Synthesis and Crystal Structures of New 1,4-Disubstituted 1,2,4-Triazoline-5-thiones

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Introduction of sulfur into the 5-position of 1,4-disubstituted quaternary 1,2,4-triazolium salts (**1**–**9**; Cl, Br, I, BF_4, PF_6, CH_3OSO_3 were used as anions) by two methods was investigated. The syntheses of nine 1,4-disubstituted 1,2,4-triazoline-5-thiones **10**–**18** are reported (**1**, **10**: $R^1 = CH_3$, $R^2 = CH_3$; **2**, **11**: $R^1 = NH_2$, $R^2 = CH_3$; **3**, **12**: $R^1 = NH_2$, $R^2 = CH(CH_3)_2$; **4**, **13**: $R^1 = N(CH_3)_2$, $R^2 = CH_3$; **5**, **14**: $R^1 = N(CH_3)_2$, $R^2 = CH(CH_3)_2$; **6**, **15**: $R^1 = CH_3$, $R^2 = NH_2$; **7**, **16**: $R^1 = OCH_2Ph$, $R^2 = CH_3$; **8**, **17**: $R^1 = OCH_2Ph$, $R^2 = CH_2CH_3$; **9**, **18**: $R^1 = CH_3$, $R^2 = CH_2Ph$). Compounds **11**–**17** represent 1-amino, 4-amino, 4-dimethylamino, and 4-benzyloxy-1,2,4-triazoline-5-thiones, whereas **10** served as a reference compound. Thione **18** was identified as an unexpected by-product in the synthesis of **16** and was also prepared independently. Thermolysis of **10** in air gave 1,4-dimethyl-1,2,4-triazolium hydrogensulfate. Crystal structures of eight 1,4-disubstituted 1,2,4-triazoline-5-thiones were determined by single-crystal X-ray diffraction. Intermolecular hydrogen bonds (C–H···S, C–H···N, N–H···N, N–H···S) were observed in the solid state. The solvent-dependent ^{1}H NMR chemical shifts of signals of **10** and **13** were satisfactorily correlated with the Kamlet-Abboud-Taft π^* and β parameters in ten solvents. From the lack of correlation with the α parameter and from the C=S bond length (average 1.67 Å) a significant contribution of a mesoionic imidazolium-2-thiolate resonance structure seems unlikely.

Key words: Crystal Structure, Desulfurization, Hydrogen Bond, Ionic Liquid, Thermolysis, Thione, Triazole

Introduction

Early examples of the title compounds have been prepared by cyclization of acyclic precursor molecules. Other substitution patterns have been obtained by rearrangement of other heterocycles or by cycloaddition. Thus, 1,4-dimethyl-1,2,4-triazoline-5-thione (**10**) [1] and 4-amino-1-methyl-1,2,4-triazoline-5-thione (**11**) [2] have been synthesized from 2,4-dimethylthiosemicarbazide and 2-methylthiocarbohydrazide, respectively, by condensation with formic acid. Although this synthetic route is facile and straightforward, it is of course limited by the availability of the respective hydrazines. In special cases, 2-hydrazino-1,3,4-thiadiazoles were found to rearrange in acid to 4-amino-1,2,4-triazoline-5-thiones [3], though the scope and limitations of this reaction are not clear because there is not much pertinent literature. More recently, cycloaddition of 1-aza-2-azoniaallenes and isothiocyanates has been reported to give substituted 1,2,4-triazoline-5-thiones [4].

In a more general approach, the thione group has been introduced by reaction of 1,4-disubstituted quaternary triazolium salts with elemental sulfur in pyridine [5, 6]. This method has been improved by addition of triethylamine and successfully employed for the synthesis of 4-amino-1-alkyl-1,2,4-triazoline-5-thiones [7] and 1-amino-4-benzyl-1,2,4-triazoline-5-thiones [8]. Another method, employing sulfur and K_2CO_3 in MeOH and frequently used for imidazoline-2-thiones [9 – 12], to our knowledge has not been applied in the triazole series so far. These thionation reactions have now been studied in more detail and are the topic of the present work. A third method, using sulfur and NaOAc in acetonitrile, is reportedly very slow [13] and was not attempted.

Typical reactions of these triazolinethiones include *S*-alkylation [14], oxidative desulfurization [5, 15, 16], and formation of metal complexes [17–20]. Charge-transfer complexes with halogens, which are common for imidazoline-2-thiones, are rare in the analogous triazole series [21]. Crystal structures of several 1,3,4-trisubstituted 1,2,4-triazoline-5-thiones, some of them with a 4-amino group [22–28], are known. However, the number of crystal structures of 1,4-disubstituted examples seems to be more limited [13, 29].

Continuing our interest in *N*-heterocyclic molecules with heteroatom substituents at the N atoms, preferably with small ones, we report the synthesis of six new, alternative syntheses of three known, as well as crystal structures of five new and three known 1,4-disubstituted 1,2,4-triazoline-5-thiones.

Results and Discussion

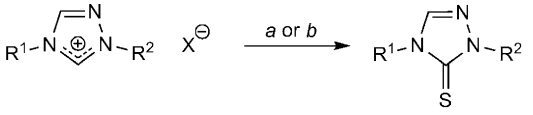
Some remarks on the synthesis of the quaternary salts and their precursors seem to be appropriate, since this chemistry is of high relevance for the contemporary field of ionic liquids (ILs). Contrary to the situation in related imidazoles, the 1- and 4-positions in 1,2,4-triazoles are not equivalent, giving rise to isomers, the concurrent presence of which can be responsible for spectacular melting point depressions of triazole-based ILs [30]. On the other hand, the enhanced nucleophilicity of position 1 in 1,2,4-triazoles allows direct quaternization of 4-amino-1,2,4-triazole which is not feasible with 1-aminoimidazole. The 4-amino group can actually be used as a protective group for the preparation of isomer-free 1-alkyl-1,2,4-triazoles [31] and ILs derived thereof [32]. Neutral 4-(dialkylamino)-1,2,4-triazoles are accessible by cyclization [33] and, more recently, a quaternary 4-(dimethylamino)-1,2,4-triazolium salt was obtained by exhaustive methylation of 4-amino-1,2,4-triazole under forceful conditions [34]. 4-Alkyl-1,2,4-triazoles in general are prepared by alkylation of 1-acetyl-1,2,4-triazole followed by removal of the acyl group. *N*-Benzyloxy-1,2,4-triazoline-5-thiones have not yet been described although the synthesis of *N*-benzyloxy-1,2,4-triazoles is known. In contrast to 1-benzyloxy-1,2,4-triazole, which can be prepared by oxidation of 1,2,4-triazole in low yield and subsequent benzylation [35], 4-benzyloxy-1,2,4-triazole can readily be obtained in satisfactory yield by a one-step cyclization reaction [36]. Starting from these inexpensive but pure precursors, the synthesis of quaternary salts was designed to avoid the generation of isomers. Introduction of two identical substituents at two nitrogen atoms of 1,2,4-triazole is of course straightforward. Thus, 1,4-dimethyl-1,2,4-triazolium methylsulfate (**1a**) was obtained in excellent yield by double methylation of 1,2,4-triazole. The iodide **1b** was preferably prepared from pure 4-methyl-1,2,4-triazole although it can also be reasonably synthesized from a crude *N*-methyl isomer mixture. Quaternary salts **2**–**5** were obtained by alkylation of 4-amino-1,2,4-triazole, whereas the new 1-amino-4-methyl-1,2,4-triazolium cation **6** (2,4-dinitrophenolate **6a** and, by ion metathesis, chloride **6b**) was synthesized by electrophilic amination of 4-methyl-1,2,4-triazole. Salts **7** and **8** were prepared by alkylation of 4-benzyloxy-1,2,4-triazole, and salt **9** by benzylation of 4-methyl-1,2,4-triazole. Four triazolium salts (**1a**, **1c**, **7** and **8**) are liquids at room temperature. We have recently reported NHC–metal complexes of **4** [34], and more carbenes may be expected from the new quaternary precursors, such as the sterically shielded 4-(dimethylamino)-1-isopropyl-1,2,4-triazolium salt **5**.

