Stable hemiaminals containing a triazole ring†

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Reactions between 4-amino-1,2,4-triazole and nitro-substituted benzaldehydes in acetonitrile under neutral conditions afford stable hemiaminals, seven of which have been structurally and spectroscopically characterized. Two Schiff bases have also been obtained after the addition of hydrochloric acid to the reaction mixture. We describe a correlation between the conformation and configuration of the hemiaminals, and conclude that the formation of these species is determined by the substituents on the phenyl ring, as well as by the presence of 4-amino-1,2,4-triazole.

Introduction

It is well known that the formation of Schiff bases from primary amines and aldehydes involves an unstable intermediate with a tetrahedral carbon atom—a hemiaminal (also known as carbinolamine).[1] As a short-lived species, these intermediates are typically observed only by spectroscopic methods at low temperatures.[2–5] To trap the hemiaminal intermediates, Rebek *et al.*[6,7] used a deep molecular cavitand. On the basis of NMR measurements, the chemical half-lives of these compounds were determined to vary from 30 min to over 100 h at ambient temperature. On the other hand, Kawamichi *et al.*[8] trapped a hemiaminal intermediate in a porous coordination network and determined its crystal structure. Dolotko *et al.*[5] observed the hemiaminal form as a short lived species in a solvent-free reaction between *o*-vanillin and *p*-toluidine. Previously, the first stable hemiaminal product was isolated as single crystals from the condensation reaction of di-2-pyridyl ketone with 4-cyclohexyl-3-thiosemicarbazide.[9]

All the above-mentioned investigations have dealt with open-chain hemiaminals. However, cyclic hemiaminals are also known, for example, the naturally occurring echinocandins have a reactive hemiaminal function due to the ornithine-5-hydroxyl group, which is responsible for its instability.[10] Moreover, some cyclic *N*-acyl hemiaminals,[11] as well as cyclic hemiaminals in a rhodium complex, have been reported.[12] Hemiaminals, in which the nitrogen atom is a part of an aromatic ring have also been observed, as in pyrrole carbinols.[13]

The above-mentioned procedures are very sophisticated; therefore, the original aim of our study was the syntheses as well as the spectroscopic and single crystal X-ray diffraction studies of new stable hemiaminals synthesised in the simplest manner (in an aprotic solvent without the addition of acid and with appropriate substrates). Crystals (**1**, **2**, **3**, **4**, **5**, **6** and **7**, Fig. 1) of seven stable hemiaminals were obtained in the reaction of 4-amino-1,2,4-triazole with respective nitro-substituted benzaldehydes [2-nitrobenzaldehyde (**1**), 3-nitrobenzaldehyde (**2**), 4-nitrobenzaldehyde (**3**), 2,4-dinitrobenzaldehyde (**4**), 2-chloro-6-nitrobenzaldehyde (**5**) and 4-chloro-3-nitrobenzaldehyde (two polymorphic forms: **6** and **7**)] in a 1 : 1 molar ratio from an acetonitrile solution.

All of the new organic compounds obtained were characterized by elemental analysis, ESI-MS, IR spectroscopy,

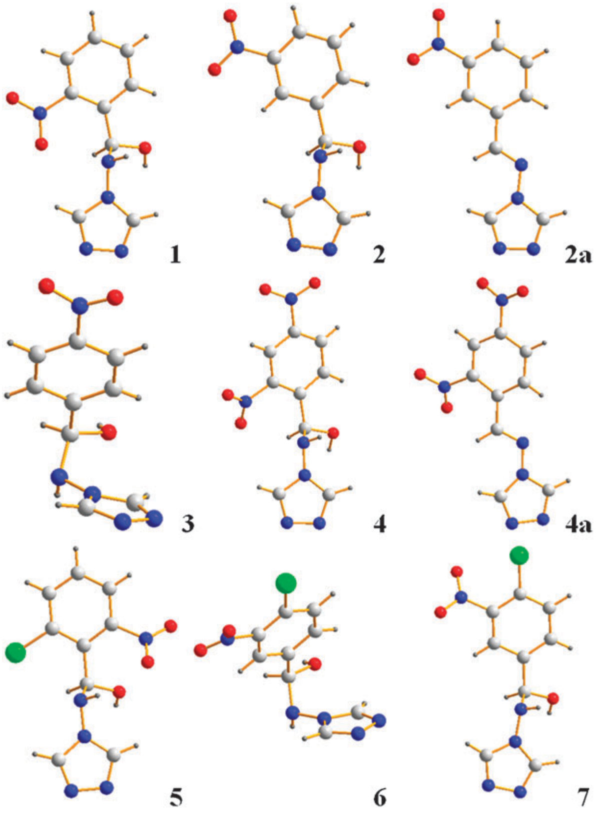

Fig. 1 Molecular structures of stable hemiaminals **1–7**, and Schiff bases **2a** and **4a**.

