Reinvestigation of the Thiazole Synthesis with Ethyl 3-Amino-2-[5-aryl-1,3,4-oxadiazol-2(3H)-ylidene]-3-thioxopropanoates and Related Reactions

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Dedicated with great appreciation to Professor Gerhard Maas on the occasion of his 60\textsuperscript{th} birthday

Treatment of the 1,3,4-oxadiazoles 3\textsubscript{a} and 3\textsubscript{b} with 3-chloropentane-2,4-dione gave the thiazoles 4\textsubscript{a} and 4\textsubscript{b}, respectively, which were methylated to furnish compounds 5\textsubscript{a} and 5\textsubscript{b}. The formation of 1,3,4-oxadiazoles using the 1,3-dithietane 1 as starting material, and the consecutive reactions mentioned above were transferred into sugar chemistry to provide the corresponding derivatives 6 – 9 in good yields. The reaction of 5\textsubscript{a} with benzyl amine, ethylene diamine and \textit{o}-phenylene diamine afforded compounds 10, 11, and 12, respectively, which possess better stabilized push-pull systems than 5\textsubscript{a}. The structures of 3\textsubscript{a}, 4\textsubscript{a}, 5\textsubscript{a}, 10, 11, and 12 were compared with the previously proposed structures I – VI, respectively. The structures of compounds 1, 3\textsubscript{b}, and 11 were confirmed by X-ray diffraction studies.

Key words: Diethyl (1,3-Dithietane-2,4-diyldiene)bis(2-cyanoacetate), Push-pull Chemistry, Hydrogen Sulfide Migration, Consecutive Ring Closure Reaction, Structural Reinvestigation

Introduction

In previous papers published in the 1970ies we reported the smooth reaction of (2\textit{E},2\textit{E})-diethyl 2,2\textsuperscript{′}-(1,3-dithietane-2,4-diyldene)bis(2-cyanoacetate) (I) (Fig. 1) with carboxylic acid hydrazides (2\textsubscript{a}, 2\textsubscript{b}) [1]. The state-of-the-art NMR and IR technique at that time gave only limited data which, for example, suggested the proposed structure I (Fig. 2) for the product of the reaction of I with benzohydrazide. In 1995, Neidlein \textit{et al.} repeated this type of reaction, and their X-ray structure analysis has shown that instead of the dihydropyrazole I the oxadiazole 3\textsubscript{a} was formed (Scheme 1), obviously by an unusual migration of hydrogen sulfide to the cyano group [2]. It is noteworthy that during the reaction no smell of hydrogen sulfide was observed.

The alleged dihydropyrazole I had been subjected to several secondary reactions, and it was feared now that the structures proposed for the resulting compounds II – VI are not correct. Therefore, we decided to repeat the formerly described reactions [3], and to reinvestigate the structures of these compounds. Furthermore, we report the extension of the 1,3-dithietane chemistry by using a sugar hydrazide instead of an aromatic hydrazide.

Fig. 1. Molecular structure of I in the crystal (ORTEP plot; displacement ellipsoids at the 50\% probability level; H atoms with arbitrary radii).
Results and Discussion

In a typical experiment the 1,3,4-oxadiazoles 3a and 3b were furnished by the reaction of 1,3-dithietane 1 with the aromatic hydrazides 2a and 2b, respectively [1].

The reaction was conducted in ethanol-chloroform solution at 60 °C, and after 30 min at r. t. the crystalline products were isolated. Analytical samples were obtained by crystallization from chloroform or ethanol. The constitution of the 1,3,4-oxadiazole 3b was confirmed by X-ray diffraction studies (Fig. 3), and all the other analytical data of 3a and 3b confirmed the structural discussion of Neidlein et al. [2].

Now, it was interesting to examine the reaction of 3a and 3b with 3-chloropentane-2,4-dione as a 1,2-dielectrophile. As previously shown [4], the reaction under basic conditions gave a mixture of two products which were converted into the products 4a and 4b, respectively, by heating under reflux with acetic anhydride for 15 min (Scheme 2). On the basis of the structure of 3a and 3b, the previously described structure II can be discarded, as the ring closure of the thiocarbamoyl group obviously gave a 4-methylthiazolyl moiety as a structural element. Comparing both structural propos-

Scheme 1. Synthesis of the ethyl 3-amino-2-(5-aryl-1,3,4-oxadiazol-2-yl)-3-thioxopropanoates 3a and 3b. Reagents and conditions: (i) CHCl3-EtOH, 60 °C, 30 min.

