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5-Chloro-3-methylthio-1,2,4-thiadiazol-2-ium Chlorides as Useful Synthetic Precursors to a Variety of 6aλ^4-Thiapentalene Systems

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ABSTRACT: *Title salts* **3** *were easily obtained by treatment of formimidoyl isothiocyanates* **1** *with a twofold excess of methanesulfenyl chloride. They showed interesting chemical behavior toward several nitrogen and carbon nucleophiles. Substitution reactions with isothioureas and acetamide in the presence of triethylamine gave the 1*H*, 6*H*-6aλ^4-thia-1,3,4,6-tetraazapentalenes* **7** *and 6*H*-6aλ^4-thia-1-oxa-3,4,6-triazapentalene* **9**, *respectively. Addition of* p*-toluidine furnished the 5-imino-thiadiazole derivatives* **10**, *which reacted further with diverse heterocumulenes to yield the corresponding thiatriaza- and tetraazapentalene species* **11**. *The* N,N′*-bis(1,2,4-thiadiazol-5-ylidene)diaminobenzenes* **13** *were also prepared and reacted with phenyl isothiocyanate. Two stable rotational isomers were separated for the 1,2-phenylene product* **14b**. *Other* π*-hypervalent sulfur compounds* **16** *were synthesized under similar conditions from salts* **3** *and methyl cyanoacetate or dimethyl malonate. The structural assignments were discussed on the basis of IR and NMR spectroscopic data and received additional support from X-ray analysis of substrate* **16a**. © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:95–105, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10106

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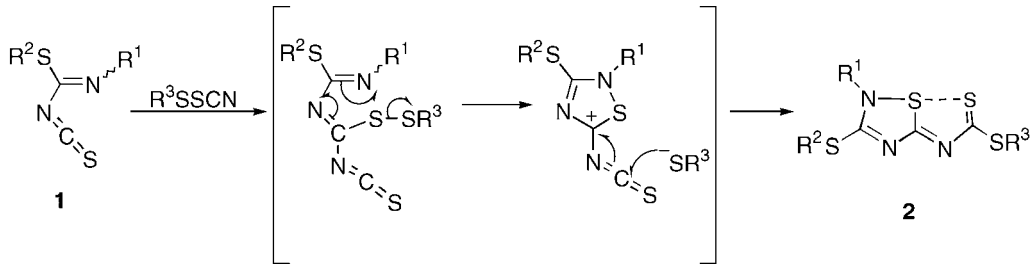
INTRODUCTION

We have previously reported [1] the reaction of sulfenyl thiocyanates with a series of (methylthio)- and (arylthio)formimidoyl isothiocyanates **1** readily forming the compounds **2**, which may be designated as 6*H*-1,6aλ^4-dithia-3,4,6-triazapentalenes. This result was explained by a nucleophilic addition to the C=S unsaturation of the heterocumulene **1**, with subsequent cyclization and displacement of the sulfenyl anion (Scheme 1).

Products **2** are members of an important class of heterocycles which are now described as three-centered hypervalent molecules with a 10 π-electron system (10-S-3 sulfuranes in the case of a central sulfur atom) [2]. Study of such isolable aromatic species has attracted much attention over the past decades because of their unique binding behavior [3–5]. It has been pointed out that their structure may be the result of the existence of a "single-bond–no-bond"



SCHEME 1

resonance between several canonical forms, represented by the three general formulas in Scheme 2. Alternatively to this proposition, a rapid equilibrium between the two valence tautomers **a** and **c** may be postulated for which the bicyclic form **b** represents only a transition state. However, there is at present no evidence for individual existence of valence isomers **a** and **c** and most of these adducts are satisfactory represented by the fused structure **b** [6,7].

Process of Scheme 1 encouraged us to investigate the utility of the imidoyl isothiocyanates **1** for the preparation of 5-chloro-1,2,4-thiadiazolium species in the presence of sulfenyl chlorides. It was expected that the 5-chlorine atom of such salts could be displaced by nucleophiles and we were particularly attracted by the possibility of obtaining diverse polyheterapentalene systems under the action of suitable reagents.

Herein report about a facile synthesis of the 5-chloro-1,2,4-thiadiazol-2-ium chlorides **3** and their use in a novel, general, and effective approach to new hypervalent sulfur compounds. In this paper, we assume the replacement nomenclature [3c] and numbering [8] corresponding to the valence formula **b** whatever the real importance of this particular resonance structure.

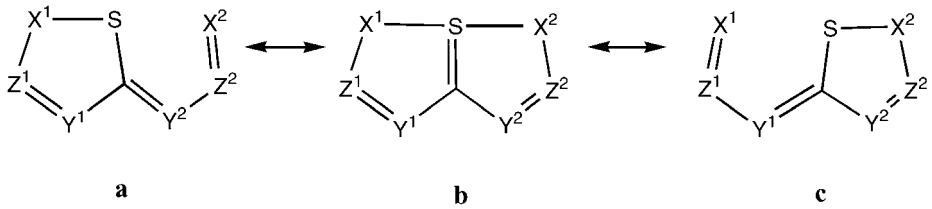
RESULTS AND DISCUSSION

Preparation of 5-Chloro-1,2,4-thiadiazol-2-ium Chlorides **3**

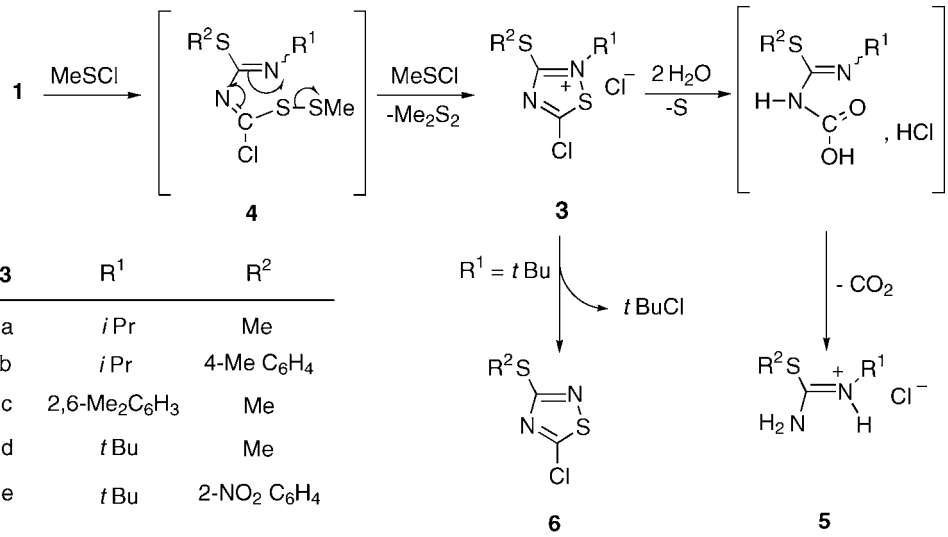
Our strategy consisted in treating the easily accessible imidoyl isothiocyanates **1** with a twofold excess of methanesulfenyl chloride, in carbon tetrachloride at room temperature. The pale-yellow solids **3**, which precipitated from the reaction medium, were collected by filtration in 80% yield or better. Large amounts of dimethyl disulfide were recovered in the filtrate supporting the stepwise mechanism via 4-chloro-4-(methyldithio)-1,3-diazabutadiene **4** as intermediate (Scheme 3).