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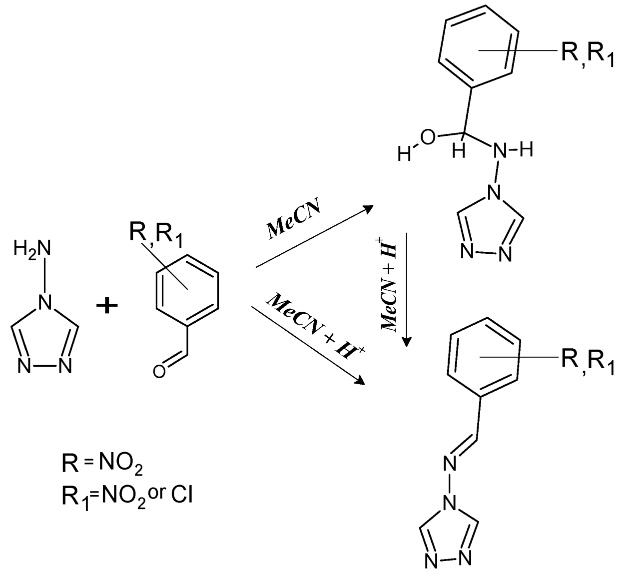


Scheme 1 General reaction scheme of hemiaminal and imine formation.

^{13}C NMR spectroscopy, ^{1}H NMR spectroscopy and X-ray single crystal analysis.

A general procedure for the syntheses of hemiaminals and Schiff bases is shown in Scheme 1.

Results

General remarks

Recently, we have studied the reaction between 4-amino-1,2,4-triazole and X-substituted benzaldehydes in ethanolic solution under neutral conditions.[14–16] For X = Cl, Br, OH, CH_3 and OCH_3, the appropriate Schiff bases were usually obtained. In the case of X = NO_2, a hemiaminal was unexpectedly detected as the sole product, albeit in a low yield. However, the yield increased considerably when the reaction was performed in an acetonitrile solution. The reaction mixture was typically stirred for 30 min at room temperature. The hemiaminals were obtained as single crystals directly from the mother liquor. To investigate the role of acidic conditions on the reaction outcome, a few drops of hydrochloric acid were added to the reaction mixture of a triazole and 3-nitrobenzaldehyde or 2,4-dinitrobenzaldehyde. This resulted in the formation of the appropriate Schiff base **2a** and **4a** (Fig. 1), respectively. A similar reaction has been already performed by Kitaev *et al.*[17]

Structure description

The molecular structures of compounds **1–7**, as well as **2a** and **4a**, consist of phenyl and triazole rings directly linked through the C1–C14–N4–N3 chain of atoms (Fig. 2). In the hemiaminals, the N4 and C14 atoms have sp^3 hybridization and both exhibit stereogenic centers. Meanwhile, in the Schiff bases, the N4 and C14 atoms are double-bonded. The respective bond lengths are presented in Table 1.

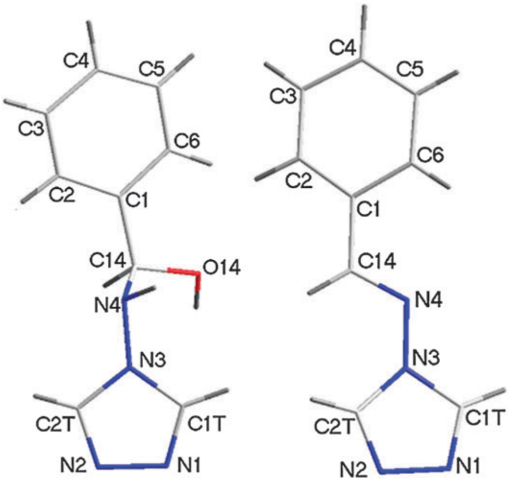


Fig. 2 General numbering scheme for the hemiaminals and Schiff bases.

Table 1 Selected bond lengths for hemiaminals **1–7**, and Schiff bases **2a** and **4a**

Compound	N4–C14	N4–N3	C14–C1	C14–O14
1	1.469(2)	1.412(2)	1.525(2)	1.408(2)
2	1.478(2)	1.416(2)	1.517(2)	1.400(2)
3	1.467(2)	1.411(2)	1.515(2)	1.406(2)
4	1.487(2)	1.412(2)	1.520(2)	1.401(2)
5				
Molecule A	1.479(5)	1.412(4)	1.525(5)	1.404(5)
Molecule B	1.472(5)	1.417(4)	1.529(5)	1.405(5)
6	1.468(2)	1.412(2)	1.513(2)	1.408(2)
7	1.474(2)	1.416(2)	1.514(2)	1.401(2)
2a	1.265(2)	1.392(2)	1.462(2)	—
4a				
Molecule A	1.258(2)	1.383(2)	1.469(3)	—
Molecule B	1.267(2)	1.398(2)	1.465(3)	—

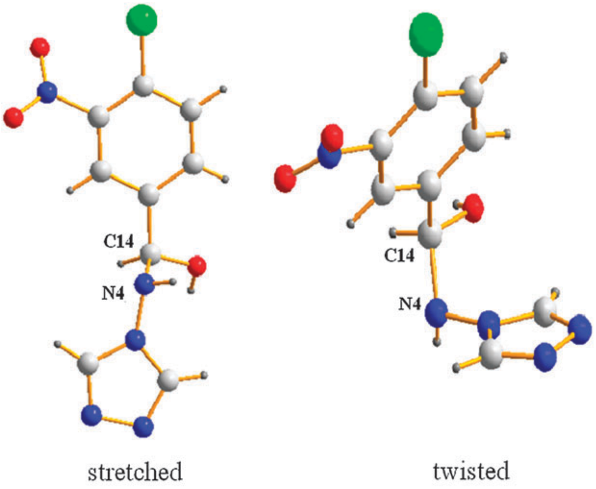


Fig. 3 Twisted (**6**) and stretched (**7**) conformations, as well as the numbering system used for the hemiaminals.