Fig. 2. Previously published, alleged structures of compounds 3a, 4a, 5a, 10, 11, and 12.

Fig. 3. Molecular structure of 3b in the crystal (ORTEP plot; displacement ellipsoids at the 50 % probability level; H atoms with arbitrary radii). There are two intramolecular hydrogen bonds in the structure. While the NH2 group at C1 has one H oriented towards O3 with a distance of 261.25(18) pm between N3 and O3, the distance between N2 and S1 is 288.99(12) pm.

of 3a and 3b, the previously described structure II can be discarded, as the ring closure of the thiocarbamoyl group obviously gave a 4-methylthiazolyl moiety as a structural element. Comparing both structural propos-
Scheme 2. Synthesis of the thiazole derivatives 4a and 4b by ring closure of compounds 3a and 3b, respectively, with 3-chloropentane-2,4-dione, and consecutive methylation. Reagents and conditions: (i) NaOEt, 20 °C, 2 h; (ii) (AcO)2O, reflux, 15 min; (iii) ethereal CH2N2, CHCl3, 20 °C, 10 min.

als II and 3a, a remarkable similarity of all the functional groups is obvious.

The tautomeric structures of 3a and 3b discussed by Neidlein et al. [2] indicated the acidity of the proton predominantly located at 3-position of the oxadiazol ring. The ring closure to the thiazoles 4a and 4b should not have a strong influence on this tautomerism. This is demonstrated by the fact that in the 1H NMR spectra of 4a and 4b a broad signal of an N-H proton appeared in the range of δ = 13.20. Consequently, the reaction of 4a and 4b with an ethereal diazomethane solution provided the 3-methyl-oxadiazols 5a and 5b, respectively, in excellent yield (80 – 90 %). Again, the differences of functionalities between both structural proposals, III and 5a, are small.

The protocol of the formation of 1,2,4-oxadiazoles by reaction of 1,3-dithietane 1 with aromatic hydrazides was now transferred to sugar hydrazides. For this reason, methyl 1,2,3,4-di-O-isopropylidene-α-D-galactopyranuronate [5] was treated with 85 % aq. hydrazine hydrate in EtOH, and the mixture was then heated under reflux for 2 h to provide the as yet unknown hydrazide 6 in nearly quantitative yield.

Scheme 3. Transfer of the reaction protocol described in Schemes 1 and 2 to the sugar hydrazide 6. Reagents and conditions: (i) CHCl3-EtOH, reflux, 10 min; (ii) NaOEt, 20 °C, 2 h; (iii) (AcO)2O, reflux, 15 min; (iv) ethereal CH2N2, CHCl3, 20 °C, 10 min.

Fortunately, β-elimination which is a typical side-reaction of galacturonates under alkaline conditions was not observed. As expected, short heating under reflux of a solution of compounds 1 and 6 in chloroform gave the 1,3,4-oxadiazole 7 in 75 % yield. Under conditions described for the formation of the thiazoles 4a, 4b and 5a, 5b, the corresponding arabinoyl derivatives 8 and 9 were obtained in 73 % and 89 % yield, respectively (Scheme 3). Unfortunately, all attempts failed to get crystals of the two compounds for X-ray diffraction studies.

To examine the previously reported reaction of alleged compound III with primary amines [3], compound 5a was heated under reflux with benzylamine in EtOH for 1 h. Instead of the originally discussed seven-membered ring IV we now proposed the formation of the 1,2,4-triazole 10 as the product of this reaction. It was found by 1H and 13C NMR investigations that neither the ester group nor the keto function of 5a was attacked by the amine. Obviously, the oxygen atom of the 1,3,4-oxadiazole was replaced by a nitrogen atom providing the triazolylidene fragment which appears to lend improved stabilization to the push-pull system.
Scheme 4. Reactions of thiazole 5a with N-nucleophiles. Reagents and conditions: (i) benzyl amine, EtOH, reflux, 1 h; (ii) 50 % aq. ethylene diamine, EtOH, reflux, 10 min; (iii) phenylene diamine, EtOH, reflux, 5 h.

in compound 10 as compared to the oxadiazolylidene fragment in 5a.