Salts **3** are hitherto unknown variations of the thiadiazolium structure. To the best of our knowledge, systems of this type have been limited to 5-aryl- and 5-(dialkylamino)-1,2,4-thiadiazolium salts through the oxidative ring closure of *N*-thionoamidino compounds in the presence of perchloric acid [4].

Thiadiazolium chlorides **3** exhibited good stability in the solid state under a dry atmosphere. Salts **3a–c** were gradually hydrolyzed on standing in air moisture, and much faster in alcohol solution, to give the isothiourea hydrochlorides **5**. We suggest a course via an unstable carbamic acid (Scheme 3). The 2-methyl-3,5-diphenyl-1,2,4-thiadiazolium salts were shown to be similarly cleaved by H_2O with elimination of sulfur [4]. The source of instability of **3d,e** lies rather in the nature of the **N**-substituent as these salts spontaneously decomposed in solution into a mixture of *tert*-butyl chloride, isobutene, and 5-chloro-1,2,4-thiadiazoles **6**. A similar isobutene evolution dominates the chemistry of the *N-tert*-butylimidazolium [9] and pyrrolium [10] salts. Patented 5-chloro-1,2,4-thiadiazoles, including 3-(alkylthio) derivatives, were previously prepared by the reaction of trichloromethylsulfenyl chloride with amidino substrates [4,11].



SCHEME 2



3	R^1	R^2
a	*i* Pr	Me
b	*i* Pr	4-Me C_6H_4
c	2,6-$Me_2C_6H_3$	Me
d	*t* Bu	Me
e	*t* Bu	2-NO_2 C_6H_4

SCHEME 3

Reactions of 5-Chloro-1,2,4-thiadiazolium Chlorides **3** *with Nitrogen Nucleophiles*

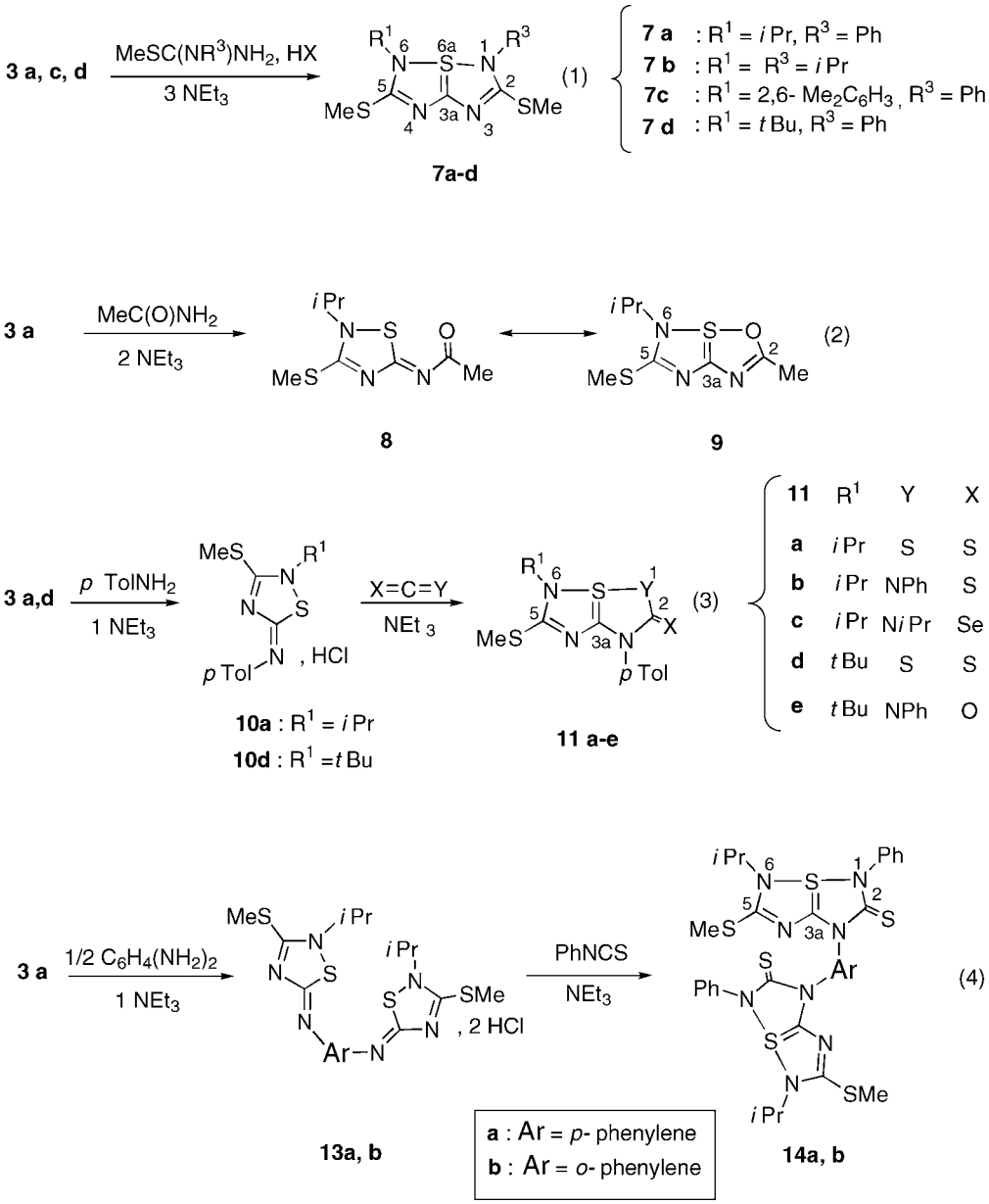
Thiadiazolium salts **3** were shown to preferentialy react with nucleophiles in the 5- and not in the 3-position. Substitutions by compounds that contain the NH_2 functional group are summarized in Scheme 4. Adducts were generally obtained in satisfying yields after a short time at room temperature in dry THF containing the specified amount of triethylamine.

Reactions with *S*-methyl isothioureas generated the 1*H*,6*H*-6aλ^4-thia-1,3,4,6-tetraazapentalenes **7** (Eq. (1)), which were characterized by elemental analysis, mass, and NMR spectroscopies with particular regard to the chemical shifts for the three endocyclic carbons. The pertinent ^{13}C NMR data are listed in Table 1 and other spectral results are recorded in the Experimental section. Interestingly, the ^{1}H and ^{13}C NMR spectra of symmetrically substituted product **7b** show the equivalence of ring carbons C2 and C5 and of substituents on the pairs of sites N1/N6 and C2/C5 (cf. Experimental section). Number and pattern of signals also remained unchanged for the ^{1}H NMR spectrum of **7b** down to −95°C in CD_2Cl_2. Such a total magnetic equivalence on the NMR time scale is consistent with a C_{2v} -symmetrical structure **b** (Scheme 2) [3c,12,13]. Relatively few examples of similar thiatetraazapentalene derivatives, without substituent on the N3 and N4 positions, have been mentioned in the literature [14,15]. They were principally prepared from 2,5-dihydro-5-imino-1,2,4-thiadiazoles and imidoyl chlorides [14].

