Derivatives of the Triaminoguanidinium Ion, 2. Prototropic Tautomerism, Crystal and Molecular Structure of *N*,*N*′,*N*″-Tris(propan-2-iminyl)guanidine [1, 2]

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Dedicated to Professor Gerhard Müller on the occasion of his 60th birthday

The title compound, $C_{10}H_{20}N_6$ (**2**), was prepared from *N*,*N*′,*N*″-triaminoguanidinium chloride. Solvent- and temperature-dependent ^{1}H NMR spectra indicating prototropic tautomerism were observed in solution. The crystal and molecular structure was determined by X-ray diffraction analysis. The compound crystallizes in the hexagonal space group $P6_3/m$. The molecules lie on crystallographic mirror planes parallel to the *a*,*b* plane, which are separated from each other by 3.37 Å. The threefold crystallographic symmetry of the molecules is due to disorder with positional averaging of individual molecules.

Key words: Triaminoguanidine, Triaminoguanidinium Salt, Variable-temperature ^{1}H NMR Spectra, Layered Crystal Structure

Introduction

Condensation of the *N*,*N*′,*N*″-triaminoguanidinium ion **1** (Fig. 1) with aromatic or aliphatic aldehydes and ketones yields *N*,*N*′,*N*″-tris(arylidenamino)- or *N*,*N*′,*N*″-tris(alkylidenamino)guanidinium salts, which can be deprotonated to form the corresponding neutral triaminoguanidine-derived trishydrazones [3 – 7]. Deprotonated forms of tris(2-hydroxybenzylidenamino)guanidinium [6 – 9] and tris[α-(hydroxyimino)alkylidenamino]guanidinium salts [10] have recently been identified as triangular ligands for transition-metal complexes with novel architectures. The solid-state structures of a few tris(2-hydroxybenzylidenamino)guanidinium salts [6, 7] have been determined; they show a planar $C(NNC)_3$ core with phenyl rings moderately tilted against this plane. To our knowledge, no crystal structures have been reported for neutral triaminoguanidine-derived trishydrazones. As the first compound of this type, we report here the crystal structure determination of the title compound **2**. For this particular compound, a completely planar molecular structure could be expected.

Results and Discussion

A synthesis of the title compound **2** from *N*,*N*′,*N*″-triaminoguanidinium chloride (**1**, X = Cl) and acetone, followed by deprotonation of the initially formed new guanidinium salt, has been published by Zelenin *et al.* [5]. In our hands, several modifications were necessary to obtain **2** in satisfactory yield and purity. In addition, our sample of **2** showed a much higher melting point than reported (154 *versus* 115 °C). The reported [5] ^{1}H NMR data for **2** (see Table 1, entry 1) are not compatible with a static molecular structure as depicted in Fig. 1. In fact, variable-temperature ^{1}H NMR spectra recorded at an operating frequency of 500.16 MHz allowed us to observe a dynamic process (Fig. 2 and Table 1). Thus, a low-temperature spectrum (220 K) in $CDCl_3$ solution showed two sharp singlet signals for the NH protons, separated sharp singlets for four methyl groups and one singlet for two methyl groups. This spectrum may be assigned to the unsymmetrical structure of **2** shown in Fig. 1 (with two accidentally isochronous methyl groups). Line broadening and coalescence of the two NH signals on one hand and of all CH_3 signals on the other hand were observed

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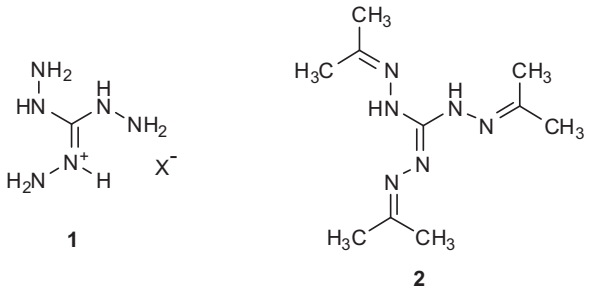


Fig. 1.