Finally, repetition of the reaction of 5a with ethylene diamine and o-phenylene diamine afforded the crystalline imidazolidinylidenes 11 and 12 in 76 % and 58 % yield, respectively (Scheme 4). Again, the driving force of the reaction is the formation of a more stabilized push-pull system in 11 and 12 than in the starting material set up by ring closure of the vicinally constituted binucleophiles. However, the postulation of structures V and VI as a result of this reaction required a reductive N–N cleavage of the hydrazide fragment in compound III which is not very plausible [3]. On the other hand, V and VI are tautomeric structures of 11 and 12, respectively. The X-ray structure analysis of compound 11 (Fig. 4) confirms the generation of the imidazolidin-2-ylidene and methylthiazolyl moieties instead of an imidazolyl and a thiazolin-2-ylidene residue in the alleged structure V.

Conclusion

The reaction of 1,3-dithietane 1 with benzohydrazide led to the 1,3,4-oxadiazole 3a instead of the previously proposed pyrazoline I. The formation of 1,3,4-oxadiazoles described first by Neidlein et al. was confirmed by X-ray diffraction studies of compound 3b. Subsequent reaction of 3a with 3-chloropentane-2,4-dione afforded compound 4a, in contrast to the earlier proposed structure II. Methylation of 4a furnished 5a instead of structure III. The reactions summarized here were successfully applied with the sugar hydrazide 6, which itself was prepared for the first time, to afford the corresponding sugar derivatives 7–9.

Finally, the nucleophilic attack of 5a by benzylamine, ethylene diamine and o-phenylene diamine gave the stabilized push-pull structures 10, 11, and 12, respectively, instead of the earlier postulated structures IV, V, and VI. Again, the structure of 11 was established by X-ray diffraction analysis.

Experimental Section

Melting points were determined with a Boetius microheating plate BHMK 05 (Rapido, Dresden) and are not corrected. Optical rotation was measured for solutions in a 2-cm cell with an automatic polarimeter GYROMAT (Dr. Kernchen Co.). $^1$H NMR spectra (250.13 MHz, 300.13 MHz, and 500.13 MHz) and $^{13}$C NMR spectra (62.89 MHz, 75.47 MHz, and 125.76 MHz) were recorded on Bruker instruments AC 250, ARX 300, and Avance 500, respectively,
with CDCl₃, CD₂OD or [D₆]DMSO as solvents. The calibration of spectra was carried out referring to solvent signals (CDCl₃: δ 1H = 7.25, δ 13C = 77.0; CD₂OD: δ 1H = 4.78, δ 13C = 49.0; [D₆]DMSO: δ 1H = 2.50, δ 13C = 39.7). δ 1H and 13C NMR signals were assigned by DEPT and two-dimensional 1H,13C COSY and 1H,13C correlation spectra (HMBC and HSQC). Mass spectra were recorded on an AMD 402/3 spectrometer (AMD Intectra GmbH). Elemental analyses were performed on a CHNS-Flash-EA-1112 instrument (Thermoquest).

All washing solutions were cooled to ~5 °C. The NaHCO₃ solution was saturated. Reactions were monitored up to the completion, indicated by a persisting yellow color of the solution, the reaction mixture was treated with acetic acid to destroy the excess of diazomethane. The solution was then diluted with the double volume of CHCl₃ and the organic layer washed with water, aq. NaHCO₃ (2 ×), and again water, dried, and concentrated. Crystallization from EtOH gave compounds 5a or 5b as yellow needles.

Ethyl 2-(5-acetyl-4-methylthiazol-2-yl)-2-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2(3H)-ylidene]acetate (4b)

