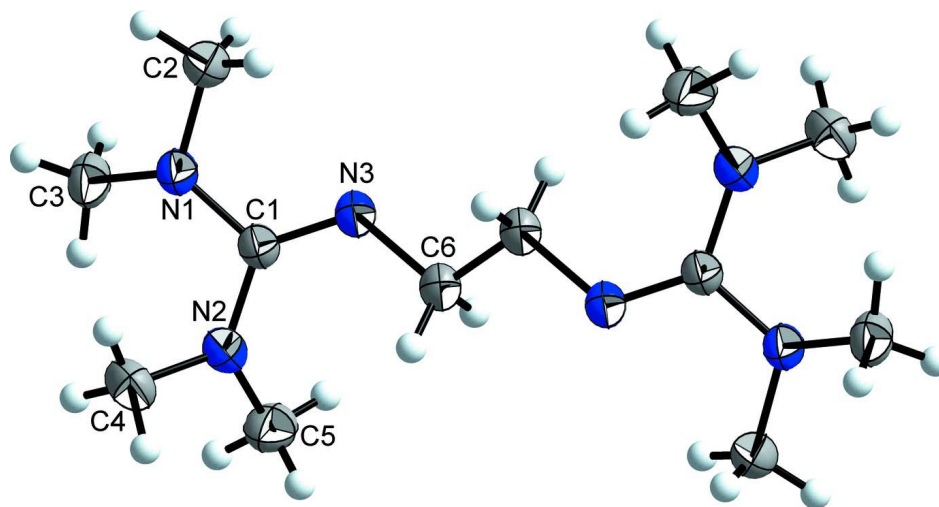

Figure 1

The structure of the title compound with atom labels and 50% probability displacement ellipsoids.

N,N,N′,N′-Tetramethyl-*N′′*-[2- (*N′,N′,N′′,N′′*-tetramethylguanidino)ethyl]guanidine

Crystal data

$C_{12}H_{28}N_6$	$F(000) = 284$
$M_r = 256.40$	$D_x = 1.118$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 7247 reflections
$a = 8.4189$ (6) Å	$\theta = 2.7–28.1°$
$b = 8.5894$ (6) Å	$\mu = 0.07$ mm^{-1}
$c = 11.0089$ (8) Å	$T = 293$ K
$\beta = 106.858$ (5)°	Polyhedral, colourless
$V = 761.88$ (10) Å^3	$0.22 \times 0.18 \times 0.15$ mm
$Z = 2$	

Data collection

Bruker–Nonius KappaCCD diffractometer	1120 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.043$
Graphite monochromator	$\theta_{max} = 28.1°$, $\theta_{min} = 2.7°$
φ scans, and ω scans	$h = -11 \rightarrow 11$
7247 measured reflections	$k = -11 \rightarrow 11$
1835 independent reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$wR(F^2) = 0.096$
Least-squares matrix: full	$S = 0.86$
$R[F^2 > 2\sigma(F^2)] = 0.036$	1835 reflections

87 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.059P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.11$ e Å^{-3}

$\Delta\rho_{min} = -0.13$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$

Extinction coefficient: 0.57 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	−0.04772 (12)	0.18588 (12)	0.32603 (9)	0.0485 (3)
N2	0.20678 (12)	0.08543 (13)	0.31899 (10)	0.0556 (3)
N3	−0.01179 (12)	0.13388 (11)	0.12955 (9)	0.0484 (3)
C1	0.05014 (13)	0.13573 (13)	0.25085 (10)	0.0434 (3)
C2	−0.22265 (16)	0.20743 (17)	0.26375 (13)	0.0607 (4)
H2A	−0.2392	0.3035	0.2173	0.091*
H2B	−0.2819	0.2105	0.3262	0.091*
H2C	−0.2631	0.1226	0.2064	0.091*
C3	0.01949 (17)	0.29870 (15)	0.42638 (12)	0.0571 (3)
H3A	0.1384	0.2914	0.4535	0.086*
H3B	−0.0228	0.2775	0.4968	0.086*
H3C	−0.0128	0.4017	0.3950	0.086*
C4	0.24173 (19)	0.01111 (18)	0.44203 (13)	0.0688 (4)
H4A	0.2972	0.0835	0.5069	0.103*
H4B	0.3116	−0.0778	0.4444	0.103*
H4C	0.1396	−0.0216	0.4563	0.103*
C5	0.35164 (16)	0.12927 (18)	0.28218 (14)	0.0664 (4)
H5A	0.3186	0.1914	0.2065	0.100*
H5B	0.4073	0.0373	0.2663	0.100*
H5C	0.4254	0.1883	0.3492	0.100*
C6	0.06621 (15)	0.04024 (13)	0.05215 (10)	0.0488 (3)
H6A	0.1385	−0.0369	0.1049	0.059*
H6B	0.1331	0.1064	0.0150	0.059*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0438 (5)	0.0632 (6)	0.0376 (5)	−0.0024 (4)	0.0103 (4)	−0.0085 (4)
N2	0.0442 (5)	0.0785 (7)	0.0409 (6)	0.0042 (5)	0.0074 (4)	0.0036 (5)