In the crystal structures of the title hemiaminals, two molecular conformations—stretched and twisted—are observed (Fig. 3). These conformations are determined by the N3–N4–C14–C1 torsion angle (Table 2). For the stretched molecule, this chain of atoms is antiperiplanar (ap) and both rings are almost parallel. For twisted molecules, this chain

Table 2 Selected torsion angles for hemiaminals **1–7**, and Schiff bases **2a** and **4a**

Compound	N3–N4–C14–C1	N3–N4–C14–O14
1	167.9(2)	−72.8(2)
2	164.1(2)	−73.7(2)
3	−64.3(2)	60.1(2)
4	174.0(2)	−65.4(2)
5		
Molecule A	−176.8(3)	−54.0(5)
Molecule B	−177.6(3)	−55.6(5)
6	−60.5(2)	63.0(2)
7	168.2(2)	−70.9(2)
2a	178.7(2)	—
4a		
Molecule A	177.2(2)	—
Molecule B	174.0(2)	—

is synclinal (sc) with both rings nearly perpendicular to each other.

Among the seven crystal structures of the hemiaminals presented here, the twisted conformation was observed in only two cases, **3** and **6**. Moreover, for the hemiaminal synthesised in a reaction of 4-amino-1,2,4-triazole and 4-chloro-3-nitrobenzaldehyde, two polymorphic forms—**6** and **7**, with both possible conformations—were found. This suggests that, while both conformations can be isolated, the stretched conformation is more common than the twisted one.

As mentioned above, the hemiaminals studied here have two stereogenic centers, at the N4 and C14 atoms, but only two of the four possible enantiomers are observed for each conformer. In the case of the stretched ones, only the *RS* and *SR* exist in solid state, while only the *RR* and *SS* enantiomers are observed for the twisted ones.

The crystal packing of the hemiaminals is determined by a variety of intermolecular interactions, such as strong O–H···$\mathrm{N_{triazole}}$, N–H···$\mathrm{N_{triazole}}$ and N–H···O hydrogen bonds, weak C–H···O and, in a few crystals, stacking interactions, all with typical lengths and angles. Among these interactions, the rather short and almost linear O–H···$\mathrm{N_{triazole}}$ hydrogen bond (with a H···N distance in the range of 1.79–1.99 Å) dominates in all crystals. In **1**, **2**, **5** and **7**, the connected molecules form infinite chains (Fig. 4). Only in **4** does this interaction connect two molecules into a dimer (Fig. 5).

In crystals of hemiaminals **1**, **2**, **5** and **7** with a stretched conformation, the O–H···N hydrogen bond links opposite enantiomers into infinite chains (*RS*–*SR*–*RS*...). Additionally, the parallel chains (except **1**) interact with each other by phenyl ring stacking. Such connected molecules form a 2D network of zipper-like structure. The geometric parameters of the stacking rings agree well with those observed by Janiak.[18] All chains in **1**, **2**, **5** and **7** are oriented along the shortest lattice vector in their crystals.

In crystals of hemiaminals **3** and **6** with a twisted conformation, the O–H···N hydrogen bond links the same enantiomers to form infinite parallel chains (Fig. 6) of molecules (*SS*–*SS*–*SS*... and *RR*–*RR*–*RR*...). Two such chains of opposite chirality interact with each other by phenyl ring stacking, forming single columns of zipper-like structure. These non-bonding interactions link molecules along one of the two shortest lattice vectors.

In **4**, the O–H···N hydrogen bonds connect two molecules with the same configuration into dimers (*SR*–*SR* and *RS*–*RS*).

All chains of molecules (in **1**, **2**, **3**, **5**, **6** and **7**) as well as dimers (in **4**) are linked into a 3D network *via* N–H···N/O hydrogen bonds and C–H···O/N weak interactions.

In both Schiff bases (**2a** and **4a**), C–H···N and C–H···O interactions are observed. These interactions join molecules into 2D sheets. Stacking interactions are present between these sheets (Fig. 7).

Discussion

Hemiaminals can be obtained in a reaction of a primary amine and an aldehyde, usually as a short-lived species. Recently, highly sophisticated methods, like trapping the intermediate product in a cavitand,[6,7] a solvent-free reaction in the solid state[5] and stabilization of these hemiaminals at low temperature in porous crystals have been used to identify such products.[7] The stabilization of the hemiaminal form can be attributed to the intramolecular O–H···N hydrogen bond.[9]

The title hemiaminals were obtained at room temperature, similar to the Schiff base formation reaction. Stable products were isolated by slow crystallization. Finally, single crystal X-ray analyses showed the presence of intermolecular hydrogen bonds and the lack of intramolecular interactions that could stabilize molecules. The parallel orientation of the column axes and the shortest lattice vectors suggest that the O–H···N intermolecular hydrogen bond does not stabilize the hemiaminal form but rather is a key factor in controlling crystal growth. We conclude that the presence of both nitro group(s) in the phenyl ring and the 1,2,4-triazole ring determine the stabilization of the hemiaminals under study. To verify this, the reaction of 2,4-dinitrobenzaldehyde and aniline was performed, but only the appropriate Schiff base was synthesized.[19] It is well known that nitro groups are strongly deactivating substituents in electrophilic aromatic substitution reactions. Also, the electron-withdrawing substituents decrease the electrophilicity of the carbonyl carbon atom.[20] Furthermore, Sayer and Jencks[21] have shown that the equilibrium constants for hemiaminal formation increase with the number of the electron-withdrawing substituents on the benzaldehyde. Our results confirm this conclusion and additionally show that the presence of the electron-rich 1,2,4-triazole ring increases the stability of intermediates.