The behavior of quaternary salts and thiones also deserves some comment. In principle, both thionation methods (Scheme 1) worked for all substrates and gave comparable results for the thiones **13**, **15** and **18**. However, the "pyridine/Et_3N method" gave superior yields for thiones **12**, **14**, **16**, and **17**, and was advantageous for thionation of the hexafluorophosphates **4** and **5** and tetrafluoroborates **7** and **8** due to avoiding their insoluble alkali salts. The "MeOH/K_2CO_3 method" gave better results for thiones **10** and **11**. In all cases, NMR spectra indicated complete consumption of starting material after the reported reaction time (typically two hours at 70 °C, with few exceptions), but the work-up procedure had to be adjusted due to the different solubilities of the thiones and accompanying salts. Thus, the product could be either precipitated by addition of water or, after removal of the solvent, isolated by extraction of the crude residue with EtOAc or by partitioning the residue between an organic solvent and water. Subsequent purification could be achieved by either sublimation from the crude residue or recrystallization of the residue or extract. Although complete conversion was achieved in all cases, the isolation and purification steps limited the yields. Interestingly, the *N*-amino-1,2,4-triazolium salts **2**, **3** and **6b** are not as prone to deamination in MeOH as

the related *N*-aminoimidazolium salts [12]. Although a by-product was observed when the thionation of 4-amino-1-isopropyl-1,2,4-triazolium bromide (**3**) was attempted in MeOH at 70 °C, it was not identical with an authentic sample of the expected deamination product 1-isopropyl-1,2,4-triazole, and the reaction in pyridine yielded pure 4-amino-1-isopropyl-1,2,4-triazoline-5-thione (**12**). No deamination occurred when the thionation of **6b** to **15** was conducted in MeOH at ambient temperature. Thionation of the 4-benzyloxy-1-methyl-1,2,4-triazolium salt **7** to **16** in methanol gave an unexpected by-product, 1-benzyl-4-methyl-1,2,4-triazoline-5-thione (**18**), as suspected from ^{13}C NMR experiments and confirmed by X-ray crystal structure determination. This incident was not fully reproducible, the by-product showed up only twice (up to 15 mol percent by NMR) in five experiments. Again, the reaction in pyridine reproducibly gave pure **16**. Conversion of the analogous ethyl derivative **8** to thione **17** was therefore performed only using the 'pyridine/Et_3N method'. For the known thiones **10** and **11** an alternative synthesis is provided which avoids the preparation of the necessary semicarbazide or carbohydrazide. The new 4-amino-1-isopropyl-1,2,4-triazoline-5-thione (**12**), the 4-(dimethylamino) derivatives **13** and **14**, and 1-amino-4-methyl-1,2,4-triazoline-5-thione (**15**), an isomer of 4-amino-1-methyl-1,2,4-triazoline-5-thione (**11**), are small molecules which are valuable building blocks for further research. It is also noteworthy that the 4-benzyloxy-1,2,4-triazoline-5-thiones **16** and **17** are the first of their kind.

Thermal rearrangements (140 °C, 60 min) involving N→S alkyl shifts in related imidazoline-2-thiones have been reported previously [37]. Nothing of this kind was observed when compounds **13**, **14** and **18** were heated at 160 °C for one hour. Interestingly, thione **10** showed some initial reaction under these conditions. Consequently, when **10** was heated in an open test tube at 160 °C for 24 h, the 1,3-dimethyl-1,2,4-triazolium cation was fully regenerated, according to ^{1}H and ^{13}C NMR spectra. No reaction occurred when **10** was heated in an argon atmosphere. Obviously, the sulfur atom was oxidized [38] by air and subsequently hydrolyzed to the hydrogensulfate anion, as indicated by IR spectroscopy and classic ion identification (Scheme 1). This product was spectroscopically identical to authentic 1,3-dimethyl-1,2,4-triazolium hydrogensulfate (**1c**) independently prepared by ion metathesis. In contrast to the analogous imidazoline-2-thione [12], the *N*-benzyloxy compound **17** did not eliminate benzaldehyde at 130 °C, but at 160 °C complete conversion to a new product was observed, as indicated by the disappearance of the CH_2O signal in both ^{1}H and ^{13}C NMR spectra. This work is in progress, and the results are to be published separately.

(a)

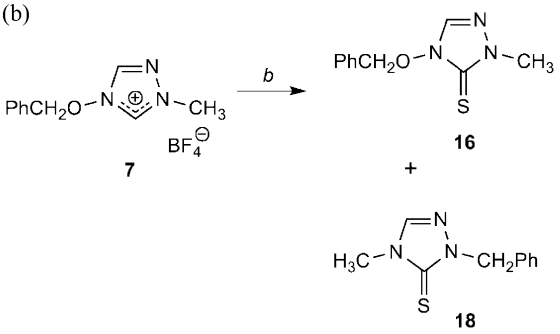


1–9 **10–18**

Salt	R^1	R^2	X	Thione	Yield, %/ method
1a	CH_3	CH_3	CH_3OSO_3	**10**	73/*b*
1b	CH_3	CH_3	I		
1c	CH_3	CH_3	HSO_4		
2	NH_2	CH_3	I	**11**	80/*b*
3	NH_2	$CH(CH_3)_2$	Br	**12**	90/*a*
4	$N(CH_3)_2$	CH_3	PF_6	**13**	72/*a*, 81/*b*
5	$N(CH_3)_2$	$CH(CH_3)_2$	PF_6	**14**	93/*a*
6a	CH_3	NH_2	DNP*		
6b	CH_3	NH_2	Cl	**15**	45/*a*, 58/*b*
7	OCH_2Ph	CH_3	BF_4	**16**	38/*a*
8	OCH_2Ph	CH_2CH_3	BF_4	**17**	40/*a*
9	CH_3	CH_2Ph	Br	**18**	77/*a*, 77/*b*

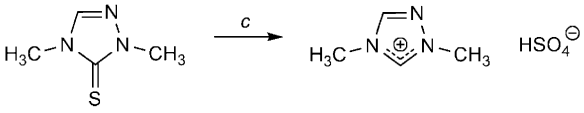
* DNP = 2,4-dinitrophenolate

(b)



7 **16** **18**

(c)



10 **1b**

Scheme 1. a) $^1/_8$ S_8, Et_3N/pyridine; b) $^1/_8$ S_8, K_2CO_3/MeOH; c) O_2/H_2O, 160 °C.

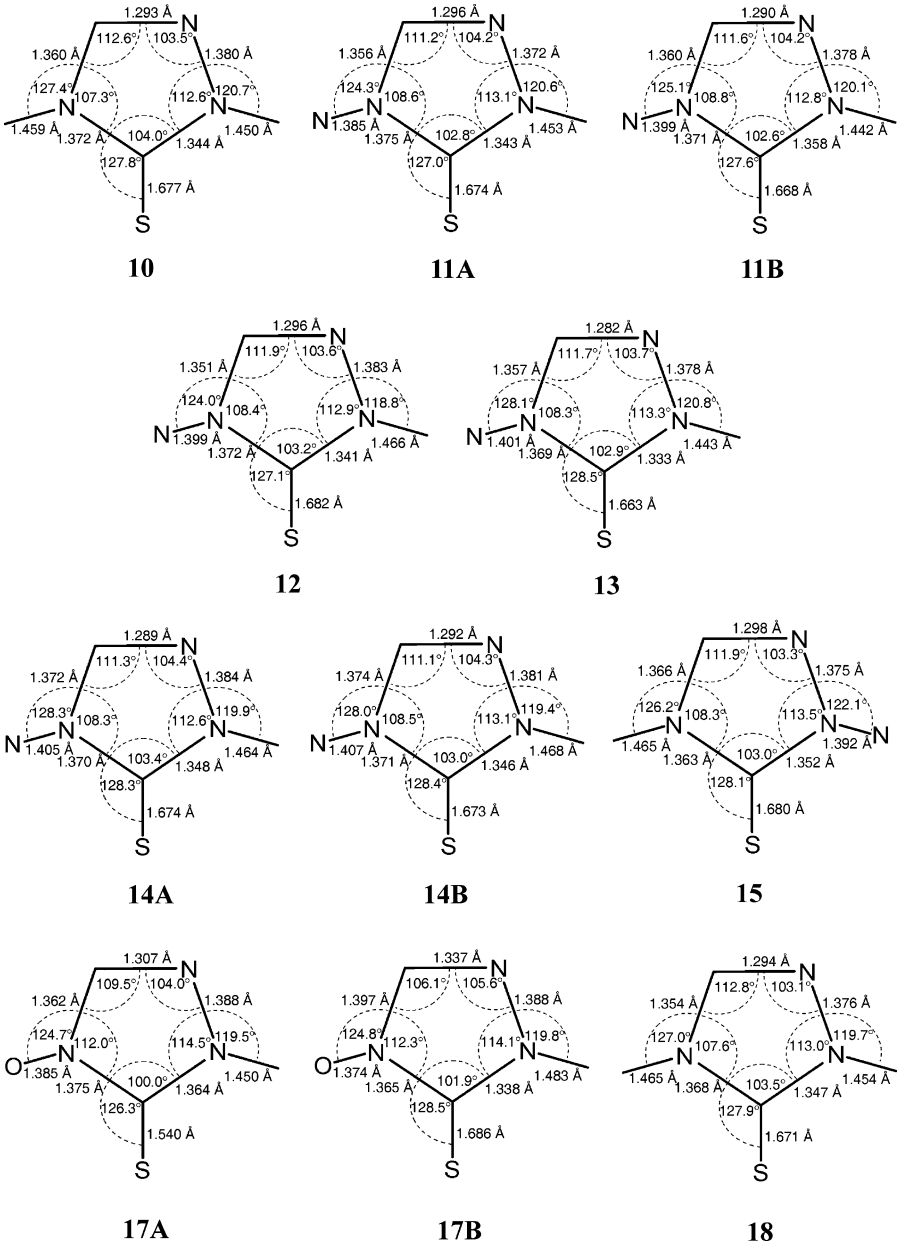


Fig. 1. Interatomic distances (Å) and angles (deg) in 1,4-disubstituted 1,2,4-triazoline-5-thiones.