Salt **3a** and acetamide were reacted to give the 5-(acetylimino)-2,5-dihydro-1,2,4-thiadiazole **8**, which may also be formulated as 6*H*-1-oxa-6aλ^4-thia-3,4,6-triazapentalene **9** (Eq. (2)). Structure **9** was assumed on the basis of NMR and IR spectral properties. Thus, the obtained adduct exhibits C2, C3a, and C5 resonances (Table 1) in consonance with those of nearly identical polyheterapentalenes [16]. It does not display the normal carbonyl vibration of *N*-acetylimidates in the 1650–1660 cm^{-1} range [17] but shows a weak band at 1635 cm^{-1} together with two strong bands in the 1500–1530 cm^{-1} region. All attempts to synthesize related dithiatriazapentalenes by treatment of salt **3a** with thioamides were unsuccessful, the substrate **7b** being essentially recovered on account of a partial hydrolysis to the transient isothiourea **5a**.

The 5-imino-2,5-dihydro-1,2,4-thiadiazole hydrochlorides **10** were readily accessible by condensation of salts **3a,d** with *p*-toluidine. They were converted into a variety of 2,3-dihydro-6aλ^4-thiapolyheterapentalenes **11** in nearly quantitative yields, using addition of heterocumulenes (Eq. (3)).

Literature synthetic pathways to analogous 5-iminothiadiazoles [4] mainly involved the oxidative cyclization of *N*-imidoylthioureas [18,19]. Hydrochloride derivatives proved to be rather stable heterocycles in contrast to their deprotonated counterparts, which underwent a rapid ring-opening process [18b]. Dipolar intermediates were implicated in their reactions with carbon disulfide [18a] and iso-, isothio-, and isoselenocyanates [5,13,18a], proceeding either on the C=N or the C=X unsaturation of such heteroallenes RNCX. Evidence for an addition of **10a** on the carbon–nitrogen double bond of phenyl isothiocyanate was found in the ready alkylation of the 2-thioxo-thiatetraazapentalene **11b** to



SCHEME 4

provide the methiodide **12b** (Scheme 5). Structures **11** were also supported by the ^{13}C NMR data reported in Table 1, in satisfying agreement with values for related polyheterapentalenes [13,18a].

In a similar manner, nucleophilic substitution on salt **3a** by 1,4- and 1,2-phenylenediamines in the presence of stoichiometric amount of triethylamine promoted the formation of the *N,N′*-bis[1,2,4-thiadiazol-5-ylidene]diaminobenzene dihydrochlorides **13**. These 1:2 adducts readily furnished the *N,N′*-phenylene-bridged bis(thiatetraazapentalene) derivatives **14** by reaction with phenyl isothiocyanate (Scheme 4, Eq. (4)).

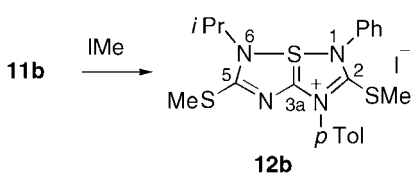
Analysis of crude solid **14b** revealed the existence of two isomers in a ratio of about 50:50, which were easily separated by a flash chromatography. ^1H NMR spectra of both isomers **14b(I)** and **14b(II)** show a singlet for the 2 equiv. methylthio groups together with a septuplet and two different doublets for the CH and the diastereotopic methyls of the 2 equiv. isopropyl groups. In the same way, ^{13}C NMR spectra of both isomers (Table 1) display two resonances in the 22–23 ppm range attributed to the methyl carbons of the isopropyl groups while only 12 signals are detected for all the other carbons of the molecule. These data were rationalized assuming the presence of two

TABLE 1 NMR Chemical Shifts and Multiplicities for the Main Carbon Atoms of 6aλ^4-Thiapentalene Systems[a,b]

	C2	*C5*	*C3a (s)*	*SCH_3 (q, ^1J = 143)*	*N1–C*[c]	*N6–C*[c]
7a	151.8 (q, $^3J = 4.9$)	156.8 (m)	169.4	13.4, 14.0	135.4 (m)	51.0 (dm)
7c	152.7 (q, $^3J = 5$)	160.4 (q, $^3J = 4$)	171.3	13.8, 14.1	135.0 (m)	144.5 (m)
7d	151.6 (q, $^3J = 5.1$)	154.4 (q, $^3J = 3.9$)	168.2	14.0, 14.8	135.3 (m)	55.4 (m)
9[d]	182.5 (q, $^2J = 6.5$)	165.5 (m)	177.5	14.1	–	50.4 (dm)
11a	203.1 (s)	162.1 (m)	169.6	13.9	–	51.6 (dm)
11b	172.5 (s)	163.2 (m)	165.4	14.0	136.2 (m)	50.9 (dm)
11c	168.2 (d, $^3J = 4.7$)	161.6 (m)	163.9	13.7	53.4 (dm)	50.6 (dm)
11d	201.9 (s)	159.9 (q, $^3J = 4.4$)	167.5	14.9	–	57.3 (m)
11e	150.7 (s)	161.1 (q, $^3J = 4.4$)	163.3	15.1	132.7 (t, $^3J = 9.5$)	57.1 (m)
12b	154.9 (q, $^3J = 5.1$)	167.8 (m)	167.1	15.4, 17.3	138.1 (m)	52.7 (dm)
14a	172.5 (s)	167.4 (m)	178.9	14.3	136.3 (m)	52.9 (dm)
14b(I)[d]	171.5 (s)	161.6 (m)	164.3	13.6	139.8 (t, $^3J = 8$)	50.6 (dm)
14b(II)[d]	171.2 (s)	163.4 (m)	164.8	14.3	140.4 (t, $^3J = 8$)	50.4 (dm)
16a[d]	170.7 (q, $^3J = 4$)	168.5 (m)	178.5	15.7	–	52.1 (dm)
16b[d]	171.6 (q, $^3J = 4$)	166.7 (m)	177.6	15.4	–	51.3 (dm)
16d[d]	170.7 (q, $^3J = 3.7$)	167.9 (q, $^3J = 4.7$)	176.5	17.5	–	61.4 (m)

[a] δ (ppm) and J (Hz) at 75.5 MHz in $CDCl_3$ solutions (except for **14a**: $CDCl_3/CF_3CO_2H$).
[b] The ring atoms are numbered in such a way that the R^1 group is at the 6-position.
[c] Carbon of the substituent connected to the specified nitrogen atom.
[d] Other selected values for **9**: δ 23.2 (q, $^1J = 128$ Hz, CH_3 on the 2 position); for **14b(I)**: δ 22.8 and 23.3 (qm, $^1J = 128$ Hz, CH_3 of the *i* Pr group); for **14b(II)**: δ 22.9 and 23.0 (qm, $^1J = 128$ Hz); for **16a**: δ 52.6 (q, $^1J = 146$ Hz), 70.4 (s, C3), 115.9 (s, CN); for **16b**: δ 51.2, 52.7 (q, $^1J = 146$ Hz), 89.6 (s, C3), 164.8 (q, $^3J = 4$ Hz, CO_2Me); and for **16d**: δ 52.6 (q, $^1J = 147$ Hz), 69.6 (s, C3), 116.1 (s, CN).