when the temperature was raised. At 330 K, the region of fast exchange was almost reached, and a spectrum showing only one (broad) NH signal and two methyl signals (each integrating for 9 H) was obtained. An approximate value for the rate constant at the coalescence temperature ($T_{coal} = 297 \pm 2$ K) for the exchange process of the two NH proton signals can be obtained using the formula $k_{coal} = (\pi/\sqrt{2})\Delta\nu$ (with $\Delta\nu$ taken as the frequency difference of the two exchanging nuclei in the region of negligibly slow exchange) [11 – 13]. With this value and the Eyring equation, the free energy of activation can be calculated. Unfortunately, the value of $\Delta\nu$ was not constant in the region of slow exchange but unexpectedly decreased from 275.0 Hz (at 260 K) to 246.6 Hz (at 220 K). Since $\Delta\nu$ in the above formula is in theory the frequency difference at T_{coal}, the use of temperature-dependent data obtained in the region of slow exchange constitutes a potential source of error. Calculation of $\Delta\nu$ at T_{coal} by linear extrapolation of the low-temperature data gave a value of 302.5 ± 1.5 Hz, from which $\Delta G^{\neq}$ (297 ± 2 K, $CDCl_3$ solution, $c = 0.045$ mol L^{-1}) $= 56.6 \pm 0.4$ kJ mol^{-1} (13.5 ± 0.1 kcal mol^{-1}) was derived.

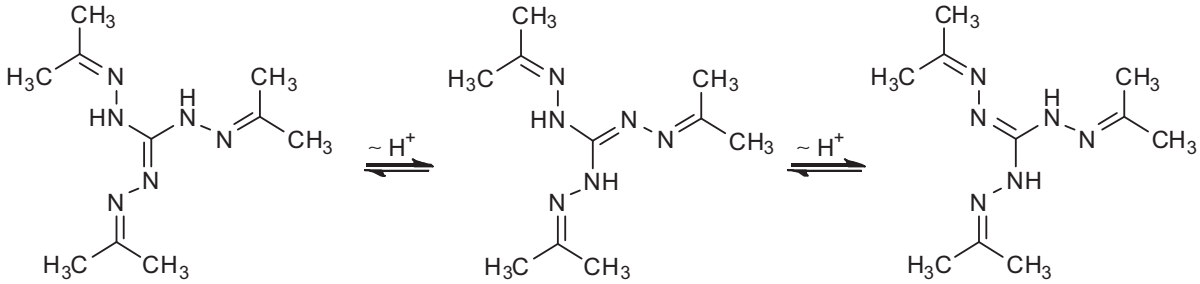
The variable-temperature (VT) ^{1}H NMR spectra of **2** in deuterated acetonitrile in the temperature range 230 – 340 K showed two signals for methyl protons, each integrating for 9 H and shifting to slightly higher δ values at elevated temperature (Table 1, entries 4 – 6). In contrast to the spectra taken in $CDCl_3$, no sign of dynamic exchange involving these two signals was seen, and a spectrum attributable to an unsymmetrical structure of **2** was not observed down to 230 K. On the other hand, the two NH protons appeared as a markedly broadened signal (2 H) over the whole temperature range down to $T \approx 250$ K, where the signal became very broad, almost disappeared on further cooling, and emerged as two, still very broad, signals at 230 K.

VT-^{1}H NMR spectra of **2** in deuterated dimethyl sulfoxide were taken in the "high-temperature" region only ($T = 300 – 360$ K; Table 1, entries 7 and 8). Two methyl signals were observed, which had an intensity

Table 1. Variable-temperature ^{1}H NMR data for compound **2**[a].

Entry	Solvent	Temperature (K)	$\delta(CH_3)$ (ppm)	δ(NH) (ppm)
1	$CDCl_3$[b]		1.80 (s, 9 H), 1.85 (s, 9 H)	8.30 (br s, 2 H)
2	$CDCl_3$	220	1.90 (s, 6 H), 1.98 (s, 3 H), 2.00 (s, 3 H), 2.06 (s, 3 H), 2.12 (s, 3 H)	8.40 (s, 1 H), 8.89 (s, 1 H)
3	$CDCl_3$[c]	300	1.96 (broadened s, 9 H), 2.01 (s, 9 H)	8.59 (very broad, 2 H)
4	CD_3CN	230	1.85 (s, H), 1.93 (s, H)	8.52/8.79 (very broad coalescing signals)
5	CD_3CN	300	1.89 (s, 9 H), 1.96 (s, 9 H)	8.59 (broad, 2 H)
6	CD_3CN	340	1.91 (s, 9 H), 1.97 (s, 9 H)	8.55 (broad, 2 H)
7	[D_6]DMSO	300	1.84 (s, 6 H), 1.94 (s, 12 H)	8.27 (br s, 1 H), 8.83 (br s, 1 H)
8	[D_6]DMSO[d]	360	1.88 (broadened s, 9 H), 1.95 (s, 9 H)	8.22/8.74 (very broad coalescing signals)
9	D_2O[e]	295	1.92 (s, 6 H), 1.97 (s, 6 H)	not observed

[a] Spectra were recorded at 500.16 MHz, except for entry 1; [b] recorded at 100 MHz, see ref. [5]; [c] data in the presence of a catalytic amount of *p*-TsOH: $\delta = 1.96$ (sharp s, 9 H), 2.01 (s, 9 H), 8.58 (very broad, 2 H); [d] data in the presence of a catalytic amount of *p*-TsOH: $\delta = 1.84$ (sharp s, 9 H), 1.94 (sharp s, 9 H), 8.63 (very broad, 2 H); [e] the compound is well soluble in water.