Crystallography

The crystallographic data and refinement details are summarized in Table 1. In contrast to the related imidazole compounds [12], there is no correlation between ring angles and the type of substituents in the triazole series. Although the corresponding bond lengths and angles in the triazole rings of the title compounds are reasonably similar (Fig. 1), crystal packings and intermolecular interactions are quite different.

Table 1. Crystallographic data and structure refinement details.

Compound	**10**	**11**	**12**	**13**	**14**	**15**	**17**	**18**
Empirical formula	$C_4H_7N_3S$	$C_3H_6N_4S$	$C_5H_{10}N_4S$	$C_5H_{10}N_4S$	$C_7H_{14}N_4S$	$C_3H_6N_4S$	$C_{11}H_{13}N_3OS$	$C_{10}H_{11}N_3S$
Formula weight	129.19	130.18	158.23	158.23	186.28	130.18	235.30	205.28
Crystal system	orthorhombic	triclinic	monoclinic,	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$Pmc2_1$	$P2_1/n$
a, Å	7.3207(3)	6.7963(8)	15.9160(11)	8.0771(3)	10.6010(6)	6.3453(3)	6.7227(3)	6.5232(4)
b, Å	12.6164(5)	6.9191(7)	5.0455(3)	9.3679(3)	20.2949(10)	12.5969(7)	7.2922(3)	20.9157(10)
c, Å	13.5211(5)	12.8169(15)	10.2886(7)	10.4681(3)	10.8624(8)	6.9318(4)	24.0879(9)	7.6361(4)
α, deg	90	97.209(9)	90	90	90	90	90	90
β, deg	90	99.809(10)	106.700(7)	90	116.562(8)	94.845(5)	90	98.802(5)
γ, deg	90	103.898(9)	90	90	90	90	90	90
Volume, Å^3	1248.82 (8)	567.72(11)	791.37(9)	792.07(4)	2090.3(2)	552.09(5)	1180.87(8)	1029.58(10)
Z	8	4	4	4	8	4	4	4
$D_{calcd.}$, g/cm^3	1.37	1.52	1.33	1.33	1.18	1.57	1.32	1.32
Absorption coefficient, mm^{-1}	3.8	0.5	0.3	0.3	2.4	0.5	2.3	0.3
F(000), e	544	272	336	336	800	272	496	432
Crystal size, mm^3	$0.40 \times 0.08 \times 0.04$	$0.50 \times 0.04 \times 0.04$	$0.36 \times 0.20 \times 0.02$	$0.28 \times 0.24 \times 0.22$	$0.36 \times 0.12 \times 0.02$	$0.44 \times 0.36 \times 0.36$	$0.31 \times 0.25 \times 0.15$	$0.36 \times 0.36 \times 0.30$
Radiation	CuK_α	MoK_α	MoK_α	MoK_α	CuK_α	MoK_α	CuK_α	MoK_α
θ range for data collection	6.6–67.5	3.1–25.4	4.0–25.3	2.9–25.4	4.4–67.4	3.4–25.3	3.7–67.2	3.3–25.4
Index ranges	$-8 \le h \le 8$	$-7 \le h \le 8$	$-19 \le h \le 15$	$-8 \le h \le 9$	$-12 \le h \le 12$	$-7 \le h \le 6$	$-7 \le h \le 5$	$-7 \le h \le 6$
	$-12 \le k \le 15$	$-5 \le k \le 8$	$-5 \le k \le 6$	$-10 \le k \le 11$	$-24 \le k \le 22$	$-15 \le k \le 12$	$-8 \le k \le 8$	$-25 \le k \le 24$
	$-15 \le l \le 16$	$-15 \le l \le 14$	$-12 \le l \le 10$	$-12 \le l \le 12$	$-10 \le l \le 12$	$-7 \le l \le 8$	$-26 \le l \le 28$	$-7 \le l \le 9$
Reflections collected	11 596	3569	4680	4824	15 148	3260	5694	6214
Independent reflections/R_{int}	1125/0.050	2067/0.042	1443/0.045	1446/0.063	3715/0.041	1010/0.031	2086/0.051	1877/0.031
Reflections [$I > 2\,\sigma(I)$]	1030	1703	1169	1176	3192	900	2017	1614
Restraints/parameters	0/75	4/159	2/99	0/95	0/247	0/82	2/236	0/128
R_1/wR_2 indices [$I > 2\,\sigma(I)$]	0.031/0.033	0.052/0.122	0.045/0.095	0.036/0.080	0.035/0.086	0.030/0.075	0.050/0.101	0.035/0.084
R_1/wR_2 indices (all data)	0.085/0.086	0.066/0.135	0.061/0.101	0.048/0.083	0.042/0.092	0.035/0.081	0.051/0.101	0.043/0.089
Goodness-of-fit on F^2	1.05	1.09	1.06	0.95	1.04	1.09	1.15	1.05
$\Delta\rho_{max/min}$, e Å^{-3}	0.19/−0.33	0.63/−0.38	0.43/−0.22	0.21/−0.27	0.22/−0.30	0.24/−0.32	0.28/−0.34	0.32/−0.22
CCDC no.	977713	977714	977715	977716	977717	977718	977719	977720

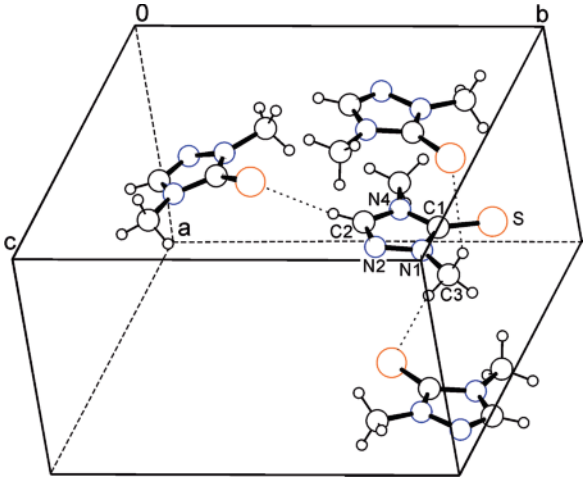


Fig. 2 (color online). Network of C–H···S contacts in the crystal structure of **10**.

A network of C–H···S contacts is found in thione **10** (Fig. 2). Columns of two independent molecules are formed in the direction of the *b* axis by N–H···S contacts in **11**. These columns are crosslinked by N–H···N hydrogen bonds (Fig. 3), similar to analogous imidazole compounds [12]. In thione **12** short N–H···N hydrogen bonds form chains in the direction of the *b* axis (Fig. 4). Weak C–H···S and C–H···N contacts are found in **13** (Fig. 5). Bifurcated C–H···S and C–H···N contacts are observed in thiones **14** (Fig. 6) and **15** (Fig. 7); in **15** there are also N–H···S hydrogen bonds present. Several attempts to solve the structure of **16** were made, but severe disorder in the crystals prohibited refinement, and only high *R* values were obtained. It was hoped that compound **17**, with an ethyl instead of a methyl group, would give better crystals. As it happens, in the asymmetric unit of **17** there are two independent 'half' molecules, which are disordered over a crystallographic mirror plane perpendicular to the *a* axis. Only the phenyl groups are ordered with C6, C9, C16, and C19 on the mirror plane and C7, C8, C17, and C18 above the plane. S_A, S_B and C2 are placed exactly on mirror planes with normal occupancies of 1.0. All other atoms of the disordered part are out of the plane with occupancies of 0.5. The disorder can be described by regular chains of molecules along the *a* axis with weak hydrogen bonds between C2–H···S_A and C12–H···S_B. Each of these chains can reverse its direction at other locations in the crystal. The disorder of the two independent molecules is shown in Fig. 8.

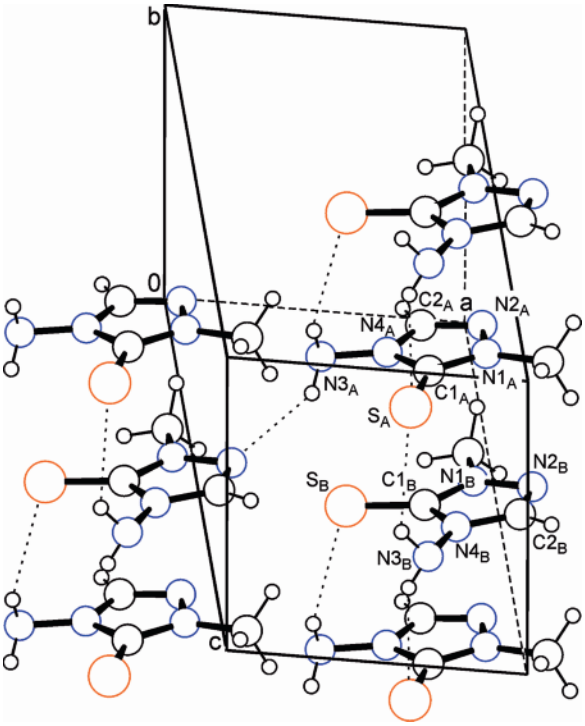


Fig. 3 (color online). Columns of two independent molecules formed by N–H···S interactions along *b* in the crystal structure of **11**.