Yield 2.89 g (72 %). – M. p. 203–205 °C (acetic acid). – 1H NMR (250.13 MHz, CDCl₃): δ = 1.47 (t, 3J = 7.0 Hz, 3 H, OCH₂CH₃), 2.46 (s, 3 H, COCH₃), 2.66 (s, 3 H, CH₃), 3.87 (s, 3 H, OCH₃), 4.39 (q, 2 H, OCH₂CH₃), 7.38, 7.97 (2 m, 4 H, C₆H₄), 13.20 (br, 1 H, NH). – 13C NMR (75.5 MHz, CDCl₃): δ = 15.1 (OCH₂CH₃), 15.4 (CH₃), 30.4 (COCH₃), 55.9 (OCH₃), 61.1 (OCH₂CH₃), 80.6 [O(NH)C=NC(2)], 114.9, 117.0, 120.8, 128.7 (NC=CS, C₆H₄, three signals are isochronic), 144.2 (NC=S), 162.2, 162.6 (O(NH)C=NC(2), O(N)=C-C₆H₅), 163.9, 166.1 (2 × C=O), 190.3 (C=S=N). – C₁⁹H₁₉N₃O₄S (404.44): calcd. C 56.85, H 4.77, N 10.47, S 7.99; found C 56.73, H 4.76, N 10.22, S 7.91.

Reaction of thiazoles 4a and 4b with diazomethane [3]

Thiazole 4a (3.71 g, 10 mmol) or 4b (4.01 g, 10 mmol) was dissolved in a minimum of chloroform and treated with an ethereal diazomethane solution. When the reaction was complete, indicated by a persisting yellow color of the solution, the reaction mixture was treated with acetic acid to destroy the excess of diazomethane. The solution was then diluted with the double volume of CHCl₃ and the organic layer washed with water, aq. NaHCO₃ (2 ×), and again water, dried, and concentrated. Crystallization from EtOH gave compounds 5a or 5b as yellow needles.
Hydrazine hydrate (85%, 0.77 g, 22 mmol) was added to a solution of methyl 1,2;3,4-di-O-isopropylidene-
α-D-galactopyranosuronate (2.88 g, 10 mmol) [4] dissolved in a minimum of EtOH with slight warming to give a clear reaction mixture. After heating under reflux for 2 h (monitored by TLC, solvent: ethylacetate 2:1) the solution was chilled to r.t. and diluted with chloroform. The organic layer was washed several times with water, dried and concentrated. Traces of hydrazine were removed by co-evaporation with toluene (5 mL) and concentrated. The residue was added to a warm solution of hydrazide (115 mg, 5 mmol) in CHCl3 to afford compound 6 (1.91 g, 95% yield) as a colorless foam.

Ethyl 3-amino-2-[5-(1,2,3,4-di-O-isopropylidene-β-D-arabinopyranosyl-5-yl)-1,3,4-oxadiazol-2(3H)-ylidene]thioxopyranonate (7)

A hot solution of diethyl 2,2'-[1,3-dithietane-2,4-diylidenebis(2-cyanoacetate) (1.55 g, 5.0 mmol) [7] in CHCl3 (5 mL) was added to a warm solution of hydrazide 6 (2.88 g, 10 mmol) in CHCl3 (10 mL). The reaction mixture was heated under reflux for 10 min, then chilled to r.t. and evaporated. The residue was crystallized from ethyl acetate to provide compound 7 (3.32 g, 75% yield) as colorless crystals.

Ethyl 2-[5-acetyl-4-methylthiazol-2-yl]-2-[5-(1,2,3,4-di-O-isopropylidene-β-D-arabinopyranosyl-5-yl)-1,3,4-oxadiazol-2(3H)-ylidene]acetate (8)

Sodium (115 mg, 5 mmol) and compound 7 (2.22 g, 5 mmol) were dissolved in abs. EtOH (15 mL), and to the reaction mixture 3-chloropentane-2,4-dione (0.67 g, 5 mmol) was added. After shaking it for 2 h at r.t., the reaction mixture was treated with acetic acid to destroy the excess of diazomethane solution. When the reaction was complete, indicated by a persisting yellow color of the solution, the reaction mixture was treated with an ethereal diazomethane solution. When the reaction was complete, indicated by a persisting yellow color of the solution, the reaction mixture was treated with acetic acid to destroy the excess of diazomethane. The solution was then diluted with the double methanol.
volume of CHCl₃, and the organic layer washed with water, aq. NaHCO₃ (2×), and again water, dried, and concentrated. The desired compound 9 (479 mg, 89%) was obtained analytically pure as a colorless foam.