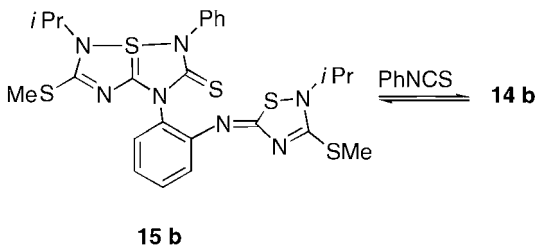
rotational isomers due to a severe steric hindrance (atropisomers [20]). Steric interactions induce a high energy barrier of one of the rotational processes around the central C–N bonds. Such an explanation was confirmed by a slow isomerization of each pure conformer **14b** on standing in $CDCl_3$ at room temperature. We obtained the same thermodynamic mixture of the above-mentioned atropisomers [21] and the thiadiazole derivative **15b** via a monoelimination of phenyl isothiocyanate (Scheme 6). Evaporation of the solution gave a residual solid that contained only the two conformers **14b** by a recombination with PhNCS! A high temperature ^{1}H NMR study (C_5D_5N, 95°C) did not show the coalescence of corresponding signals but promoted the fast formation of **15b** and decomposition by-products. Only one isomer was observed for the para-phenylene counterpart **14a**, which does not offer the same restricted rotation.



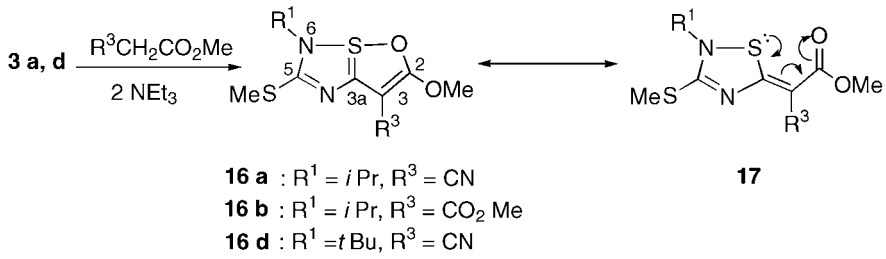
SCHEME 5

Reactions of 5-Chloro-1,2,4-thiadiazolium Chlorides **3** *with Active Methylene Anions*

Under similar conditions, treatment of substrates **3a,d** with triethylammonium salts of methyl cyanoacetate and dimethyl malonate afforded compounds which may be designated as 6*H*-1-oxa-6aλ^4-thia-4,6-diazapentalenes **16** (Scheme 7). In principle, the methyl 2-(1,2,4-thiazol-5-ylidene)cyanoacetates **17a,d** corresponding to monocyclic form **a** in Scheme 2 would be a mixture of *Z*/*E* isomers but only one stereoisomer was detected in the reaction medium from **3a,d** and cyanoacetic ester. Structures **16** were further supported by ^{13}C NMR (Table 1) and IR spectroscopies as well as X-ray crystallographic determination of **16a**.



SCHEME 6



16 a : R^1 = *i* Pr, R^3 = CN
16 b : R^1 = *i* Pr, R^3 = CO_2 Me
16 d : R^1 = *t* Bu, R^3 = CN

SCHEME 7

The prominent feature of IR spectra of **16a,d** is the appearance of a strong absorption band at about 1625 cm^{-1}. Such a carbonyl stretchching vibration is markedly affected with regard to the typical conjugated ester frequency in the 1655–1670 cm^{-1} region as previously reported for ethyl 2-(1,3-dithiol-2-ylidene)cyanoacetates [22] and alkyl 2-(5*H*-1,2,3-dithiazol-5-ylidene)cyanoacetates [23]. In the same way, thermostable adduct **16b** exhibits spectral data and strong $[M]^+$ in good agreement with the assigned structure.

The single crystal X-ray analysis of **16a** confirmed the expected coplanar structure of the heterapentalene framework, as depicted in Fig. 1 [24]. The angle between the thiadiazole ring and the isoxathiole reference plane was calculated to be 0.8(3)° and the heteroatoms of the N—S—O arrangement are approximately in a straight line with a 167.5(3)° bond angle. Other important result is the contact distance between the S and O atoms (2.395 Å), which is much shorter than the sum of the van der Waals radii (3.30 Å). The relatively short interatomic S—O distance, together with the coplanarity of the system, suggest the existence of a no-bond interaction by σ-delocalization. The C3a—S6a length (1.746 Å) lies in the range expected for thiapentalenes [3–5].

However, as suggested by one of the referees, the crystal data may be also considered in terms of the open-chain form **17a** where conjugated heteroatoms are held together by fractional S^+ and O^- charges (Scheme 7). Such monocyclic structure is rather consistent with the distance observed between the thiadiazole S and N6 atoms (1.724 Å), which is nearly equal to the sum of the covalent radii of

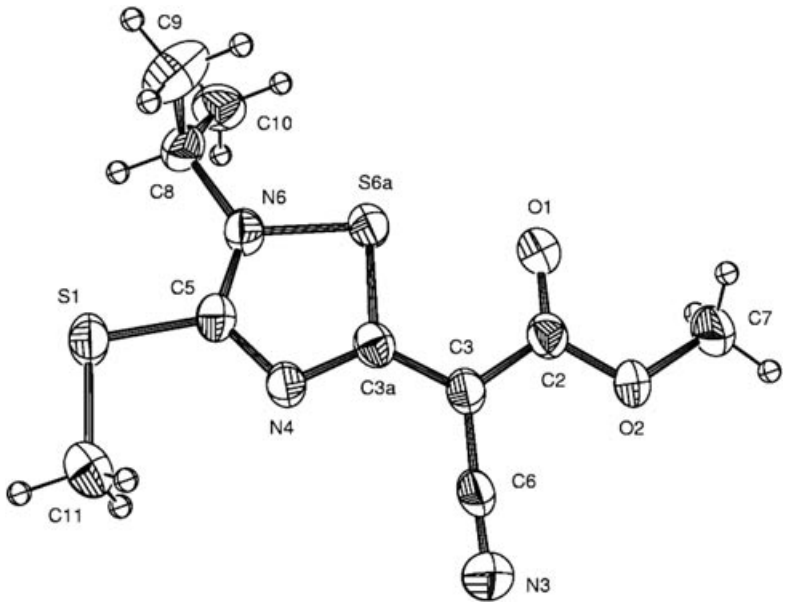


FIGURE 1 Solid-state molecular structure of **16a**. Selected bond lengths (Å): N6–C5 1.326 (8), C5–N4 1.331 (7), N4–C3a 1.344 (8), C3a–S6a 1.746 (6), S6a–N6 1.724 (5), C3a–C3 1.394 (8), C3–C2 1.422 (8), C2–O1 1.228 (7), O1–S6a 2.395 (5). Selected bond angles (°): N6–C5–N4 117.5 (5), C5–N4–C3a 109.4 (5), N4–C3a–S6a 114.4 (4), C3a–S6a–N6 87.2 (3), S6a–N6–C5 111.4 (4), S6a–C3a–C3 119.0 (4), C3a–C3–C2 117.2 (5), C3–C2–O1 121.9 (6), N4–C3a–C3 126.6 (5), O1–S6a–N6 167.5 (3); dihedral angle (N6–C5–N3–C3a–S6a/O1–C2–C3–C3a–S6a) 0.8 (3).

sulfur and nitrogen (1.74 Å). This molecular N—S dimension corresponds to a typical two-center two-electron bond length and agrees favorably with that of a structurally comparable 5-(benzoylimino)-2,5-dihydro-1,2,4-thiadiazole [25]. In the same way, the open structure **8** should be preferred over the bicyclic **9** (Scheme 4).