In crystals of **18**, typical C–H···π interactions [39, 40] between the triazole and benzene rings are observed, linking the molecules in the direction of the crystallographic *c* axis (Fig. 9). The six $H_{triazole}\cdots C_{ar}$ distances range from 2.79 to 2.90 Å, and the distance between the triazole H atom and the plane of the aromatic ring was found to be 2.485 Å. The distance between the H atom and the ring centroid is 2.488 Å, and the C–H···centroid angle is 172°. Weak C–H···S contacts link the molecules into chains parallel to the *a* axis. The details of the C–H···S, C–H···N, N–H···S, N–H···N hydrogen bonds are summarized in Table 2.

The C=S bond lengths in seven of the thiones range from 1.66 to 1.68 Å in agreement with the accepted value of 1.68 Å in thioureas [41]. The C=S bond lengths in the two independent molecules of the *N*-benzyloxy derivative **17** are 1.540 and 1.686 Å, respectively, but this structure is severely disordered, and the measurements possibly do not represent typical values. In any case, there is no elongated C–S bond. The average value for compounds containing

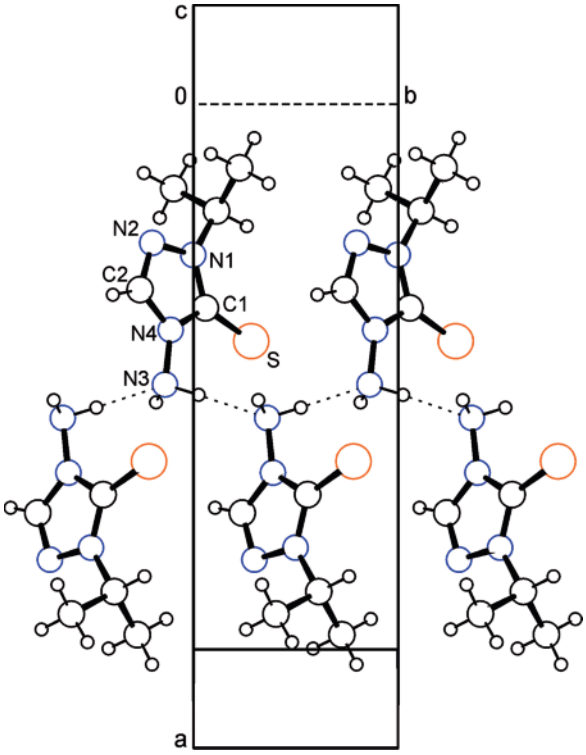


Fig. 4 (color online). Crystal structure of **12** showing a chain of N–H···N hydrogen bonds along *b*.

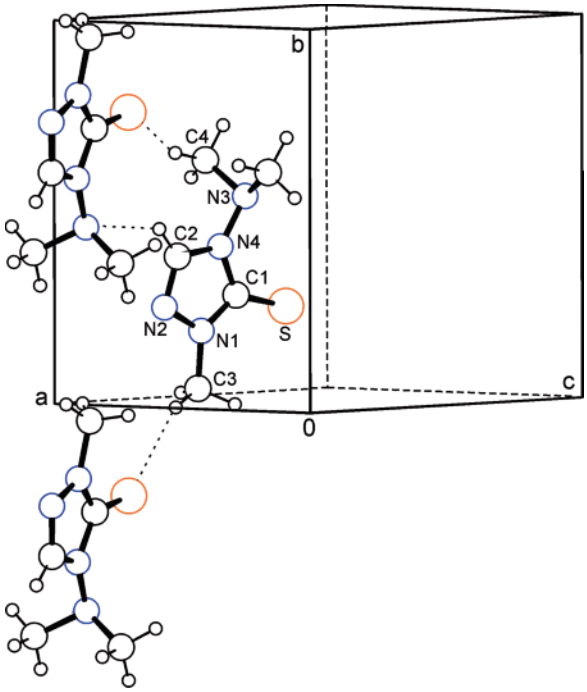


Fig. 5 (color online). Interactions in the crystal structure of **13**.

a propanethione fragment is 1.67 Å [12]. Thus, there is no evidence for a significant triazolium-5-thiolate resonance contribution (Scheme 2) in the solid state. Mesoionic structures of this type have also been postulated for imidazoline-2-thiones [42–45], but have recently been dismissed due to lack of evidence [12]. In 2,3-diphenyltetrazoline-5-thione, however, the increased C–S bond length of 1.70 Å [46] supports a mesoionic contribution.

^{1}H NMR spectroscopy

The ^{1}H NMR signals of the thiones are shifted upfield from those of the quaternary precursor salts by 0.4–0.9 ppm, which may be attributed to the loss of cationic character. It is noteworthy that ^{1}H NMR chemical shifts of the triazolinethiones depend quite significantly on the solvent (even more than in the imidazole series [12]). It seemed to be of interest to analyze this behavior in terms of the Kamlet–Abboud–Taft parameters [47] of solvent properties, *i. e.* (hydrogen bond donor) acidity α [48], (hydrogen bond acceptor) basicity β [49], and dipolarity/polarizability π^* [50, 51]. Thus, spectra of 1,4-dimethyl-1,2,4-triazoline-5-thione (**10**) and 4-(dimethylamino)-1-methyl-1,2,4-triazoline-5-thione (**13**) were recorded in ten common NMR solvents covering a wide range of these parameters. The parameters for non-deuterated solvents from a recent compilation [52] were applied to unravel the individual contributions of the terms in the linear solvation energy relationship (LSER) [47] by multiple regression analysis:

$$\delta(^1\mathrm{H}) = \delta_0 + s\pi^* + a\alpha + b\beta$$

From the data the following equations were derived (standard errors of δ_0, s, and b, correlation coefficient r, relative standard deviation σ of the correlation, and number N of data points given).

For **10**: $\delta(^1\mathrm{H}) = (7.420 \pm 0.116) + (0.390 \pm 0.180)\pi^* + (0.892 \pm 0.158)\beta$
$(r = 0.95,\ \text{rel. } \sigma = 1.24\,\%,\ N = 10)$.

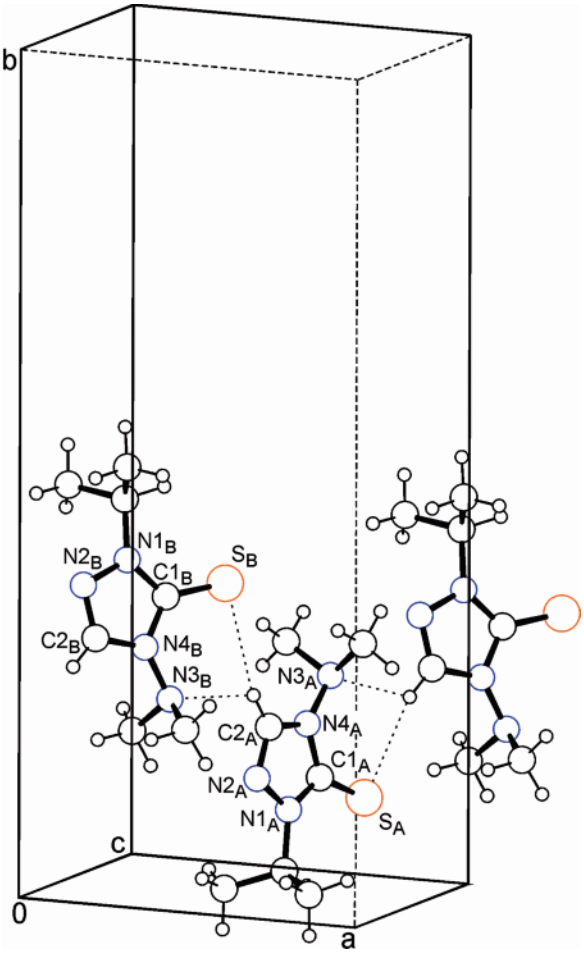


Fig. 6 (color online). Bifurcated C–H···S and C–H···N contacts in the crystal structure of **14**.

For **13**: $\delta(^1\mathrm{H}) = (7.114 \pm 0.171) + (0.887 \pm 0.267)\pi^* + (0.977 \pm 0.234)\beta$
$(r = 0.95,\ \text{rel. } \sigma = 1.81\,\%,\ N = 10)$.