Scheme 1. Degenerate prototropic equilibria of **2**.

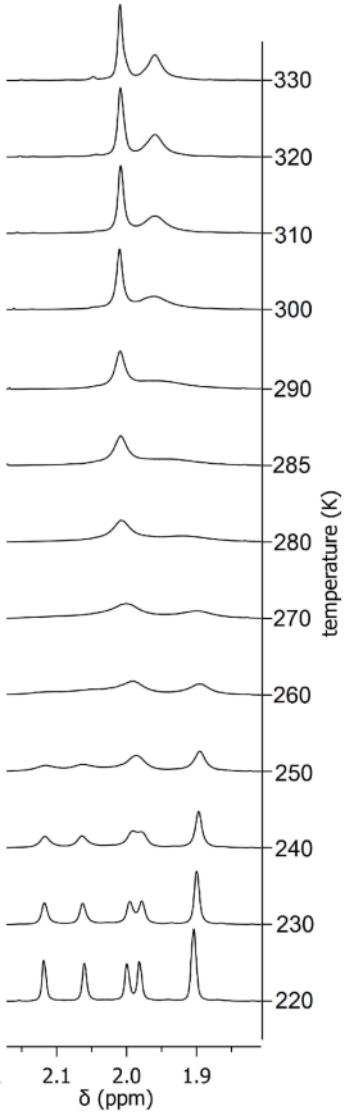


Fig. 2. Variable-temperature ^{1}H NMR spectra of **2** (in $CDCl_3$, 500.16 MHz); region of the methyl resonances.

ratio of 6 : 12 at 300 K and of 9 : 9 at 360 K. This change results from the coalescence between the signal for two methyl groups at $\delta = 1.84$ ppm and one of the four methyl groups contributing to the signal at 1.94 ppm. The NH protons appeared as two broadened signals at 300 K and were in the coalescence region at 360 K.

In principle, temperature-dependent NMR spectra of **1** can result from stereodynamic factors as well as prototropic tautomerism. Useful information on the stereodynamics of hydrazones and guanidines is found in ref. [13]. Stereodynamics to be considered in this molecule include (a) the rotation around guanidine C−N single bonds, (b) geometrical isomerization at the guanidine C=N double bond, and (c) geometrical isomerization at the hydrazone C=N bond. The last-mentioned process is likely not to take place in the temperature range of the present study; it has been reported that geometrical isomerization of several N-substituted acetone hydrazones requires much higher temperatures in inert solvents (*e. g.*, $\Delta G^{\neq} = 23.9$ kcal mol^{-1} for acetone *N*,*N*-dimethylhydrazone in 1,2,4-trichlorobenzene at 170 °C [14]). The barrier to rotation around the guanidine C−N single bond, which have partial double bond character due to $n-\pi$ conjugation, is difficult to estimate; based on available data for ureas and pentasubstituted amidinium salts [13, 15], one may assume that the barrier is significantly lower than the one measured for **2**. In addition, the observed solvent dependency of the NMR spectra excludes this process as the rate-limiting one.

$\Delta G^{\neq}$ values for the geometrical isomerization at the guanidine C=N bond cover a wide range, whith electron-withdrawing substituents at the imino nitrogen atom lowering the barrier considerably. Examples for $(Me_2N)_2C{=}N{-}R$ are as follows: < 10 (R = acyl, NO_2, CN), 12.1 (Ph), 18.7 (CH_3), > 25 kcal mol^{-1}