All the hemiaminals under study have two stereogenic centers because the C14 and N4 atoms have sp^3 hybridization and four different substituents; the fourth substituent on N4 is a lone electron pair. Geometrical analysis of both stereogenic centers in all hemiaminals shows that this lone pair and a hydroxyl group have an ap orientation. We have found an analogous correlation in the geometrical analysis of the hemiaminal obtained by Kurup *et al.*[9] The main reason for this observation lies in the repulsive stereoelectronic effect. This phenomenon is similar to the anomeric effect[22] known for compounds with a C–X–C–Y structural fragment, where X = N, O or S, and Y = F, Cl, Br, O, N or S, but we did not observe a shortening of the C–X (in our hemiaminals' N4–C14) or an elongation of C–Y (in our hemiaminals'

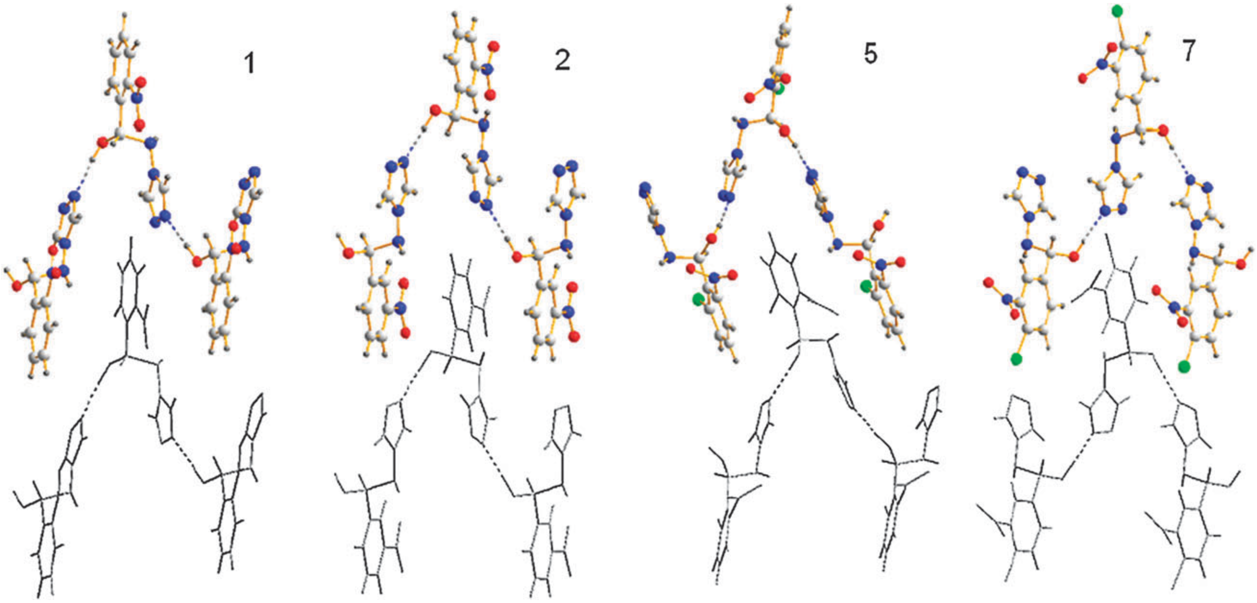


Fig. 4 The O–H···N hydrogen bonds in stretched hemiaminals that determine the packing motif of the crystal structures of compounds **1**, **2**, **5** and **7**, connecting the molecules into zipper-like chains. Dashed lines indicate hydrogen bonds.

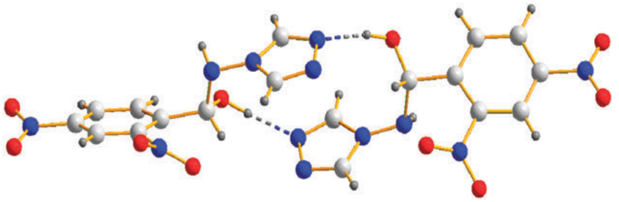


Fig. 5 Dimer formation in the crystal packing of **4** through O–H···N hydrogen bonds.

C14–O14) bond, which are typical for an anomeric effect. This observation should be correlated with the conformation and configuration of hemiaminals, in which stretched conformers have an *RS* or *SR* configuration, while the twisted ones have an *RR* or *SS* configuration.

Transformation of a stretched molecule into a twisted one (Scheme 2) may be realized in the course of two low energetic processes:[23] rotation about the C–N single bond and inversion of configuration on the N atom. During the possible rotation about the C14–N4 bond (Fig. 8a), the lone electron pair on the N4 atom approaches the hydroxyl group (Fig. 8b) but the repulsion between them causes an inversion of configuration on the nitrogen atom (Fig. 8c). The rotation and inversion, both being low-energetic processes, must be highly conjugated in order to cause the observed stereoelectronic effect.