Both the standard deviations and correlation coefficients are very satisfactory. It was to be expected that a thiolate would be affected by the hydrogen bond donating strength of the solvents. However, the influence of the α term was found to be negligible. Interestingly, the β term is predominant (more than in the imidazole series [12]), and the resulting correlation of calculated *vs*. observed values is shown in Fig. 10. The dimethylamino compound **13** displayed higher sensitivity than the dimethyl compound **10**. Obviously,

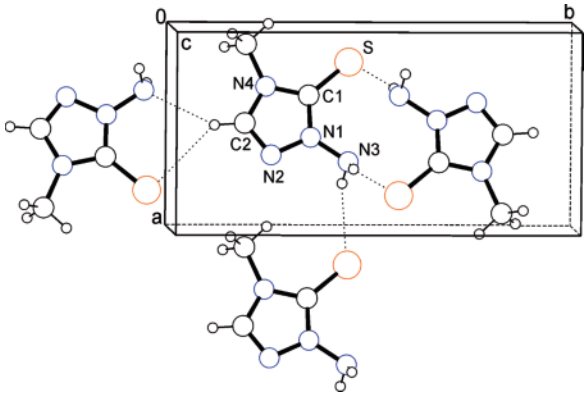


Fig. 7 (color online). Crystal structure of **15** showing N–H···S hydrogen bonds as well as bifurcated C–H···S and C–H···N contacts.

here the C–H···solvent interactions dominate. In contrast, the α term constituted the major contribution to the observed solvatochromism of unquestionable 2,3-diaryltetrazolium-5-thiolates [53]. Thus, there is no evidence of involvement of a mesoionic triazolium-5-thiolate resonance structure here (Scheme 2).

Conclusion

Fundamental groundwork has been laid for a general synthetic approach, with few limitations, providing an extension of the methodic repertory for the preparation of 1,2,4-triazoline-5-thiones. There is, however, no general procedure for isolation and purification. It must be noted that some of the experiments were conducted on a small scale, and yields were not fully optimized. A compilation of 1,2,4-triazoline-5-thione ring geometries and hydrogen bond interactions in the crystalline state is presented. The thiones are valuable building blocks for substituted triazolium compounds *via* *S*-methyl derivatives. The bifunctional amino-thiones offer access to new annelated heterocyclic systems. The thiones are also interesting ligands on their own. Many metal complexes of 1,3-disubstituted imidazoline-2-thiones are known, but comparatively few examples with 1,4-disubstituted triazoline-5-thiones. Thus, the new thiones open new fields, and the results of our ongoing research will be published in due course. Certainly, this work has erased some blank areas from the map of heterocycle territory.

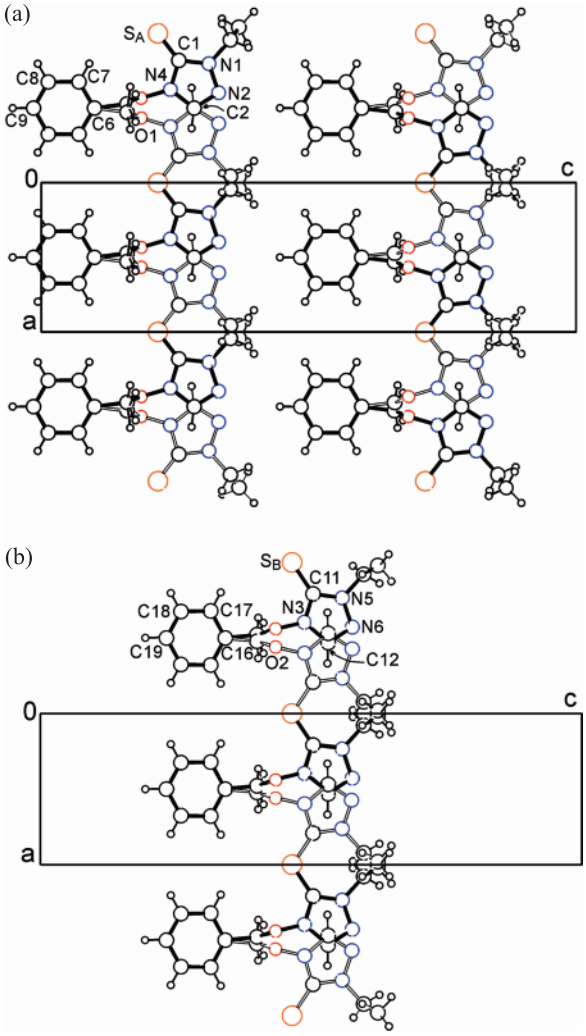


Fig. 8 (color online). Disordered structure of the two independent molecules A and B of **17**.

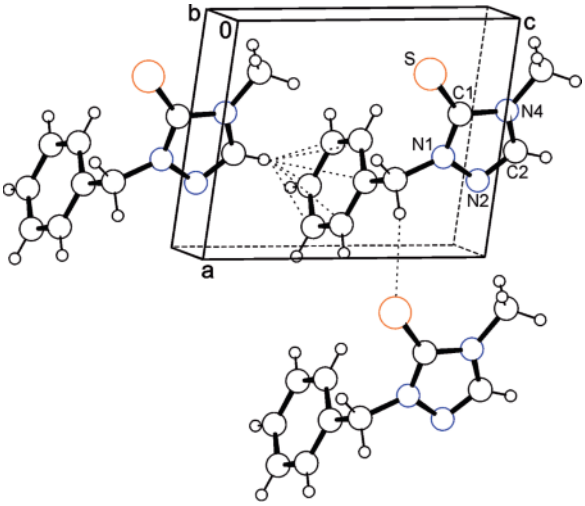


Fig. 9 (color online). Typical C–H···π interactions in the crystal structure of **18**.

Experimental Section

NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. IR spectra were obtained with a Nicolet 5700 FT instrument. High resolution mass spectra were measured with a Finnigan MAT 95 mass spectrometer. 1,2,4-Triazole, 4-amino-1,2,4-triazole, and 4-methyl-1,2,4-triazole-3-thiol were purchased from Sigma-Aldrich and used as received. 4-Methyl-1,2,4-triazole was prepared by two methods, desulfurization of 4-methyl-1,2,4-triazole-3-thiol [54, 55] or *via* 1-acetyl-1,2,4-triazole [56 – 58]. In one step, desulfurization yielded the purest product in highest yield. 4-Benzyloxy-1,2,4-triazole was obtained by cyclization of *O*-benzylhydroxylamine and dimethylformamide azine [36]. *O*-(2,4-Dinitrophenyl)hydroxylamine (DNPH) was prepared according to the published procedure [59]. Synthesis of 1,4-dimethyl-1,2,4-triazolium methylsulfate (**1a**) from 1-methyl-1,2,4-triazole has been reported [60], and there are known procedures for the synthesis of 1,4-dimethyl-1,2,4-triazolium iodide (**1b**) from either 1,2,4-triazole or 1-methyl-1,2,4-triazole [61 – 65]. We prepared **1a** from 1,2,4-triazole and **1b** from 4-methyl-1,2,4-triazole in one step and much shorter reaction times. The quaternary precursor salts 4-amino-1-methyl-1,2,4-triazolium iodide (**2**) [66], 4-amino-1-isopropyl-1,2,4-triazolium bromide (**3**) [66] and 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**4**) [34] were prepared as previously described. We scored a quantitative yield of **3** by refluxing the starting materials for 5 weeks.

*1,4-Dimethyl-1,2,4-triazolium methylsulfate (**1a**)*

1,2,4-Triazole (5.0 g, 72 mmol) was dissolved in 25 % methanolic NaOMe (16.5 mL). The solvent was evaporated, and the colorless residue was powdered and vacuum-dried to constant weight. *Caution: the following reaction is very exothermic!* The sodium triazolide was suspended in CH_3CN (25 mL), and dimethyl sulfate (13.7 mL, 145 mmol) was added dropwise during 40 min with stirring at such a rate as to keep the temperature below 70 °C. Higher temperature gave a brown product. The mixture was stirred for an additional hour at 70 °C, cooled and filtered. The volatiles were removed from the filtrate under reduced pressure at 50 °C to yield 14.8 g (98 %) of a colorless, viscous oil; $n_D^{20} = 1.469$.

Table 2. Hydrogen bonding geometries (Å, deg).