[α]D²⁵ = −134.2 (c = 1.0, CHCl₃). – ¹H NMR (250.13 MHz, CDCl₃): δ = 1.34 (t, 3J = 7.0 Hz, 3 H OCH₂CH₃), 1.33, 1.36, 1.46, 1.55 (4 s, 12 H 2 × C(CH₃)₂), 2.47 (s, 3 H COCH₃), 2.62 (s, 3 H CH₂), 3.63 (s, 3 H NCH₃), 4.29 (q, 2 H OCH₂CH₃), 4.44 (m, 1 H 2-H), 4.56 (dd, 1 H 3J₁₂ = 7.6 Hz, 3-H), 4.75 (dd, 1 H 3J₂₅ = 1.8 Hz, 4-H), 5.06 (d, 1 H 5-H), 5.67 (d, 1 H 3J₁₂ = 4.9 Hz, H-1). – ¹³C NMR (125.8 MHz, CDCl₃): δ = 14.4 (OCH₂CH₃), 18.3 (CH₃), 24.4, 24.6, 25.7, 26.0 (2 × C(CH₃)₃), 29.6 (COCH₃), 30.7 (NCH₃), 60.0 (OCH₂CH₃), 64.4 (C-5), 70.4 (C-2), 70.5 (C-4), 71.2 (C-3), 74.5 [O(NH)C(C=C)], 96.5 (C-1), 109.5, 110.7 (2 × (C(CH₃)₂), 126.2 (NC=CS), 157.4 (NC=CS), 157.9, 164.0 (O(NH)C(C=C)), O(N=CC(Na)), 165.5, 166.0 (2 × O=C), 190.4 (C(S)=N). – C₂H₅₃N₂O₅S (537.58): calcld. C 53.62, H 5.81, N 7.82, S 5.96; found C 53.37, H 0.61, N 7.58, S 5.71.

Ethyl 2-(5-acetyl-4-methylthiazol-2-yl)-2-[imidazolidin-2-ylidene]acetate (10) [3]

Benzylamine (643 mg, 6 mmol) was added to a solution of compound 8a (1.16 g, 3 mmol) in EtOH (25 mL). The resulting reaction mixture was heated under reflux for 1 h, chilled to r.t., and evaporated. The residue was dissolved in chloroform (100 mL), and the organic layer was washed with water (50 mL), aq. NaHCO₃ (2 × 50 mL), and again water (50 mL), dried, and evaporated. The yellow residue was purified by column chromatography (chloroform : acetone = 1:1) to furnish compound 10 (1.21 g, 85%) as a syrup.

M. p. 89–91 °C (ethyl acetate–heptane). – ¹H NMR (250.13 MHz, CDCl₃): δ = 1.21 (m, 3 H OCH₂CH₃), 2.44 (s, 3 H CH₂), 2.60 (s, 3 H CH₃), 3.86 (s, 3 H NCH₃), 4.16 (m, 2 H OCH₂CH₃), 5.21 (dd, 2 H 2J = 18 Hz H₂C₂NC(C), 6.71, 7.12, 7.50 (3 m, 10 H H₂C₂NC(C), H₂C₂NC(C)). – ¹³C NMR (125.8 MHz, CDCl₃): δ = 15.1 (OCH₂CH₃), 18.6 (CH₃), 30.7 (COCH₃), 38.3 (NCH₃), 50.6 (H₂C₂NC(C), 58.7 (OCH₂CH₃), 124.1, 126.9, 128.2, 128.5, 128.9, 129.1, 131.5, 133.6 (O(NH)C(C≡C)), (NC=CS), 2 × C=O, six signals are isochronous). 153.0 (NC=CS), 155.0, 158.9 (N(NCH₃)C≡C(C), N≡CN=C.CH₃), 164.9, 168.9 (2 × O=C=O), 190.0 (C(S)=N). – C₂H₅₃N₂O₅S (574.75): calcld. C 59.46, H 4.99, N 12.24, S 9.34; found C 59.18, H 5.08, N 12.0, S 9.47.

Ethyl 2-(5-acetyl-4-methylthiazol-2-yl)-2-[imidazolidin-2-ylidene]acetate (11) [3]

Phenyldiamine (648 mg, 6 mmol) was added to a solution of compound 8a (1.16 g, 3 mmol) in EtOH (30 mL), and the resulting reaction mixture was heated under reflux for 5 h. After chilling the mixture to r.t., the crystals were filtered off and washed several times with cold EtOH. Product 12 (721 mg, 70%) was obtained as yellow needles.