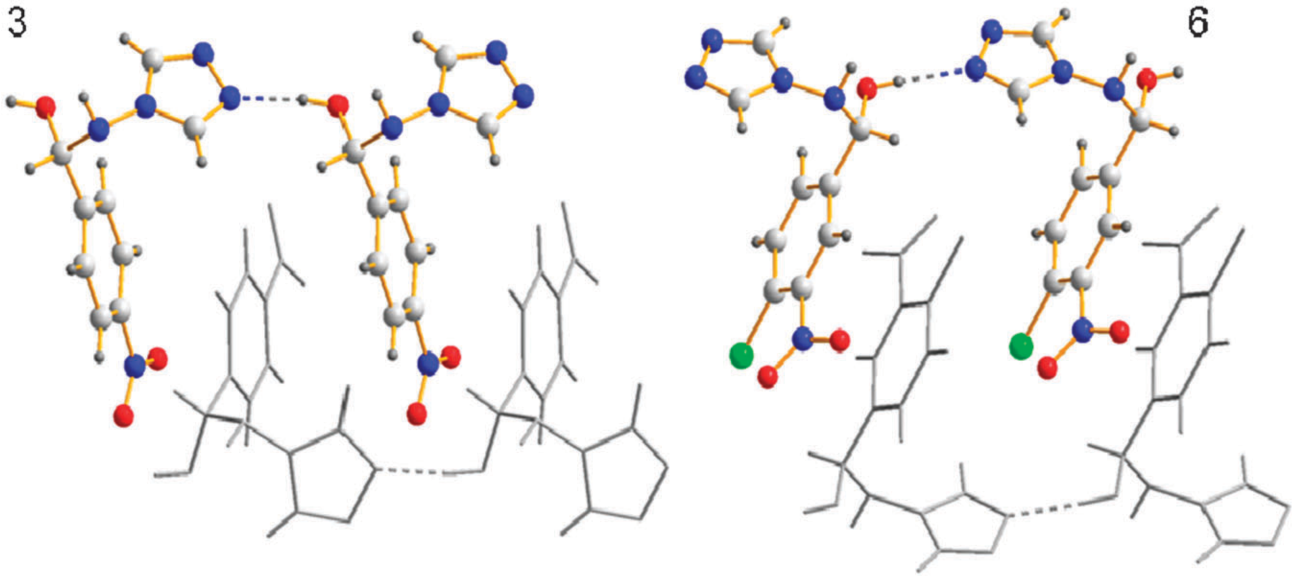


Fig. 6 Illustration of the O–H···N hydrogen bonds in twisted hemiaminals **3** and **6**, connecting aromatic rings into zipper-like chains.

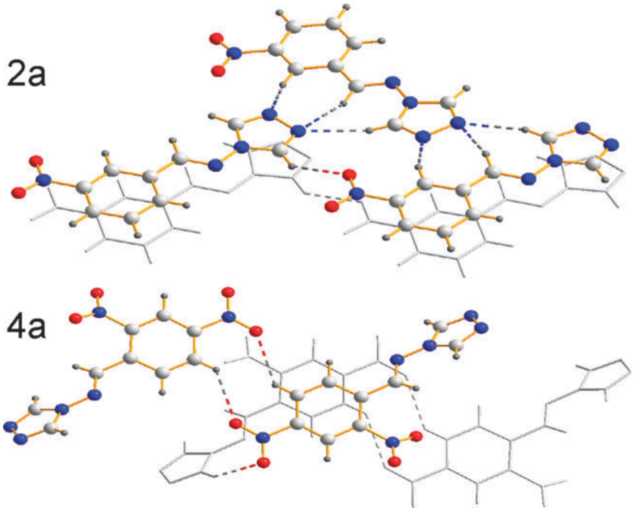
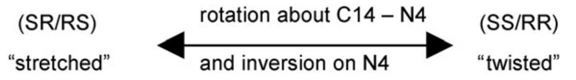


Fig. 7 Intermolecular C–H···O/N and stacking interactions between molecules of Schiff bases of **2a** and **4a**.



Scheme 2 Configurational and conformational changes resulting from the inversion of configuration on nitrogen atom N4.

Conclusion

We have developed a new, general method for the efficient preparation of stable hemiaminals *via* the reaction of nitro-substituted benzaldehydes with 4-amino-1,2,4,-triazole. The reaction mechanism can be considered as a multi-step process with hemiaminal formation, protonation of a hydroxyl group, dehydration and imine formation. It is well known that acidic conditions influence the final product as much as the choice of substrate does. Therefore, we used neutral solvent reaction conditions and connected 4-amino-1,2,4-triazole with benzaldehyde derivatives containing electron-withdrawing substituents that decrease the electrophilicity of the carbonyl carbon atom.

The crystal structures of the presented hemiaminals have two stereogenic centers on both the C14 carbon atom and N4 nitrogen atom. The lone electron pair on the N4 nitrogen atom and the hydroxyl group on the C14 carbon atom have an ap orientation due to a repulsive stereoelectronic effect (similar to an anomeric effect). Moreover, we have correlated this observation with both the configuration and conformation of the hemiaminals.

In summary, the subtle connection of nitrobenzaldehyde derivatives with 4-amino-1,2,4-triazole gave a new simple route to stable hemiaminals with two chiral centers, and with highly correlated conformations and configurations.

Experimental

Materials and physical measurements

All reactions were performed using commercially available reagents. All solvents were purchased from either POCh or Aldrich and were used without further purification. NMR spectra were recorded on a Bruker-500 spectrometer. Infrared spectra were recorded using KBr pellets on a Bruker IFS66 FT-IR spectrometer. Elemental analyses were carried out at the microanalytical laboratory of the University of Wrocław.

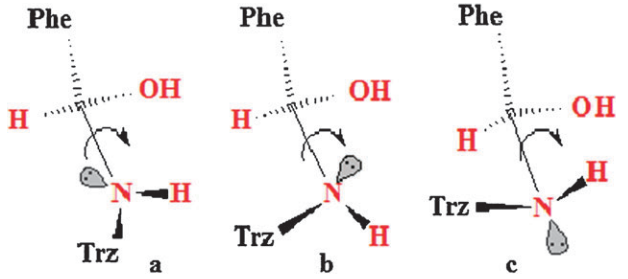


Fig. 8 Possible rotation about C14–N4 *vs.* configuration inversion on nitrogen atom N4.