Compound	Interaction	H···A	D···A	D–H···A	Symmetry codes (A)
10	C2–H···S	2.8123(4)	3.636(2)	145.6(1)	$-x, -1/2+y, 3/2-z$
	C3–H···S	2.8113(4)	3.769(2)	166.0(1)	$1/2-x, 2-y, 1/2+z$
	C3–H···S	2.9002(4)	3.672(2)	136.4(1)	$-1/2+x, y, 3/2-z$
11	$N3_A$–H···$N2_B$	2.39(3)	3.122(4)	147(3)	$-1+x, y, z$
	$N3_A$–H···S_B	2.79(3)	3.491(3)	146(3)	$x, 1+y, z$
	$C2_A$–H···$N3_A$	2.686(2)	3.539(4)	149.8(2)	$1-x, 1-y, 1-z$
	$N3_B$–H···S_A	2.84(4)	3.444(4)	133(3)	x, y, z
	$N3_B$–H···S_A	2.79(2)	3.526(4)	149(3)	$x, -1+y, z$
	$C2_B$–H···$N3_B$	2.660(3)	3.539(4)	154.2(2)	$2-x, 1-y, 2-z$
12	N3–H···N3	2.17(2)	3.094(3)	168(2)	$1-x, 1/2+y, 1/2-z$
13	C2–H···N3	2.628(2)	3.380(3)	136.4(1)	$3/2-x, 1-y, -1/2+z$
	C3–H···S	2.8314(6)	3.781(3)	158.2(2)	$3/2-x, -y, -1/2+z$
	C4–H···S	2.8911(6)	3.797(3)	154.0(2)	$3/2-x, 1-y, -1/2+z$
14	$C2_A$–H···S_B	2.8612(5)	3.784(2)	163.9(1)	$x, 1/2-y, 1/2+z$
	$C2_A$–H···$N3_B$	2.628(2)	3.267(3)	125.0(1)	$x, 1/2-y, 1/2+z$
	$C2_B$–H···S_A	2.7274(4)	3.651(2)	164.6(1)	$-1+x, 1/2-y, -1/2+z$
	$C2_B$–H···$N3_A$	2.615(2)	3.223(2)	122.3(1)	$-1+x, 1/2-y, -1/2+z$
15	N3–H···S	2.80(3)	3.592(2)	162(2)	$1+x, y, z$
	N3–H···S	2.65(3)	3.499(2)	158(2)	$1-x, 1-y, 1-z$
	C2–H···S	2.9395(5)	3.695(2)	137.5(1)	$1-x, -1/2+y, 1/2-z$
	C2–H···N3	2.705(2)	3.457(3)	136.6(1)	$1-x, -1/2+y, 1/2-z$
17	C2–H···S_A	2.92(3)	3.754(2)	150(3)	$1+x, y, z$
	C12–H···S_B	2.800(1)	3.56(2)	138.1(7)	$1+x, y, z$
18	C4–H···S	2.8300(5)	3.809(2)	170.2(1)	$1+x, y, z$

– ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.37$ (s, 3H), 3.88 (s, 3H), 4.04 (s, 3H), 9.06 (s, 1H), 9.92 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 34.0$, 38.6, 53.1, 143.6, 145.4 ppm. – IR (neat): $\nu = 3090$ w, 1590 m, 1211 s, 1059 m, 998 s, 732 s, 577 s cm^{-1}. – HRMS (FAB): $m/z = 98.0836$ (calcd. 98.0713 for $C_4H_8N_3$, $[M]^+$).

*1,4-Dimethyl-1,2,4-triazolium iodide (**1b**)*

A solution of 4-methyl-1,2,4-triazole (0.55 g, 6.6 mmol) and CH_3I (2.1 g, 15 mmol) in MeOH (1.5 mL) was heated in a pressure vessel (bath temperature 100 °C) for 1 h. After cooling the solvent was evaporated. The residue was suspended in Et_2O, filtered and dried to yield a gray powder (1.27 g, 85 %). The spectroscopic data were as previously reported [49].

*1,4-Dimethyl-1,2,4-triazolium hydrogensulfate (**1c**)*

A solution of 1,4-dimethyl-1,2,4-triazolium iodide (**1b**) (0.50 g, 2.2 mmol) in H_2O (3 mL) was added dropwise to a stirred solution of Ag_2SO_4 (0.35 g, 1.1 mmol) and H_2SO_4 (2.22 mL 0.5 M, 1.1 mmol) in H_2O (15 mL) at 50 °C. The mixture was stirred for 30 min and filtered (0.45 μm). The volatiles were removed from the filtrate under reduced pressure at 50 °C to yield a colorless oil (0.43 g, 99 %); $n_D^{20} = 1.487$. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.90$ (s, 3H), 4.06 (s, 3H), 5.0 (br, 1H), 9.13 (s, 1H), 10.20 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 33.9$, 38.5, 143.8, 145.3 ppm. – IR (neat): $\nu = 1590$ m, 1159 s, 1022 s, 835 s, 734 m, 658 m, 622 m, 569 s cm^{-1}.

*4-(Dimethylamino)-1-isopropyl-1,2,4-triazolium hexafluorophosphate (**5**)*

A mixture of 4-amino-1-isopropyl-1,2,4-triazolium bromide (**3**) (2.0 g, 9.7 mmol) and dimethyl sulfate (1.83 mL, 2 equiv.) was stirred at 100 °C for 12 h. The solution was allowed to cool to 20 °C, and H_2O (6 mL) was added. A solution of NH_4PF_6 (1.57 g, 9.7 mmol) in H_2O (4 mL) was added, and the colorless precipitate was stirred for 10 min, filtered off, washed with H_2O (4 mL), and dried. Yield: 2.2 g (76 %). M. p. 151 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 1.51$ (d, $J = 6.6$ Hz, 6H), 2.95 (s, 6H), 6.70 (sept, $J = 6.6$ Hz, 1H), 9.62 (s, 1H), 10.48 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 21.0$ (2C), 47.7 (2C), 55.8, 140.6, 142.4 ppm. – IR (neat): $\nu = 3154$ w, 1561 w, 1469 w, 1129 w, 1072 w, 985 w, 885 w, 817 s, 655 m, 555 s cm^{-1}. – $C_7H_{15}F_6N_4P$ (300.18): calcd. C 28.01, H 5.04, N 18.66; found C 27.90, H 4.85, N 18.42.

*1-Amino-4-methyl-1,2,4-triazolium 2,4-dinitrophenolate (**6a**)*

A solution of 4-methyl-1,2,4-triazole (1.08 g, 13 mmol) and DNPH (2.60 g, 13 mmol) in CH_2Cl_2 (20 mL) was stirred at 20 °C for 4 d. The product precipitated and was collected by filtration, washed with CH_2Cl_2 (5 mL) and Et_2O (5 mL),

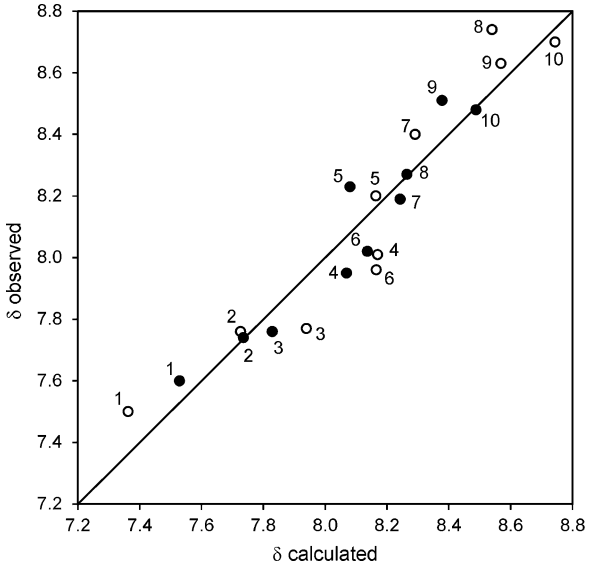
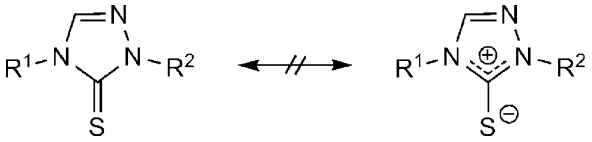


Fig. 10. Correlation of calculated and observed ^{1}H NMR shifts of 1,4-dimethyl-1,2,4-triazoline-5-thione **10** (•) and 4-(dimethylamino)-1-methyl-1,2,4-triazoline-5-thione **13** (○) in different solvents: (1) CCl_4, (2) $CDCl_3$, (3) CD_2Cl_2, (4) CD_3CN, (5) [D_6]acetone, (6) [D_8]THF, (7) CD_3OD, (8) D_2O, (9) [D_7]DMF, (10) [D_6]DMSO.



Scheme 2.

and dried to yield 2.45 g (67 %) of a yellow powder. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.84$ (s, 3H), 6.32 (d, $J =$ 9.7 Hz, 1H), 7.41 (s, 2H), 7.77 (dd, $J = 9.7$ Hz, $J = 3.1$ Hz, 1H), 8.59 (d, $J = 3.1$ Hz, 1H), 8.98 (s, 1H), 9.98 ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 34.1$, 125.0, 126.5, 127.4, 136.0, 140.7, 143.4, 170.3 ppm. – IR (neat): $\nu = 3294$ w, 3236 w, 3081 m, 2988 m, 1595 s, 1550 m, 1525 s, 1475 m, 1431 m, 1371 m, 1307 s, 1258 s, 1175 m, 1128 s, 983 m, 834 s, 710 m, 654 m, 618 s cm^{-1}. – $C_9H_{10}N_6O_5$ (282.21): calcd. C 38.30, H 3.57, N 29.78; found C 38.28, H 3.42, N 29.40.