M. p. 236–238 °C (acetone). – ¹H NMR (250.13 MHz, [D₆]DMSO): δ = 1.37 (t, 3J = 7.0 Hz, 3 H OCH₂CH₃), 2.45 (s, 3 H CH₂), 2.74 (s, 3 H CH₃), 4.39 (q, 2 H OCH₂CH₃), 7.27, 7.68 (2 m, 4 H C₈H₄), 13.00 (br, 2H, NH). – ¹³C NMR (75.5 MHz, [D₆]DMSO): δ = 15.0 (OCH₂CH₃), 18.4 (CH₃), 30.3 (COCH₃), 59.7 (OCH₂CH₃), 78.4 [NH(NH)C(C≡C)], 112.1, 123.0, 124.8, 130.3 (NC=CS, C₈H₄, three signals are isochronous). 150.0 [NH(NH)C(C≡C)], 155.9 (NC=CS), 165.9, 167.8 (2 × O=C=O), 189.9 (C(S)=N). – C₁₁H₁₃N₂O₅S (343.40): calcld. C 59.46, H 4.99, N 12.24, S 9.34; found C 59.18, H 5.08, N 12.0, S 9.47.

X-Ray structure determinations

Data collections were performed using an X8Apex diffractometer system with MoKα radiation and a CCD area detector. The structures were solved with Direct Methods and refined against F² (program system used: Bruker SHELXTL [8]).

Crystal structure data of 1: Crystal size: 0.025 × 0.21 × 0.6 mm³, triclinic crystal system, space group P1, a = 4.9450(2), b = 6.7471(3), c = 10.5470(5) Å, α = 82.926(3), β = 81.722(2), γ = 84.299(2), V = 344.38(3) Å³, Z = 1, T = 293 K, μ(MoKα) = 4.0 cm⁻¹, θ range for data collection 3.93–25.00°, index ranges (h k l) = ±5, ±8, ±12, 10317 measured reflections, 1201 independent reflections, Rint = 0.0301, GOF (F²) = 1.135, R1/wR1 [I ≥ 2σ(I)] = 0.0329/0.0871, R1/wR1 (all data) = 0.0376/0.0951, Δρmax
(max/min) = 0.0304/−0.0244 e Å⁻³. Remarks: All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into theoretical positions, and these positions were then refined with a riding model.

**Crystal structure data of 3b:** Crystal size: 0.10 × 0.12 × 0.35 mm³, triclinic crystal system, space group P1, a = 7.3134(3), b = 9.1288(4), c = 11.5577(4) Å, α = 85.551(2)°, β = 83.651(2)°, γ = 69.2677(2)°, V = 718.52(5) Å³, Z = 2, T = 173 K, µ(MoKα) = 2.48 cm⁻¹, θ range for data collection 2.91 – 25.00°, index ranges (h, k, l) = ±8, ±10, ±13, 22641 measured reflections, 2512 independent reflections, Rint = 0.0295, GOF (F²) = 1.086, R1/wR2 [I ≥ 2σ(I)] = 0.0345/0.0824, R1/wR2 (all data) = 0.0533/0.0912, Δρ_{fin} (max/min) = 0.197/−0.180 e Å⁻³. Remarks: All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at N2 and N3 were elucidated from a difference map, and their positions were refined freely. The other hydrogen atoms were put into theoretical positions, and these positions were then refined with a riding model.

**Crystal structure data of 11:** Crystal size: 0.04 × 0.12 × 0.58 mm³, monoclinic crystal system, space group P2₁/n, a = 10.1322(2), b = 7.3519(2), c = 19.1581(4) Å, β = 102.032(1)°, 3.45 – 27.50°, index ranges (h, k, l) = ±13, ±9, ±24, 27433 measured reflections, 3203 independent reflections, Rint = 0.0496, GOF (F²) = 1.022, R1/wR2 [I ≥ 2σ(I)] = 0.0345/0.0824, R1/wR2 (all data) = 0.0533/0.0912, Δρ_{fin} (max/min) = 0.283/−0.191 e Å⁻³. Remarks: All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at N2 and N3 were elucidated from a difference map, and their positions were refined freely. The other hydrogen atoms were put into theoretical positions, and these positions were then refined with a riding model.

CCDC 728522 (1), 728523 (3b), and 728524 (11) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.