In conclusion, the reactivity of the readily available 5-chloro-1,2,4-thiadiazol-2-ium salts **3** was shown to be exclusively determined by the nucleophilic substitution of the chlorine atom. Reagents having two active hydrogen atoms were used for the one-step synthesis of new heterocycles, whose spectroscopic data and X-ray analysis suggest an hybridization between the canonical structures outlined in Scheme 2, with a great contribution from *b*. The formation and separation of two atropisomers in the case of compound **14b** also deserve to be emphasised.

EXPERIMENTAL

NMR spectra: Bruker AM 300 WB spectrometer (300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C) in $CDCl_3$ solution (internal standard Me_4Si) at room temperature unless otherwise indicated. *HRMS*: Centre Régional de Mesures Physiques de l'Ouest; Varian MAT 311 instrument, electron impact mode using a potential of 70 eV, except for compounds **12–15**: MS/MS ZabSpec TOF Micromass spectrometer, ionization mode positive LSIMS with Cs^+, matrix *m* NBA; only mass-spectral fragments with relative intensities of 10% or more are reported. *IR spectra*: Perkin-Elmer 1420 spectrophotometer, suspensions in nujol. *Elemental analyses*: Analytical laboratory, CNRS. *Solvents*: Carbon tetrachloride was dried over calcium chloride and distilled; tetrahydrofuran (THF) and dichloromethane were freshly distilled from NaH and P_2O_5, respectively.

Starting Materials: The imidoyl isothiocyanates **1** were conveniently prepared as previously described [1] from the insertion reaction of isocyanides R^1NC into the S—Cl bond of sulfenyl chlorides R^2SCl followed by the addition of ammonium thiocyanate in CCl_4 solution. The isopropyl isoselenocyanate [13b] and *S*-methyl-*N*-phenylisothiourea hydroiodide [26] were obtained according to known procedures.

Preparation of 5-Chloro-1,2,4-thiadiazol-2-ium Salts **3**

Methanesulfenyl chloride (3.3 g, 40 mmol) was dissolved in CCl_4 (10 ml) and added dropwise to a CCl_4 solution (30 ml) of imidoyl isothiocyanate **1** (20 mmol). A yellowish material precipitated immediately. The mixture was stirred at room temperature for 1 h. The salts **3** were collected by filtration, washed with anhydrous diethyl ether, dried in vacuo, and used for next reactions without further workup. They showed very low solubility in apolar solvents and were hygroscopic. For example, **3a** was allowed to stand overnight in the solid state under atmospheric moisture to give the isothiourea hydrochloride **5a**, which was recrystallized from CH_2Cl_2/diethyl ether. NMR spectra of salt **3d** were unable to be recorded because of the rapid elimination of *tert*-butyl chloride in $CDCl_3$ solution. This instability problem even prevented the salt **3e** to be isolated from the CCl_4 medium. After removal of the solvent, the 5-chloro-1,2,4-thiadiazoles were purified by distillation under reduced pressure (**6d**) or recrystallization from petroleum ether (**6e**).

*5-Chloro-2-isopropyl-3-(methylthio)-1,2,4-thiadiazol-2-ium Chloride (***3a***).* m.p. 184°C dec. (95% yield). ^{1}H NMR δ 1.68 (d, 6H, $J = 6.6$ Hz), 2.95 (s, 3H), 4.59 (m, 1H). ^{13}C NMR δ 16.6 (q, $^1J = 145$ Hz), 23.0 (qm, $^1J = 130$ Hz), 55.7 (dm, $^1J = 143$ Hz), 169.9 (m, C2), 179.3 (s, C5).

*5-Chloro-2-isopropyl-3-[(4-methylphenyl)thio]-1,2,4-thiadiazol-2-ium Chloride (***3b***).* m.p. 171°C (88% yield). ^{1}H NMR δ 1.76 (d, 6H, $J = 6.8$ Hz), 2.45 (s, 3H), 4.76 (m, 1H), 7.30, 7.55 (2d, 4H, $J = 7.8$ Hz).

*5-Chloro-2-(2,6-dimethylphenyl)-3-(methylthio)-1,2,4-thiadiazol-2-ium Chloride (***3c***).* m.p. 192–196°C dec. (80% yield). ^{1}H NMR δ 2.16 (s, 6H), 2.87 (s, 3H), 7.25 (m, 3H).

*2-tert-Butyl-5-chloro-3-(methylthio)-1,2,4-thiadiazol-2-ium Chloride (***3d***).* m.p. 135°C (96% yield). MS *m/z* (rel. int.): 166 [M-*t* BuCl]$^+$ (10), 131 (100), 105 (12), 99 (30).

*N-Isopropyl(methylthio)formamidine Hydrochloride (***5a***).* m.p. 154°C (62% yield). IR 3160, 1643, 1583 cm^{-1}. ^{1}H NMR δ 1.32 (d, 6H, $J = 6.4$ Hz), 2.79 (s, 3H), 3.77 (m, 1H), 8.90 (l, 2H), 9.55 (d, NH, $J = 7$ Hz). Anal. calcd. for $C_5H_{13}ClN_2S$: C, 35.61; H, 7.72; N, 16.62; S, 18.99. Found: C, 35.72; H, 7.71; N, 16.70; S, 18.54.

*5-Chloro-3-(methylthio)-1,2,4-thiadiazole (***6d***).* b.p. 50°C/0.025 Torr (Büchi Kugelrohr apparatus) (65% yield). ^{1}H NMR δ 2.70 (s). ^{13}C NMR δ 14.7 (q, $^1J = 142$ Hz), 172.0 (q, $^3J = 5$ Hz, C3), 173.2 (s, C5). MS *m/z* (rel. int.): 166 [M]$^+$ (80), 131 (20), 105 (50),

95 (100), 90 (40), 85 (30), 73 (30). Anal. calcd. for $C_3H_3ClN_2S_2$: C, 21.62; H, 1.80; Cl, 21.32; N, 16.81; S, 38.43. Found: C, 21.66; H, 1.76; Cl, 21.19; N, 16.65; S, 38.35.