*1-Amino-4-methyl-1,2,4-triazolium chloride (**6b**)*

A suspension of the dinitrophenolate **6a** (2.40 g, 8.5 mmol) in 1 M HCl (70 mL) was stirred at 80 °C for 1 h. The solids were filtered off, well washed with hot 1 M HCl (2 × 20 mL) and hot H_2O (20 mL), and the filtrate was taken to dryness under reduced pressure. The product was recrystallized from MeOH and washed with Et_2O. Yield: 1.03 g (90 %). M. p. 194 – 196 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.86$ (s, 3H), 9.10 (s, 1H), 10.17 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 34.2$, 140.4, 143.4 ppm. – IR (neat): $\nu = 3214$ m, 3107 m, 3002 m, 1528 w, 1179 m, 1061 m, 987 m, 901 m, 651 m, 619 s, 461 m cm^{-1}.

*4-Benzyloxy-1-methyl-1,2,4-triazolium tetrafluoroborate (**7**)*

A solution of 4-benzyloxy-1,2,4-triazole (0.80 g, 4.6 mmol) and Me_3O^+ BF_4^- (0.71 g, 1.05 equiv.) in CH_2Cl_2 (4 mL) was stirred at room temperature for 20 h. MeOH (0.1 mL) was added, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 5 mL) to yield 1.03 g (81 %) of crude **7** as a syrup. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 4.04$ (s, 3H), 5.52 (s, 2H), 7.4 – 7.5 (m, 5H), 9.53 (s, 1H), 10.60 (s, 1H) ppm.

*4-Benzyloxy-1-ethyl-1,2,4-triazolium tetrafluoroborate (**8**)*

A solution of 4-benzyloxy-1,2,4-triazole (1.0 g, 5.7 mmol) and Et_3O^+ BF_4^- (1.14 g, 1.05 equiv.) in CH_2Cl_2 (5 mL) was stirred at room temperature for 17 h. MeOH (0.3 mL) was added, and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 5 mL) to yield 1.54 g of crude **8** as a syrup which was used in the next step without purification. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 1.46$ (t, $J = 7.3$ Hz, 3H), 4.36 (q, $J = 7.3$ Hz, 2H), 5.55 (s, 2H), 7.50 (m, 5H), 9.55 (s, 1H), 10.65 (s, 1H) ppm.

*1-Benzyl-4-methyl-1,2,4-triazolium bromide (**9**)*

A solution of 4-methyl-1,2,4-triazole (0.32 g, 3.9 mmol) and benzyl bromide (0.50 mL, 1.1 equiv.) in CH_3CN (5 mL) was refluxed for 21 h. On cooling, the product crystallized and was collected by filtration and dried. Yield: 0.72 g (74 %). M. p. 158 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.91$ (s, 3H), 5.66 (s, 2H), 7.38 – 7.43 (m, 5H), 9.21 (s, 1H), 10.32 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 34.2$, 54.5, 128.8 (5C), 133.4, 143.2, 145.8 ppm. – IR (neat): $\nu = 2988$ w, 2940 w, 1582 m, 1457 w, 1357 w, 1152 m, 999 w, 912 w, 721 s, 695 s, 640 m, 621 m, 614 m cm^{-1}.

*1,4-Dimethyl-1,2,4-triazoline-5-thione (**10**)*

A mixture of 1,4-dimethyl-1,2,4-triazolium methylsulfate (**1a**) (1.0 g, 4.8 mmol), sulfur (153 mg, 1.0 equiv.) and K_2CO_3 (0.79 g, 1.2 equiv.) in MeOH (7 mL) was stirred at 70 °C (bath temperature) for 2 h. Insoluble material was removed by filtration and washed with MeOH. The solvent was evaporated, and the residue was dissolved in hot H_2O (2 mL). On cooling to 5 °C, fine needles precipitated and were collected by filtration. The mother liquor was concentrated and cooled to give a second crop of the product which was dried over P_2O_5. Yield: 0.45 g (73 %). Single crystals were obtained by slow evaporation of a tetrachloromethane

solution. M. p. 92 °C (lit. 93 °C [1]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.44 (s, 3H), 3.64 (s, 3H), 8.46 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 32.4, 36.1, 141.4, 165.5 ppm. – IR (neat): ν = 3109 w, 3040 w, 1533 w, 1389 m, 1357 s, 1227 m, 1171 m, 1049 m, 977 m, 846 m, 768 m, 628 s cm^{-1}.

*4-Amino-1-methyl-1,2,4-triazoline-5-thione (**11**)*

A mixture of 4-amino-1-methyl-1,2,4-triazolium iodide (**2**) (1.0 g, 4.4 mmol), sulfur (142 mg, 1.0 equiv.) and K_2CO_3 (0.73 g, 1.2 equiv.) in MeOH (7 mL) was stirred at 70 °C (bath temperature) for 2 h. The solvent was removed under reduced pressure, and the residue was recrystallized from hot H_2O (6 mL). Yield: 0.46 g (80 %). Single crystals were obtained from pyridine at room temperature. M. p. 140 – 142 °C (lit. 139 °C [2], 142 °C [7]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.64 (s, 3H), 5.74 (br s, 2H), 8.52 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 36.6, 140.9, 165.4 ppm. – IR (neat): ν = 3269 m, 3177 w, 3113 w, 3034 w, 2940 w, 1604 m, 1531 w, 1473 m, 1388 m, 1331 m, 1235 m, 1213 m, 1153 m, 1060 w, 1003 m, 962 m, 846 s, 784 m, 666 w, 627 s cm^{-1}.

*4-Amino-1-isopropyl-1,2,4-triazoline-5-thione (**12**)*

A mixture of 4-amino-1-isopropyl-1,2,4-triazolium bromide (**3**) (1.0 g, 4.8 mmol), sulfur (155 mg, 1.0 equiv.) and Et_3N (0.67 mL, 1.0 equiv.) in pyridine (5 mL) was stirred at 70 °C for 2 h. The volatiles were evaporated under reduced pressure, and the residue was partitioned between 0.1 M HCl (10 mL) and EtOAc (4 mL). The aqueous phase was extracted with EtOAc (2 × 3 mL). The combined organic extracts were washed with brine (3 mL) and taken to dryness under reduced pressure to yield **12** (0.69 g, 90 %) as an off-white powder which could be recrystallized from hot H_2O. Single crystals were obtained from pyridine-H_2O (2 : 1) at −20 °C. M. p. 104 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.29 (d, J = 6.7 Hz, 6H), 4.87 (sept, J = 6.7 Hz, 1H), 5.75 (br s, 2H), 8.53 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.5 (2C), 50.1, 141.0, 164.1 ppm. – IR (neat): ν = 3278 w, 3169 w, 3097 w, 3036 w, 2978 w, 2946 w, 1639 m, 1538 w, 1433 s, 1397 m, 1332 s, 1220 m, 1125 m, 975 m, 876 m, 755 m, 637 m, 566 m cm^{-1}. – HRMS (EI): m/z = 158.0560 (calcd. 158.0621 for $C_5H_{10}N_4S$, [M]$^+$).

*4-(Dimethylamino)-1-methyl-1,2,4-triazoline-5-thione (**13**)*

a) A mixture of 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**4**) (1.0 g, 3.7 mmol), sulfur (118 mg, 1.0 equiv.) and Et_3N (0.51 mL, 1.0 equiv.) in pyridine (5 mL) was stirred at 70 °C for 2 h. The volatiles were evaporated under reduced pressure, and the residue was partitioned between 1 M HCl (2 mL) and EtOAc (5 mL). The organic phase was repeatedly washed with 1 M HCl (3 × 2 mL) and taken to dryness under reduced pressure to yield **13** (0.42 g, 72 %).

b) A mixture of 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**4**) (1.0 g, 3.7 mmol), sulfur (118 mg, 1.0 equiv.) and K_2CO_3 (0.61 g, 1.2 equiv.) in MeOH (5 mL) was refluxed for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in H_2O (10 mL). The aqueous phase was extracted with EtOAc (3 × 3 mL). The combined organic extracts were washed with H_2O (2 × 3 mL), brine (3 mL) and taken to dryness under reduced pressure to yield **13** (0.47 g, 81 %) as an oil which soon solidified. Recrystallization from hot H_2O resulted in unacceptable losses. Sublimation at 55 °C/0.1 mbar gave 0.45 g (77 %) colorless crystals. Single crystals were obtained from pyridine-Et_2O (1 : 1) at −20 °C. M. p. 72 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.93 (s, 6H), 3.61 (s, 3H), 8.69 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 35.8, 44.4 (2C), 139.4, 163.2 ppm. – IR (neat): ν = 3079 w, 3016 w, 2967 w, 2876 w, 2833 w, 2797 w, 1460 m, 1444 m, 1368 s, 1350 m, 1235 w, 1187 m, 1156 m, 1144 m, 1098 w, 1022 m, 970 m, 918 m, 889 m, 747 m, 677 m, 631 s cm^{-1}. – HRMS (EI): m/z = 158.0526 (calcd. 158.0621 for $C_5H_{10}N_4S$, [M]$^+$).