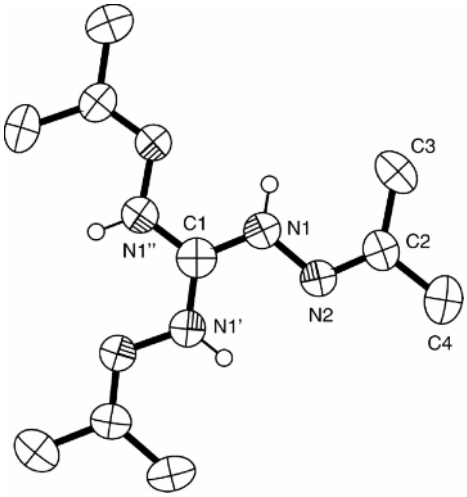


Fig. 3. Structure of compound **2** in the crystal, with 50% probability displacement ellipsoids. Methyl hydrogen atoms have been omitted. The two NH hydrogen atoms are disordered over three positions. See text for discussion of the observed symmetry. Bond lengths (Å) and angles (deg): C1–N1 1.332(2), N1–N2 1.382(2), N2–C2 1.282(2), C2–C3 1.495(3), C2–C4 1.489(3); N1–C1–N1′ 120.0, C1–N1–N2 116.9(1), N1–N2–C2 115.5(2), N2–C2–C3 125.1(2), N2–C2–C4 117.4(2), C3–C2–C4 117.5(2).

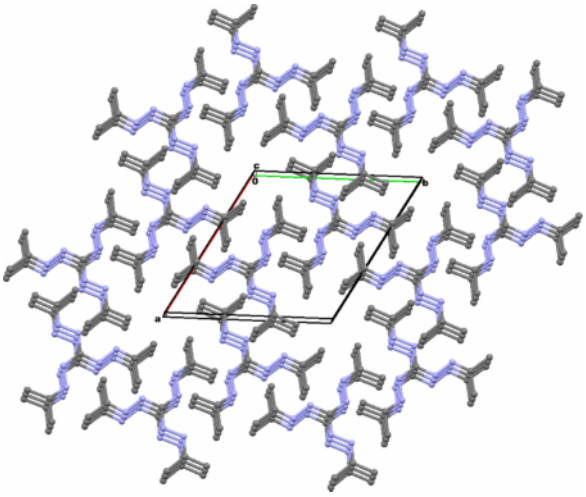


Fig. 4 (color online). Packing diagram of **2** in the crystal, viewed approximately perpendicular to the a,b plane. Molecules within the stacks are separated by a distance of $z \pm 1$. Each stack is surrounded by three adjacent stacks displaced by $c/2$.

(OMe, NMe_2) [16]. Considering the rationalization of these substituent effects, it is likely that the iminyl moiety as a substituent at the imino nitrogen of **2** is not able to stabilize a negative charge by resonance and therefore resembles more a methoxy substituent, corresponding to a $\Delta G^{\neq}$ value that would be significantly higher than the value determined here for guanidine **2**. It has also been reported that the geometrical isomerization of 1,1,3,3-tetramethyl-2-phenylguanidine, which proceeds *via* the N-inversion mechanism, is independent of solvent polarity but decreases in protic solvents such as CD_3OD [15].

Prototropic tautomerism, which is well known for the guanidine system, is likely to be the dynamic process that accounts for the temperature-dependent NMR spectra described above. Prototropic equilibria between three identical molecules (Scheme 1) generate a time-averaged, C_3-symmetrical structure that agrees with the observation of only two CH_3 signals and one NH signal in the region of fast exchange. In contrast to the solvent's influence on the E/Z isomerization at the C=N bond (see preceding paragraph), the dynamic process for **2** is accelerated by polar solvents (CD_3CN and [D_6]DMSO *vs.* $CDCl_3$) as well as by a protic solvent (D_2O). In fact, we observe that the process is fastest in D_2O solution, and a complete H/D exchange occurs within a few minutes at ambient temperature. Incidentally, the experimentally determined $\Delta G^{\neq}$ value (55.6 kJ mol^{-1}) is in close agreement with the data reported for the complete exchange between NH and NH_2 protons in *N*-methoxyguanidine, *N*-formylguanidine, and *N*-(trichloromethylcarbimidoyl)guanidine [17].

Prototropic tautomerism of guanidines has often been discussed in the literature [18, 19], but it seems that detailed investigations on the mechanism of the

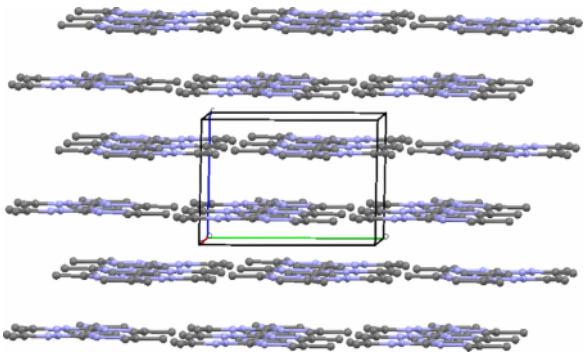


Fig. 5 (color online). Packing motif of **2** in the crystal, showing layers parallel to the a,b plane and separated by $c/2$.