*5-Chloro-3-[(2-nitrophenyl)thio]-1,2,4-thiadiazole (***6e***).* m.p. 87°C (55% yield). IR 1585, 1564, 1513 cm^{-1}. ^{13}C NMR δ 125.6, 127.5, 129.3, 133.4, 134.5, 149.2 (arom.C), 168.4 (s, C3), 174.3 (s, C5). MS *m/z*(rel. int.): 273 $[M]^+$ (80), 227 (60), 209 (50), 192 (65), 174 (100). Anal. calcd. for $C_8H_4ClN_3O_2S_2$: C, 35.10; H, 1.46; Cl, 12.98; N, 15.35; S, 23.40. Found: C, 35.09; H, 1.56; Cl, 12.98; N, 15.39; S, 23.67.

Reactions of Thiadiazolium Salts **3** *with Nitrogen Nucleophiles*

In a general procedure, salt **3** (5 mmol) was added to a solution of amino compound and triethylamine in THF (50 ml). Quantities of the amino nucleophile were the following: 1.47 g, 5 mmol for *S*-methyl-*N*-phenylisothiourea hydroiodide; 0.84 g, 5 mmol for *S*-methyl-*N*-isopropylisothiourea hydrochloride **5a**; 0.3 g, 5 mmol for acetamide; 0.54 g, 5 mmol for *p*-toluidine; 0.27 g, 2.5 mmol for 1,4- and 1,2-phenylenediamines. Three, 2, or 1 equiv. (0.5 g) of triethylamine were used as specified in Scheme 4. The suspension was stirred at room temperature for 2 h. A mixture of triethylammonium chloride and 5-iminothiadiazole hydrochlorides **10,13** was collected by filtration and slightly washed with H_2O to remove the ammonium salt. In other cases, concentration of the filtrate after elimination of the triethylammonium chloride gave a residue that was purified by recrystallization from methanol (**7a,c,d**) or flash chromatography on silica gel using diethyl ether/petroleum ether (2:1) as eluent (**7b, 9**). Selected ^{13}C NMR data for compounds **7a,c,d** and **9**: see Table 1.

6-Isopropyl-2,5-di(methylthio)-1-phenyl-6aλ^4*-thia-1,3,4,6-tetraazapentalene (***7a***).* m.p. 107°C (69% yield). ^1H NMR δ 1.31 (d, 6H, $J = 6.6$ Hz), 2.19, 2.54 (2s, 6H), 3.82 (m, 1H), 7.45 (m, 5H). MS calcd. for $C_{14}H_{18}N_4S_3$ *m/z*: 338.0694 $[M]^+$, found 338.0694; *m/z* (rel. int.): 338 (6), 291 (76), 265 (11), 249 (100). Anal. calcd. C, 49.70; H, 5.32; N, 16.56; S, 28.40. Found: C, 49.50; H, 5.33; N, 16.78; S, 28.69.

1,6-Diisopropyl-2,5-di(methylthio)-6aλ^4*-thia-1,3,4,6-tetraazapentalene (***7b***).* Orange viscous oil (75% yield). ^1H NMR δ 1.44 (d, 12H, $J = 6.6$ Hz), 2.70 (s, 6H), 4.10 (m, 2H); at −95°C (CD_2Cl_2) δ 1.40 (d), 2.59 (s), 4.02 (m). ^{13}C NMR δ 12.6 (q, $^1J = 143$ Hz), 22.4 (qm, $^1J = 127$ Hz), 48.4 (dm, $^1J = 136$ Hz), 160.8 (m, C2 and C5), 171 (s, C3a). MS calcd. for $C_{11}H_{20}N_4S_3$ *m/z*: 304.0850 $[M]^+$, found 304.0851; *m/z* (rel. int.): 304 (15), 289 (10), 257 (100), 215 (45), 173 (95).

6-(2,6-Dimethylphenyl)-2,5-di(methylthio)-1-phenyl-6aλ^4*-thia-1,3,4,6-tetraazapentalene (***7c***).* m.p. 187°C (59% yield). ^1H NMR δ 2.10 (s, 6H), 2.15, 2.52 (2s, 6H), 6.98 (m, 3H), 7.45 (m, 5H). MS calcd. for $C_{19}H_{20}N_4S_3$ *m/z*: 400.0850 $[M]^+$, found 400.0850; *m/z* (rel. int.): 400 (16), 353 (100), 327 (10), 280 (14), 248 (27). Anal. calcd. C, 57.00; H, 5.00; N, 14.00; S, 24.00. Found: C, 56.92; H, 4.98; N, 14.05; S, 24.23.

6-tert-Butyl-2,5-di(methylthio)-1-phenyl-6aλ^4*-thia-1,3,4,6-tetraazapentalene (***7d***).* m.p. 135°C (65% yield). ^1H NMR δ 1.47 (s, 9H), 2.19, 2.52 (2s, 6H), 7.40 (m, 5H). MS calcd. for $C_{15}H_{20}N_4S_3$ *m/z*: 352.0850 $[M]^+$, found 352.0851; *m/z* (rel. int.): 352 (2), 305 (38), 249 (100). Anal. calcd. C, 51.12; H, 5.68; N, 15.90; S, 27.27. Found: C, 51.06; H, 5.73; N, 15.99; S, 27.01.

6-Isopropyl-2-methyl-5-(methylthio)-1-oxa-6aλ^4*-thia-3,4,6-triazapentalene (***9***).* m.p. 112°C (pentane/diethyl ether) (56% yield). IR 1635, 1530, 1502 cm^{-1}. ^1H NMR δ 1.52 (d, 6H, $J = 6.6$ Hz), 2.41, 2.80 (2s, 6H), 4.40 (m, 1H). MS calcd. for $C_8H_{13}N_3OS_2$ *m/z*: 231.0500 $[M]^+$, found 231.0496; *m/z* (rel. int.): 231 (60), 216 (100), 174 (40), 147 (60). Anal. calcd. C, 41.56; H, 5.63; N, 18.18. Found: C, 41.31; H, 5.49; N, 17.96.

*2-Isopropyl-5-[(4-methylphenyl)imino]-3-(methylthio)-2,5-dihydro-1,2,4-thiadiazole Hydrochloride (***10a***).* m.p. 205–207°C (CH_2Cl_2/diethyl ether) (70% yield). ^1H NMR δ 1.55 (d, 6H, $J = 6.6$ Hz), 2.35, 2.86 (2s, 6H), 4.43 (m, 1H), 7.18, 7.62 (2d, 4H, $J = 8.3$ Hz), 13.00 (l, NH). ^{13}C NMR δ 16.3 (q, $^1J = 144$ Hz), 21.0 (qt, $^1J = 127$ Hz, $^3J = 4.3$ Hz), 22.7 (qm, $^1J = 129$ Hz), 53.2 (dm, $^1J = 141$ Hz), 120.3, 129.6, 135.1, 135.5 (arom. C), 169.3 (m, C3), 170.7 (s, C5). MS calcd. for $C_{13}H_{17}N_3S_2$ *m/z*: 279.0864 $[M - HCl]^+$, found 279.0867; *m/z* (rel. int.): 279 (100), 237 (60), 190 (20), 164 (65). Anal. calcd. for $C_{13}H_{18}ClN_3S_2$: C, 49.45; H, 5.71; N, 13.31; S, 20.29. Found: C, 49.39; H, 5.88; N, 13.35; S, 20.33.