*4-(Dimethylamino)-1-isopropyl-1,2,4-triazoline-5-thione (**14**)*

A solution of 4-(dimethylamino)-1-isopropyl-1,2,4-triazolium hexafluorophosphate (**5**) (0.50 g, 1.7 mmol), sulfur (53 mg, 1.0 equiv.) and Et_3N (0.23 mL, 1.0 equiv.) in pyridine (2 mL) was stirred at 70 °C for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc (10 mL). The organic phase was washed with 1 M HCl (4 × 2 mL) and H_2O (2 × 1 mL) and taken to dryness under reduced pressure to yield **14** (0.30 g, 97 %). Recrystallization from hot H_2O involved heavy losses, but sublimation at 75 °C/0.1 mbar gave 0.29 g (93 %) colorless crystals. Single crystals were obtained from H_2O. M. p. 95 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.27 (d, J = 6.7 Hz, 6H), 2.93 (s, 6H), 4.95 (sept, J = 6.7 Hz, 1H), 8.69 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.4 (2C), 44.5 (2C), 48.9, 139.5, 162.0 ppm. – IR (neat): ν = 3071 w, 3005 w, 2984 w, 2871 w, 1529 w, 1410 s, 1363 s, 1347 s, 1327 s, 1221 m, 1115 w, 1038 w, 1021 w, 991 m, 916 w, 885 m, 831 w, 686 m, 642 m, 592 s cm^{-1}. – HRMS (EI): m/z = 186.0970 (calcd. 186.0934 for $C_7H_{14}N_4S$, [M]$^+$).

*1-Amino-4-methyl-1,2,4-triazoline-5-thione (**15**)*

a) A solution of 1-amino-4-methyl-1,2,4-triazolium chloride (**6b**) (0.30 g, 2.2 mmol), sulfur (72 mg, 1.0 equiv.) and

Et_3N (0.31 mL, 1.0 equiv.) in pyridine (2 mL) was stirred at 70 °C for 2 h. The volatiles were evaporated under reduced pressure, and the residue was partitioned between 1 M HCl (3 mL) and EtOAc (8 mL). The aqueous phase was extracted with EtOAc (2 mL). The combined organic extracts were washed with 1 M HCl (2 × 2 mL) and brine (2 mL) and taken to dryness under reduced pressure to yield **15** as an off-white powder (0.13 g, 45 %).

b) A mixture of 1-amino-4-methyl-1,2,4-triazolium chloride (**6b**) (0.30 g, 2.2 mmol), sulfur (72 mg, 1.0 equiv.) and K_2CO_3 (0.37 g, 1.2 equiv.) in MeOH (3 mL) was stirred for 4 h at room temperature. The solids were filtered off, washed well with MeOH, and the filtrate was taken to dryness under reduced pressure. The product was recrystallized from hot H_2O (2 mL) and dried. Single crystals were obtained from H_2O. Yield: 0.17 g (58 %). M. p. 134 °C (dec.). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.44$ (s, 3H), 6.12 (s, 2H), 8.33 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 32.8$, 138.0, 162.9 ppm. – IR (neat): $\nu = 3255$ m, 3151 m, 3104 m, 3049 w, 2953 w, 1629 m, 1537 m, 1446 m, 1415 m, 1338 s, 1245 w, 1218 m, 1088 w, 1015 m, 937 m, 875 s, 775 m, 667 m, 628 s, 507 m cm^{-1}. – HRMS (EI): $m/z = 130.0326$ (calcd. 130.0308 for $C_3H_6N_4S$, $[M]^+$).

*4-Benzyloxy-1-methyl-1,2,4-triazoline-5-thione (**16**)*

A mixture of crude 4-benzyloxy-1-methyl-1,2,4-triazolium tetrafluoroborate (**7**) (0.50 g, 1.8 mmol), sulfur (58 mg, 1.0 equiv.) and Et_3N (0.25 mL, 1.0 equiv.) in pyridine (2 mL) was stirred at room temperature for 76 h. The product was precipitated by addition of H_2O (10 mL), collected by filtration, washed with H_2O (2 mL), and dried under vacuum. Yield: 0.15 g (38 %). Crystals were obtained from aqueous acetone. M. p. 102 – 104 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.76$ (s, 3H), 5.41 (s, 2H), 7.29 (s, 1H), 7.41 (m, 5H) ppm. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.64$ (s, 3H), 5.36 (s, 2H), 7.42 – 7.49 (m, 5H), 8.68 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 36.4$, 79.0, 128.7 (2C), 129.5, 130.0 (2C), 133.0, 137.7, 161.1 ppm. – IR (neat): $\nu = 3133$ w, 1456 m, 1398 m, 1362 m, 1348 m, 1147 m, 960 m, 915 m, 818 m, 747 s, 703 s, 677 m, 651 m, 616 s, 578 m, 533 m cm^{-1}. – HRMS (EI): $m/z = 221.0634$ (calcd. 221.0617 for $C_{10}H_{11}N_3OS$, $[M]^+$).

*4-Benzyloxy-1-ethyl-1,2,4-triazoline-5-thione (**17**)*

A mixture of crude 4-benzyloxy-1-ethyl-1,2,4-triazolium tetrafluoroborate (**8**) (1.5 g, 5.2 mmol), sulfur (165 mg, 1.0 equiv.) and Et_3N (0.72 mL, 1.0 equiv.) in pyridine (5 mL) was stirred at 70 °C for 2 h. Addition of H_2O (35 mL) precipitated an oil which was stirred overnight at room temperature until it solidified. The product was filtered off, washed with H_2O and dried in a vacuum. Yield: 0.49 g (40 %). Single crystals were obtained from CH_3CN. M. p. 63 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.26$ (t, $J = 7.2$ Hz, 3H), 4.10 (q, $J = 7.2$ Hz, 2H), 5.38 (s, 2H), 7.42 – 7.50 (m, 5H), 8.67 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta =$ 12.9, 43.8, 79.0, 128.6 (2C), 129.5, 130.0 (2C), 132.9, 137.8, 160.5 ppm. – IR (neat): $\nu = 3112$ w, 1444 m, 1420 s, 1348 s, 1301 m, 1189 m, 1145 m, 952 s, 741 s, 699 s, 665 s, 618 s, 579 m, 538 s cm^{-1}. – HRMS (FAB): $m/z = 236.0829$ (calcd. 236.0852 for $C_{11}H_{14}N_3OS$, $[M+H]^+$).

*1-Benzyl-4-methyl-1,2,4-triazoline-5-thione (**18**)*

a) A mixture of 1-benzyl-4-methyl-1,2,4-triazolium bromide (**9**) (0.15 g, 0.59 mmol), sulfur (19 mg, 1.0 equiv.) and K_2CO_3 (98 mg, 1.2 equiv.) in MeOH (1 mL) was stirred at 70 °C for 2 h. Addition of H_2O (2 mL) gave a clear solution which on cooling to 20 °C deposited the crystalline product. Yield: 93 mg (77 %).

b) A mixture of 1-benzyl-4-methyl-1,2,4-triazolium bromide (**9**) (0.40 g, 1.6 mmol), sulfur (51 mg, 1.0 equiv.) and Et_3N (0.22 mL, 1.0 equiv.) in pyridine (2 mL) was stirred at 70 °C for 2 h. The product was precipitated by addition of H_2O (4 mL), collected by filtration, washed with H_2O (4 mL), and dried in a vacuum. Yield: 0.25 g (77 %). Single crystals were obtained from aqueous acetone. M. p. 118 – 120 °C (lit. 118 – 119 °C [67]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.48$ (s, 3H), 5.31 (s, 2H), 7.31 (m, 5H), 8.50 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta =$ 32.5, 51.5, 127.8, 127.9 (2C), 128.5 (2C), 135.9, 141.7, 165.9 ppm. – IR (neat): $\nu = 3144$ w, 1546 m, 1447 m, 1414 s, 1351 s, 1216 m, 1099 m, 1017 m, 794 m, 734 s, 703 s, 665 m, 630 m, 579 m, 531 m cm^{-1}. – HRMS (EI): $m/z = 205.0603$ (calcd. 205.0668 for $C_{10}H_{11}N_3S$, $[M]^+$).

*Oxidative desulfurization of **10** to 1,4-dimethyl-1,2,4-triazolium hydrogensulfate (**1c**)*

In an open test tube, thione **10** (50 mg) was heated at 160 °C for 24 h. On cooling the product (40 mg, 53 %) was obtained as a colorless liquid. The spectroscopic data were matching those of authentic **1c**.

Crystal structure determination

X-Ray diffraction data were collected with an Oxford Diffraction Gemini-R Ultra diffractometer using MoK_α ($\lambda =$ 0.7107 Å) or CuK_α radiation ($\lambda = 1.5418$ Å), as noted in Table 1, at 173 K. Absorption corrections were applied in all cases (multi-scan). The crystal structures were solved by Direct Methods and refined by full-matrix least-squares techniques [68, 69]. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The Flack parameter x of the non-centrosymmetric crystal structure of **13** was 0.0(3).

CCDC 977713–977720 contain 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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