N3	0.0528 (6)	0.0556 (6)	0.0351 (5)	0.0067 (4)	0.0099 (4)	−0.0028 (4)
C1	0.0434 (6)	0.0495 (6)	0.0357 (6)	−0.0011 (4)	0.0090 (5)	−0.0028 (4)
C2	0.0463 (7)	0.0865 (9)	0.0482 (7)	0.0030 (6)	0.0121 (6)	−0.0075 (6)
C3	0.0635 (8)	0.0643 (8)	0.0439 (7)	−0.0071 (6)	0.0162 (6)	−0.0122 (5)
C4	0.0686 (9)	0.0823 (9)	0.0476 (8)	0.0144 (7)	0.0043 (7)	0.0078 (7)
C5	0.0458 (7)	0.0868 (10)	0.0662 (9)	−0.0047 (6)	0.0155 (7)	−0.0165 (7)
C6	0.0518 (7)	0.0576 (7)	0.0361 (6)	0.0056 (5)	0.0115 (5)	−0.0016 (5)

Geometric parameters (Å, º)

N1—C1	1.3945 (14)	C3—H3B	0.9600
N1—C2	1.4449 (16)	C3—H3C	0.9600
N1—C3	1.4550 (15)	C4—H4A	0.9600
N2—C1	1.3837 (15)	C4—H4B	0.9600
N2—C5	1.4422 (16)	C4—H4C	0.9600
N2—C4	1.4483 (17)	C5—H5A	0.9600
N3—C1	1.2852 (15)	C5—H5B	0.9600
N3—C6	1.4589 (13)	C5—H5C	0.9600
C2—H2A	0.9600	C6—C6^i	1.516 (2)
C2—H2B	0.9600	C6—H6A	0.9700
C2—H2C	0.9600	C6—H6B	0.9700
C3—H3A	0.9600		
C1—N1—C2	117.02 (10)	H3A—C3—H3C	109.5
C1—N1—C3	119.32 (9)	H3B—C3—H3C	109.5
C2—N1—C3	113.16 (10)	N2—C4—H4A	109.5
C1—N2—C5	121.12 (11)	N2—C4—H4B	109.5
C1—N2—C4	123.22 (10)	H4A—C4—H4B	109.5
C5—N2—C4	114.76 (11)	N2—C4—H4C	109.5
C1—N3—C6	119.87 (10)	H4A—C4—H4C	109.5
N3—C1—N2	126.52 (10)	H4B—C4—H4C	109.5
N3—C1—N1	119.28 (11)	N2—C5—H5A	109.5
N2—C1—N1	114.14 (10)	N2—C5—H5B	109.5
N1—C2—H2A	109.5	H5A—C5—H5B	109.5
N1—C2—H2B	109.5	N2—C5—H5C	109.5
H2A—C2—H2B	109.5	H5A—C5—H5C	109.5
N1—C2—H2C	109.5	H5B—C5—H5C	109.5
H2A—C2—H2C	109.5	N3—C6—C6^i	109.70 (12)
H2B—C2—H2C	109.5	N3—C6—H6A	109.7
N1—C3—H3A	109.5	C6^i—C6—H6A	109.7
N1—C3—H3B	109.5	N3—C6—H6B	109.7
H3A—C3—H3B	109.5	C6^i—C6—H6B	109.7
N1—C3—H3C	109.5	H6A—C6—H6B	108.2
C6—N3—C1—N2	15.52 (18)	C2—N1—C1—N3	10.45 (16)
C6—N3—C1—N1	−161.37 (10)	C3—N1—C1—N3	−132.01 (12)
C5—N2—C1—N3	46.34 (18)	C2—N1—C1—N2	−166.81 (11)
C4—N2—C1—N3	−145.11 (14)	C3—N1—C1—N2	50.74 (15)

| C5—N2—C1—N1 | −136.65 (12) | C1—N3—C6—C6[i] | 138.63 (13) |
| C4—N2—C1—N1 | 31.90 (17) | | |

Symmetry code: (i) −*x*, −*y*, −*z*.