*2-tert-Butyl-5-[(4-methylphenyl)imino]-3-(methylthio)-2,5-dihydro-1,2,4-thiadiazole Hydrochloride (***10d***).* m.p. 184–186°C (CH_2Cl_2/diethyl ether) (76% yield). ^1H NMR δ 1.77 (s, 9H), 2.32, 2.84 (2s, 6H), 7.15, 7.60 (2d, 4H, $J = 8.2$ Hz). ^{13}C NMR δ 18.1

(q, $^1J = 144$ Hz), 21.0 (qt, $^1J = 127$ Hz, $^3J = 4.3$ Hz), 24.9 (qm, $^1J = 129$ Hz), 62.8 (m), 120.4, 129.6, 135.2, 135.3 (arom. C), 166.7 (q, $^3J = 4.7$ Hz, C3), 169.2 (s, C5). MS calcd. for $C_{14}H_{19}N_3S_2$ *m/z*: 293.1020 $[M - HCl]^+$, found 293.1025; *m/z* (rel. int.): 293 (19), 237 (100), 190 (17).

*N,N′-Bis[2-isopropyl-3-(methylthio)-2,5-dihydro-1,2,4-thiadiazol-5-ylidene]-benzene-1,4-diamine Dihydrochloride (***13a***).* m.p. 278–282°C (CH_2Cl_2/diethyl ether) (76% yield). ^{1}H NMR δ 1.57 (d, 12H, $J = 6.6$ Hz), 2.90 (s, 6H), 4.46 (m, 2H), 7.80 (s, 4H). ^{13}C NMR δ 16.3 (q, $^1J = 145$ Hz), 22.8 (qm, $^1J = 129$ Hz), 53.4 (dm, $^1J = 142$ Hz), 121.0 (d, $^1J = 165$ Hz), 135.0 (m), 169.3 (m, C3), 170.9 (s, C5). MS calcd. for $C_{18}H_{25}N_6S_4$ *m/z*: 453.1024 $[M - HCl - Cl]^+$, found 453.1013. Anal. calcd. for $C_{18}H_{26}Cl_2N_6S_4$: C, 41.14; H, 4.95; N, 16.00. Found: C, 41.09; H, 4.96; N, 15.92.

*N,N′-Bis[2-isopropyl-3-(methylthio)-2,5-dihydro-1,2,4-thiadiazol-5-ylidene]-benzene-1,2-diamine Dihydrochloride (***13b***).* m.p. 210–212°C (CH_2Cl_2/diethyl ether) (77% yield). IR 3360, 1583, 1550 cm^{-1}. ^{1}H NMR δ 1.54 (d, 12H, $J = 6.6$ Hz), 2.69 (s, 6H), 4.40 (m, 2H), 7.45 (m, 4H), 12.00 (l, NH). MS calcd. for $C_{18}H_{25}N_6S_4$ *m/z*: 453.1024 $[M - HCl - Cl]^+$, found 453.1008; calcd. for $C_{18}H_{25}N_6S_3$ *m/z*: 421.1303 $[M - HCl - Cl - S]^+$, found 421.1324. Anal. calcd. for $C_{18}H_{26}Cl_2N_6S_4$: C, 41.14; H, 4.95; N, 16.00. Found: C, 41.37; H, 4.89; N, 16.29.

Addition of Heterocumulenes to 5-(Arylimino)-2,5-Dihydro-1,2,4-Thiadiazole Hydrochlorides **10, 13**

Salt **10a,d** (2.5 mmol) was added to a solution of triethylamine (0.3 g, 3 mmol) and carbon disulfide (1 ml) or appropriate iso-, isothio-, or isoselenocyanate (2.7 mmol) in anhydrous CH_2Cl_2 (35 ml). The mixture was stirred at room temperature for 1 h and concentrated in vacuo. Trituration of the residue with methanol allowed the filtration of the polyheterapentalenes **11a–e**. Compound **11b** was quantitatively alkylated by iodomethane in CH_2Cl_2 for 3 h at room temperature. After removal of the solvent, the crude methiodide **12b** was recrystallized from CH_2Cl_2/diethyl ether.

In a similar way, the synthesis of the phenylene-linked bis(thiatetraazapentalene) derivatives **14a,b** was performed from a mixture of dihydrochloride **13a,b** (0.8 g, 1.5 mmol), phenyl isothiocyanate (0.46 g, 3.4 mmol), and triethylamine (0.4 g, 4 mmol) in CH_2Cl_2 (40 ml). Compound **14a** rapidly precipitated (20 min) from the reaction medium as stable and colorless solid, which is quite insoluble in all usual solvents. It was washed with boiling acetone. The procedure for the purification of **14b** was the same as described for products **11**. The two isomers were separated by a column chromatography on silica-gel, using CH_2Cl_2/diethyl ether (10:1) as eluent or by a selective dissolution in acetone [isomer **(I)** insoluble, isomer (**II**) soluble].

A $CDCl_3$ solution of pure sample **14b**(**I**) or **14b**(**II**) was maintained at room temperature for 48 h to generate the two starting conformers **14b** in addition with phenyl isothiocyanate and monoelimination product **15b** [**14b**(**I**)/**14b**(**II**)/**15b** ≈ 18:42:40 by ^{1}H NMR estimation]. Compound **15b** was only identified in this mixture by NMR spectroscopies [^{1}H NMR δ 1.26, 1.31 (2d, 6H, $J = 6.5$ Hz), 1.42, 1.43 (2d, 6H, $J = 6.6$ Hz), 2.33, 2.70 (2s, 6H), 4.00, 4.25 (2m, 2H), 7.25–7.55 (m, 9H); selected ^{13}C NMR values: δ 131.8 (l), 140.3 (t, $^3J = 8.5$ Hz), 150.0 (l), 162.5 (m), 164.7 (s), 167.3 (s), 168.3 (m), 172.3 (s)].

*2,3-Dihydro-6-isopropyl-3-(4-methylphenyl)-5-(methylthio)-1,6aλ^4-dithia-3,4,6-triazapentalene-2-thione (***11a***).* m.p. 136–138°C (MeOH) (90% yield). IR 1530, 1040 cm^{-1}. ^{1}H NMR δ 1.44 (d, 6H, $J = 6.5$ Hz), 2.13, 2.42 (2s, 6H), 3.96 (m, 1H), 7.13, 7.32 (2d, 4H, $J = 8.3$ Hz). Anal. calcd. for $C_{14}H_{17}N_3S_4$: C, 47.32; H, 4.79; N, 11.83; S, 36.06. Found: C, 47.44; H, 4.86; N, 11.72; S, 35.89.

*2,3-Dihydro-6-isopropyl-3-(4-methylphenyl)-5-(methylthio)-1-phenyl-6aλ^4-thia-1,3,4,6-tetraazapentalene-2-thione (***11b***).* m.p. 168–170°C (MeOH) (87% yield). ^{1}H NMR δ 1.44 (d, 6H, $J = 6.6$ Hz), 2.37, 2.44 (2s, 6H), 4.05 (m, 1H), 7.25–7.55 (m, 9H). MS calcd. for $C_{20}H_{22}N_4S_3$ *m/z*: 414.1007 $[M]^+$, found 414.0983; *m/z* (rel. int.): 414 (1), 279 (80), 237 (50), 135 (100). Anal. calcd. C, 57.97; H, 5.31; N, 13.53; S, 23.19. Found: C, 58.27; H, 5.47; N, 13.63; S, 23.21.