Table 2. Crystal structure data for **2**.

	2
Formula	$C_{10}H_{20}N_6$
M_r	224.32
Crystal size, mm^3	$0.26 \times 0.10 \times 0.08$
Crystal system	hexagonal
Space group	$P6_3/m$
a, Å	10.6383(10)
b, Å	10.6383(10)
c, Å	6.7415(6)
V, Å^3	660.74(10)
Z	2
D_{calcd}, g cm^{-3}	1.13
μ(MoK_α), mm^{-1}	0.6
F(000), e	244
Radiation	CuK_α
Temperature, K	150 (2)
hkl range	$-11 \le h \le +12$, $-7 \le k \le 12$, $-8 \le l \le +2$
θ range, deg	4.80 – 73.67
Refl. measd / unique / R_{int}	1401 / 487 / 0.0174
Param. refined / restraints	35 / 0
$R(F)$ / $wR(F^2)^{a,b}[I > 2\sigma(I)]$	0.0464 / 0.1348
$R(F)$ / $wR(F^2)^{a,b}$ (all refls.)	0.0538 / 0.1424
GoF $(F^2)^c$	1.137
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.15 / −0.14

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = \left[\sigma^2(F_o^2) + (AP)^2 + BP\right]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

proton shift interconverting the individual tautomers are scarce. For a discussion of possible mechanisms of proton transfer in guanidines, see lit. [20]. For cyanoguanidine ("dicyandiamide"), an IR spectroscopic study suggested the presence of at least two tautomers in solution [21]. The four-membered transition state for an intramolecular proton transfer (N···H···N) between the two major tautomers has an energy of at least 170 kJ mol^{-1} according to DFT calculations, which excludes an interconversion by this mechanism around room temperature [21]. The observed influence of the solvent on the temperature-dependence of the ^{1}H NMR spectra of **2** suggests a solvent-assisted prototropy for the more polar solvents, acetonitrile and dimethyl sulfoxide, involving deprotonation of an amino N−H with formation of a resonance-stabilized [N$^-$−C=N] anion followed by reprotonation at the imine nitrogen atom. On the other hand, the rate acceleration in the presence of a catalytic amount of *p*-toluenesulfonic acid would include protonation at the basic imine nitrogen and solvent-assisted deprotonation at the other N−H bond of the [HN$^+$=C−NH] intermediate. It should be added that in both intermediates, the bond order of the imine C=N bond will be reduced; consequently the barrier to E/Z isomerization at this bond will be lowered compared to the neutral guanidine, so that this process may in fact be involved in the molecular dynamics which give rise to the VT NMR spectra. With water as the solvent, both dissociative processes of H transfer could be operating (*i. e.* water could act both as a base and an acid), but a non-dissociative process, in which proton transfer occurs in a complex made up of a molecule of **2** and several water molecules, cannot be excluded *a priori*. Detailed investigations on the different mechanistic pathways were beyond the scope of this study.

An X-ray crystal structure determination of **2** revealed the molecular structure shown in Fig. 3. The molecular plane, comprising all atoms except the methyl hydrogen atoms, coincides with a crystallographic mirror plane, and the position of the central carbon atom C1 has point symmetry $\bar{6}$. The apparent C_{3h} symmetry of the molecule is higher than expected for the chemical structure of **2**. The threefold crystallographic symmetry of the molecule is due to positional averaging of individual molecules rotated in the molecular plane by 120 or 240°. This disorder could not be resolved. As a consequence, the observed C–N bond lengths of the CN_3 unit (1.332 Å) represent only averaged values. For comparison, the C–N bond lengths in the symmetrical cation of *N*,*N*′,*N*″-triaminoguanidinium chloride (**1**, X = Cl), which have partial double bond character due to delocalization of the positive charge, have been reported to be 1.325(2) Å (X-ray diffraction data [22]) and 1.324(4) – 1.336(4) Å (neutron diffraction data [23]). Similarly, in *N*,*N*′,*N*″-tris(benzylamino)guanidinium salts, the C–N bond lengths are in the range 1.321(3) – 1.333(3) Å [1]. In contrast, the C=N and the C–N bond lengths in several substituted guanidines are distinctly different [18]. The following recent examples of pentaalkylguanidines are illustrative: 1.285(2) *vs.* 1.384(2) – 1.395(1) Å in *N*,*N*,*N*′,*N*′-tetramethyl-*N*″-[2-(*N*′,*N*′,*N*″,*N*″-tetramethylguanidino)ethyl]guanidine [24] and 1.282(2) *vs.* 1.392(2) – 1.399(2) Å in 1,1,3,3-tetramethyl-2-[2-(tritylsulfanyl)ethyl]guanidine [25]. Unresolved superposition of prototropic tautomers has also been suggested to explain the experimentally observed equalized C–N bond lengths of *N*-cyanoguanidine as compared to the data of the individual tautomers obtained from quantum chemical calculations [21].