X-Ray crystallography

Single crystal X-ray diffraction data were collected on a Kuma KM4CCD[24] κ-axis diffractometer with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å)[24] at 100 K (**1–7**), 230 K (**2a**) and 295 K (**4a**) using an Oxford Cryosystem adapter.[25] Data collection: CrysAlis CCD;[26] data reduction: CrysAlis RED; program used to solve the structures: SHELXS97;[27] program used to refine the structures: SHELXL97;[27] software used to prepare material for publication: SHELXL97; molecular graphics software: DIAMOND.[28]

Syntheses

General procedure for syntheses of hemiaminals

A mixture of an appropriate nitrobenzaldehyde and 4-amino-1,2,4-triazole (molar ratio 1 : 1) in acetonitrile or ethanol was stirred at r.t. for 30 min. The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether and then dried in air.

General procedure for syntheses of Schiff bases

A mixture of the appropriate nitrobenzaldehyde and 4-amino-1,2,4-triazole (molar ratio 1 : 1) and 3 drops of hydrochloric acid in ethanol was stirred at r.t. for 4 h. The crystals were filtered off, washed with a small amount of ethanol and diethyl ether, and then dried in air.

(2-Nitrophenyl)(4*H*-1,2,4-triazole-4-ylamino)methanol (1)

Upon standing of the reaction mixture for 3 h at room temperature, yellow crystals of (2-nitrophenyl)(4*H*-1,2,4-triazol-4-ylamino)methanol were deposited (0.89 g, 76%), mp 123–124 °C. Calculated: C 45.96, H 3.82, N 29.78%; found: C 46.13, H 3.60, N 30.06%. MS: (*m*/*z*) 236.1 $[M]^+$. ^{1}H NMR (500 MHz, DMSO): δ 8.25 (s, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 4.6 Hz, 1H), 6.05–5.93 (m, 1H). ^{13}C NMR (125 MHz, DMSO): δ 79.4, 124.1, 128.0, 129.7, 132.8, 133.0, 143.4, 148.3. IR (KBr, cm^{-1}): 3445sh, 3194sh, 3089sh, 2996m, 2850m, 1557m, 1515vs, 1441w, 1338vs, 1254w, 1191s, 1067vs, 1039vs, 980m, 953w, 879m, 860s, 788s, 717vs, 639vs.

Crystal data: M = 235.21, crystal system: monoclinic, space group: $P2_1/c$, a = 11.591(4), b = 10.437(4), c = 8.892(3) Å, β = 105.27(2)°, V = 1037.7(6) Å^3, Z = 4, crystal size: 0.23 × 0.15 × 0.12 mm, ρ_c = 1.506 g cm^{-3}, μ = 0.117 mm, θ_{max} = 30.00°, reflections: 13472, independent: 2995, R_{int} = 0.0976, R_1 = 0.0689, wR_2 = 0.1450, GoF = 1.188.

(3-Nitrophenyl)(4*H*-1,2,4-triazole-4-ylamino)methanol (2)

Upon standing of the reaction mixture for 2 d at room temperature, yellow crystal plates of (3-nitrophenyl)(4*H*-1,2,4-triazol-4-lamino)methanol were deposited (0.91 g, 78%), mp 141–143 °C. Calculated: C 45.96, H 3.82, N 29.78%; found: C 45.86, H 3.78, N 29.91%. MS: (*m*/*z*) 236.1 [M]$^+$. ^{1}H NMR (500 MHz, DMSO) δ 8.43 (s, 2H), 8.34 (s, 1H), 8.20 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.48 (d, J = 6.7 Hz, 1H), 6.92 (s, 1H), 5.67 (d, J = 6.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 82.5, 121.4, 123.0, 129.7, 133.4, 142.2, 143.9, 147.6. IR (KBr, cm^{-1}): 3429sh, 3206sh, 3117sh, 2937sh, 2856sh, 2736sh, 1582w, 1520vs, 1481m, 1423w, 1353vs, 1309m, 1202m, 1096m, 1070vs, 1056vs, 979m, 953m, 927m, 882s, 759m, 729s, 674s, 636sh, 587sh.

Crystal data: M = 235.21, crystal system: monoclinic, space group: $P2_1/c$, a = 12.316(4), b = 10.616(3), c = 7.863(3) Å, β = 92.39(3)°, V = 1027.2(6) Å^3, Z = 4, crystal size: 0.20 × 0.13 × 0.12 mm, ρ_c = 1.521 g cm^{-3}, μ = 0.119 mm, θ_{max} = 30.00°, reflections: 15102, independent: 2988, R_{int} = 0.0527, R_1 = 0.0482, wR_2 = 0.1232, GoF = 1.099.

(*N*-(3-Nitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (2a)

Upon standing of the reaction mixture for 2 weeks at room temperature, colorless crystals (needles) of (*N*-(3-nitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) were deposited (0.35 g, 54%), mp 240–241 °C. Calculated: C 49.76, H 3.23, N 32.26%; found: C 49.58, H 3.15, N 32.25%. MS: (*m*/*z*) 218.1 [M]$^+$. ^{1}H NMR (500 MHz, DMSO) δ 9.32 (s, 1H), 9.28 (d, J = 0.4 Hz, 2H), 8.64 (s, 1H), 8.43 (dd, J = 8.2, 2.2 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 122.5, 126.4, 130.9, 133.8, 134.1, 139.0, 148.2, 156.0. IR (KBr, cm^{-1}): 3440sh, 3139m, 3085sh, 3058sh, 1611m, 1578w, 1524vs, 1470m, 1360vs, 1330m, 1287m, 1219m, 1168s, 1110w, 1081w, 1061vs, 978m, 929w, 870w, 848m, 807m, 736s, 679s, 621s, 596m.

Crystal data: M = 217.20, crystal system: monoclinic, space group: $P2_1/c$, a = 3.870(2), b = 10.917(4), c = 23.019(7) Å, β = 94.18(3)°, V = 969.7(7) Å^3, Z = 4, crystal size: 0.59 × 0.13 × 0.09 mm, ρ_c = 1.487 g cm^{-3}, μ = 0.112 mm, θ_{max} = 28.77°, reflections: 8490, independent: 2367, R_{int} = 0.0296, R_1 = 0.0422, wR_2 = 0.1053, GoF = 0.966.

(4-Nitrophenyl)(4*H*-1,2,4-triazole-4-ylamino)methanol (3)

Upon standing of the reaction mixture for 4 d at room temperature, yellow crystals (needles) of (4-nitrophenyl)-(4*H*-1,2,4-triazol-4-lamino)methanol were deposited (0.81 g, 69%), mp 145–147 °C. Calculated: C 45.96, H 3.82, N 29.78%; found: C 46.28, H 3.50, N 30.02%. MS: (*m*/*z*) 236.1 [M]$^+$. ^{1}H NMR (500 MHz, DMSO) δ 8.41 (s, 2H), 8.24 (m, J = 8.7 Hz, 2H), 7.76 (m, J = 8.8 Hz, 2H), 7.48 (d, J = 6.6 Hz, 1H), 6.90 (d, J = 5.4 Hz, 1H), 5.65 (t, J = 6.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 82.6, 123.2, 128.0, 143.9, 147.15, 147.24. IR (KBr, cm^{-1}): 3423sh, 3166sh, 3089sh, 2983sh, 2858sh, 2769sh, 1607m, 1569m, 1515vs, 1417w, 1349vs, 1291m, 1214w, 1199w, 1168m, 1107m, 1070s, 1050vs, 990m, 949s, 856vs, 755s, 739s, 688s, 630vs.

Crystal data: M = 235.21, crystal system: monoclinic, space group: Cc, a = 6.948(2), b = 20.546(6), c = 7.362(2) Å, β = 93.56(3)°, V = 1048.9(7) Å^3, Z = 4, crystal size: 0.38 × 0.23 × 0.12 mm, ρ_c = 1.489 g cm^{-3}, μ = 0.116 mm, θ_{max} = 31.99°, reflections: 6722, independent: 1791, R_{int} = 0.0210, R_1 = 0.0328, wR_2 = 0.0870, GoF = 1.057.

(2,4-Dinitrophenyl)(4*H*-1,2,4-triazole-4-amino)methanol (4)

Upon standing of the reaction mixture for 2 h at room temperature, yellow crystals of (2,4-dinitrophenyl)(4*H*-1,2,4-triazol-4-ylamino)methanol were deposited (1.17 g, 84%), mp 122–123 °C. Calculated: C 38.57, H 2.85, N 30.00%; found: C 38.93, H 2.66, N 30.12%. MS: (*m*/*z*) 281.1 [M]$^+$. ^{1}H NMR (500 MHz, DMSO) δ 8.73 (d, J = 2.3 Hz, 1H), 8.54 (dd, J = 8.6, 2.3 Hz, 1H), 8.27 (s, 2H), 8.04 (d, J = 8.6 Hz, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.39 (d, J = 5.5 Hz, 1H), 6.12–6.01 (m, 1H). ^{13}C NMR (125 MHz, DMSO): δ 79.1, 119.7, 127.1, 129.9, 139.3, 143.4, 147.5, 148.1. IR (KBr, cm^{-1}): 3432sh, 3299sh, 3120sh, 2888sh, 2755sh, 1607s, 1532vs, 1496s, 1348vs, 1253w, 1189s, 1148m, 1078s, 1056vs, 978m, 908w, 803m, 716s, 632s, 569m.

Crystal data: M = 280.21, crystal system: orthorhombic, space group: $Pccn$, a = 14.202(4), b = 14.267(4), c = 11.223(3) Å, V = 2274(1) Å^3, Z = 8, crystal size: 0.22 × 0.15 × 0.11 mm, ρ_c = 1.637, μ = 0.137 g cm^{-3}, θ_{max} = 29.50°, reflections: 26651, independent: 3151, R_{int} = 0.0548, R_1 = 0.0481, wR_2 = 0.1141, GoF = 1.161.

(*N*-(2,4-Dinitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (4a)

The title compound crystallized directly from the solution to afford (*N*-(2,4-dinitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (0.47 g, 60%), mp 182–184 °C. Upon standing of reaction mixture for 2 weeks at the room temperature, colorless crystals (needles) were deposited. Calculated: C 41.22, H 2.29, N 32.06%; found: C 41.24, H 2.15, N 32.04%. MS: (*m*/*z*) 263.1 [M]$^+$. ^{1}H NMR (500 MHz, DMSO) δ 9.42 (s, 1H), 9.26 (s, 2H), 8.87 (d, J = 2.3 Hz, 1H), 8.70 (dd, J = 8.6, 2.3 Hz, 1H), 8.30 (d, J = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 120.4, 128.3, 131.1, 131.8, 139.1, 148.5, 148.8, 152.4. IR (KBr, cm^{-1}): 3446sh, 3098sh, 3038sh, 1611m, 1593m, 1529vs, 1459s, 1344vs, 1219w, 1208w, 1197w, 1170m, 1157m, 1050s, 920m, 855m, 832m, 771m, 740m, 711m, 676w, 614m, 515w.