The molecules form layers which are parallel to the *a*,*b* plane and are separated by a distance of $c/2 =$ 3.381 Å (Figs. 4 and 5). Although this spacing is in the typical range of contact distances of neighboring conjugated π systems – for example, adjacent layers in the crystal lattice of graphite are separated by 3.354 Å [26] – there is no close π contact between adjacent layers due to the ABAB sequence of layers. A comparison of the crystal structure of **2** and of triaminoguanidinium chloride (**1**, X = Cl) is interesting: the latter also crystallizes in space group $P6_3/m$ and forms a layered crystal structure. In contrast to **2**, however, the planar cations (C_{3h} symmetry) are stacked directly over one another with a spacing of only 3.109(1) Å between adjacent layers [22].

In summary, we have reported the first solid-state structure of an *N*,*N*′,*N*″-triaminoguanidine-derived trishydrazone. Due to positional disorder in the crystal, the planar molecules of **2** build up hexagonal crystals, which contain an ABAB… sequence of layers separated by a van der Waals distance of 3.381 Å. The temperature- and solvent-dependent ^{1}H NMR spectra of **2** are likely related to a prototropic tautomerism resulting in an equilibrium of three identical molecular structures. When the exchange between the three structures is fast on the NMR time scale, a spectrum corresponding to a time-averaged C_3-symmetrical structure is obtained.

Experimental Section

For general instrumentation, see ref. [1].

*N,N′,N″-Tris(propan-2-iminyl)guanidine (**2**)*

A solution of *N*,*N*′,*N*″-triaminoguanidinium chloride (**1**, X = Cl; 5.00 g) in acetone (100 mL) was stirred at room temperature for four days. The solvent was evaporated and the solid residue was dissolved in aqueous NaOH (1 M, 15 mL). The solution was extracted with ethyl acetate (5 × 15 mL), the combined organic extracts were washed with a small volume of water and dried ($MgSO_4$). After filtration and evaporation of the solvent, a bright orange solid was obtained which was triturated with diethyl ether to leave the product as a colorless solid, m. p. 154 °C (4.16 g, 52% yield). – IR (KBr): ν = 3366 (m), 3344 (m), 2982 (m), 2910 (m), 2847 (m), 1639 (s), 1527 (s), 1433 (s), 1359 (s), 1328 (s), 1268 (m), 1255 (m), 1243 (s), 1141 (m), 1097 (s), 1046 (s), 842 (m), 693 (s) cm^{-1}. – ^{1}H NMR: see Table 1. – ^{13}C NMR (100.62 MHz, [D$_6$]DMSO, T = 298 K): δ = 24.95 (CH_3), 99.58 (N= $C(CH_3)_2$), 150.18 ($(NH)_2C$=N) ppm. – $C_{10}H_{20}N_6$ (224.17): calcd. C 53.55, H 8.99, N 37.47; found C 53.52, H 8.86, N 37.58.

X-Ray structure determination

Needle-shaped single crystals were obtained by slow evaporation of a solution of **2** in acetone. Data collection was performed with an Oxford Diffraction diffractometer (SuperNova, Dual Source, Atlas CCD). Software for structure solution and refinement: CrysAlis PRO [27], SHELXS/L-97 [28, 29]; molecule plots: ORTEP-3 [30, 31] and MERCURY [32]. In the refinement procedure, the hydrogen atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density, with d(C–H) = 0.98 Å and U(H) set to 1.5 U_{eq}(C). The NH hydrogen atom was placed in a calculated position with d(N–H) = 0.88 Å and U(H) set to 1.2 U_{eq}(N); the occupancy factor was fixed at 0.667 to account for the disorder of two hydrogen atoms over three symmetry-equivalent positions. Further details are provided in Table 2.

CCDC 909637 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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