Crystal data: M = 262.20, crystal system: monoclinic, space group: $P2_1/c$, a = 16.286(5), b = 7.007(2), c = 19.746(6) Å, β = 91.24(3)°, V = 2253(1) Å^3, Z = 8, crystal size: 0.19 × 0.13 × 0.10 mm, ρ_c = 1.546 g cm^{-3}, μ = 0.126 mm, θ_{max} = 28.75°, reflections: 31807, independent: 5577, R_{int} = 0.0578, R_1 = 0.0488, wR_2 = 0.1308, GoF = 0.952.

(2-Chloro-6-nitrophenyl)(4*H*-1,2,4–triazole–4-amino) methanol (5)

Upon standing of the reaction mixture for 3 d at room temperature, yellow crystals (plates) of (2-chloro-6-nitrophenyl)-(4*H*-1,2,4-triazole-4-ylamino)methanol were deposited (0.93 g, 69%), mp 148–150 °C. Calculated: C 40.08, H 2.96, N 25.98%; found: C 40.39, H 2.83, N 26.19%. MS: (m/z) 270.0 $[M]^+$. ^{1}H NMR (500 MHz, DMSO) δ 8.28 (s, 2H), 8.03 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 2.3 Hz, 1H), 7.72 (dd, J = 8.6, 2.4 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.24 (d, J = 5.5 Hz, 1H), 6.07–5.91 (m, 1H). ^{13}C NMR (125 MHz, DMSO): δ 82.0, 122.7, 130.0, 130.8, 132.9, 133.6, 143.7, 150.6. IR (KBr, cm^{-1}): 3429sh, 3316sh, 3140sh, 3107sh, 2890sh, 2760sh, 1594w, 1530vs, 1442m, 1369s, 1295w, 1272w, 1215w, 1192m, 1087m, 1056s, 979m, 908w, 873m, 802m, 765m, 722m, 631s, 583w, 474w.

Crystal data: M = 269.65, crystal system: monoclinic, space group: $P2_1/c$, a = 12.882(4), b = 8.440(3), c = 21.129(7) Å, β = 100.04(3)°, V = 2262(1) Å^3, Z = 8, crystal size: 0.18 × 0.12 × 0.10 mm, ρ_c = 1.584 g cm^{-3}, μ = 0.347 mm, θ_{max} = 30.00°, reflections: 25378, independent: 6273, R_{int} = 0.1096, R_1 = 0.0789, wR_2 = 0.1660, GoF = 1.103.

(4-Chloro-3-nitrophenyl)(4*H*-1,2,4-triazole-4-ylamino) methanol (6 and 7)

Upon standing of the reaction mixture for 2 weeks at room temperature, yellow crystals (needles) of (4-chloro-3-nitrophenyl)(4*H*-1,2,4-triazole-4-ylamino)methanol were deposited (0.85 g, 63%), mp 133–134 °C. Calculated: C 40.08, H 2.96, N 25.98%; found: C 40.14, H 2.88, N 26.06%. MS: (m/z) 270.0 $[M]^+$. ^{1}H NMR (500 MHz, DMSO) δ 8.44 (s, 2H), 8.13 (s, 1H), 7.80 (s, 2H), 7.49 (d, J = 6.6 Hz, 1H), 6.98 (d, J = 5.5 Hz, 1H), 5.63 (t, J = 6.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 81.9, 123.7, 124.5, 131.4, 132.1, 141.0, 143.8, 147.1. IR (KBr, cm^{-1}): 3141sh, 3085sh, 2979sh, 2868sh, 1693w, 1606m, 1528vs, 1476m, 1449w, 1393m, 1346vs, 1321s, 1285m, 1204w, 1177w, 1124w, 1066vs, 986m, 946s, 893m, 860s, 822m, 754m, 671m, 923vs, 555m.

Crystal data **6**: M = 269.65, crystal system: monoclinic, space group: $P2_1/n$, a = 7.143(2), b = 21.329(6), c = 7.429(2) Å, β = 94.31(3)°, V = 1128.6(5) Å^3, Z = 4, crystal size: 0.24 × 0.14 × 0.12 mm, ρ_c = 1.587 g cm^{-3}, μ = 0.348 mm, θ_{max} = 28.64°, reflections: 7678, independent: 2699, R_{int} = 0.0195, R_1 = 0.0350, wR_2 = 0.0954, GoF = 1.103.

Crystal data **7**: M = 269.65, crystal system: monoclinic, space group: $P2_1/c$, a = 12.386(4), b = 10.764(3), c = 8.407(3) Å, β = 93.08(2)°, V = 1119.2(6) Å^3, Z = 4, crystal size: 0.20 × 0.15 × 0.10 mm, ρ_c = 1.600 g cm^{-3}, μ = 0.351 mm, θ_{max} = 25.06°, reflections: 11195, independent: 1985, R_{int} = 0.0259, R_1 = 0.0286, wR_2 = 0.0755, GoF = 1.052.

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