*2,3-Dihydro-1,6-diisopropyl-3-(4-methylphenyl)-5-(methylthio)-6aλ^4-thia-1,3,4,6-tetraazapentalene-2-selone (***11c***).* m.p. 176°C (MeOH) (93% yield).^{1}H NMR δ 1.46, 1.51 (2d, 12H, $J = 6.6$ Hz), 2.30, 2.43 (2s, 6H), 4.00, 5.10 (2m, 2H), 7.25, 7.30 (2d, 4H, $J = 8.6$ Hz). MS calcd. for $C_{17}H_{24}N_4S_2Se$ *m/z*: 428.0608 $[M]^+$, found 428.0593; *m/z* (rel. int.): 428 (20), 278 (100), 236 (45), 190 (10). Anal. calcd. C, 47.78; H, 5.62; N, 13.11; S, 14.99. Found: C, 47.53; H, 5.61; N, 13.13; S, 14.97.

*6-tert-Butyl-2,3-dihydro-3-(4-methylphenyl)-5-(methylthio)-1,6aλ^4-dithia-3,4,6-triazapentalene-2-thione (***11d***).* m.p. 151°C (MeCN) (90% yield). ^{1}H NMR δ 1.57 (s, 9H), 2.10, 2.44 (2s, 6H), 7.12, 7.32

(2d, 4H, $J = 8.4$ Hz). Anal. calcd. for $C_{15}H_{19}N_3S_4$: C, 48.78; H, 5.15; N, 11.38; S, 34.68. Found: C, 49.09; H, 5.27; N, 11.61; S, 34.25.

*6-tert-Butyl-2,3-dihydro-3-(4-methylphenyl)-5-(methylthio)-6aλ⁴-thia-1,3,4,6-tetraazapentalene-2-one (***11e***).* m.p. 182°C (MeOH) (87% yield). IR 1685, 1590, 1530 cm^{-1}. ^1H NMR δ 1.62 (s, 9H), 2.37, 2.40 (2s, 6H), 7.10–7.70 (m, 9H). Anal. calcd. for $C_{21}H_{24}N_4OS_2$: C, 61.16; H, 5.82; N, 13.59; S, 15.53. Found: C, 61.18; H, 5.91; N, 13.85; S, 15.78.

*6-Isopropyl-3-(4-methylphenyl)-2,5-di(methylthio)-1-phenyl-6aλ⁴-thia-1,3,4,6-tetraaza-1H,3H,6H-pentalenium Iodide (***12b***).* m.p. 173–175°C. ^1H NMR δ 1.58 (d, 6H, $J = 6.7$ Hz), 2.06, 2.48, 2.51 (3s, 9H), 4.35 (m, 1H), 7.38–7.65 (m, 9H). MS calcd. for $C_{21}H_{25}N_4S_3$ *m/z*: 429.1241 $[M - I]^+$, found 429.1237.

*1,4-Bis[2,3-dihydro-6-isopropyl-5-(methylthio)-1-phenyl-6aλ⁴-thia-1,3,4,6-tetraaza-2-thioxopentalene-3-yl]-benzene (***14a***).* m.p. 226–228°C (98% yield). ^1H NMR ($CDCl_3/CF_3CO_2H$) δ 1.63 (d, 12H, $J = 6.6$ Hz), 2.41 (s, 6H), 4.36 (m, 2H), 7.15 (m, 4H), 7.35 (m, 6H), 7.99 (s, 4H). Anal. calcd. for $C_{32}H_{34}N_8S_6$: C, 53.19; H, 4.71; N, 15.51. Found: C, 53.44; H, 4.69; N, 15.20.

1,2-Bis[2,3-dihydro-6-isopropyl-5-(methylthio)-1-phenyl-6aλ⁴-thia-1,3,4,6-tetraaza-2-thioxopentalene-3-yl]-benzene (80% yield) **14b(I)**. m.p. 159–161°C (EtOH). ^1H NMR δ 1.27, 1.42 (2d, 12H, $J = 6.6$ Hz), 2.37 (s, 6H), 3.96 (m, 2H), 7.20–7.45 (m, 10H), 7.62 (m, 2H), 7.95 (m, 2H). MS calcd. for $C_{32}H_{34}N_8S_6$ *m/z*: 722.1231 $[M]^+$, found 722.1233; *m/z* (rel. int.): 722 (80), 588 (50), 453 (100), 419 (20), 291 (30). Oily crude **14b(II)**: ^1H NMR δ 1.47, 1.48 (2d, 12H, $J = 6.6$ Hz), 2.50 (s, 6H), 4.05 (m, 2H), 7.20–7.40 (m, 10H), 7.66 (m, 2H), 7.85 (m, 2H). MS found 722.1221; the same fragments as described for **14b(I)**.

Reactions of Thiadiazolium Salts **3** *with Active Methylene Compounds*

Salt **3a,d** (5 mmol) was added to a solution of triethylamine (1.2 g, 12 mmol) and methyl cyanoacetate (0.55 g) or dimethyl malonate (0.72 g, 5.5 mmol) in dry THF (30 ml). The suspension was stirred at room temperature for 0.5 h and the triethylammonium chloride was filtered off. Concentration of the filtrate left a brownish residual syrup, which was washed twice with petroleum ether and triturated with MeOH to afford the polyheterapentalenes **16** as the insoluble portion.

*3-Cyano-6-isopropyl-2-methoxy-5-(methylthio)-1-oxa-6aλ⁴-thia-4,6-diazapentalene (***16a***).* m.p. 173°C (MeOH) (59% yield). IR 2205, 1620 cm^{-1}. ^1H NMR δ 1.50 (d, 6H, $J = 6.6$ Hz), 2.82, 3.85 (2s, 6H), 4.40 (m, 1H). MS calcd. for $C_{10}H_{13}N_3O_2S_2$ *m/z*: 271.0449 $[M]^+$, found 271.0446; *m/z* (rel. int.): 271 (63), 229 (100), 197 (71). Anal. calcd. C, 44.28; H, 4.79; N, 15.49; S, 23.61. Found: C, 44.34; H, 4.79; N, 15.30; S, 23.31.

*6-Isopropyl-2-methoxy-3-(methoxycarbonyl)-5-(methylthio)-1-oxa-6aλ⁴-thia-4,6-diazapentalene (***16b***).* m.p. 136°C (MeOH) (42% yield). IR 1685, 1585 cm^{-1}. ^1H NMR δ 1.52 (d, 6H, $J = 6.6$ Hz), 2.87, 3.86, 3.90 (3s, 9H), 4.35 (m, 1H). MS calcd. for $C_{11}H_{16}N_2O_4S_2$ *m/z*: 304.0551 $[M]^+$, found 304.0524; *m/z* (rel. int.): 304 (100), 273 (19), 262 (23), 231 (82), 230 (43), 204 (31). Anal. calcd. C, 43.42; H, 5.26; N, 9.21. Found: C, 43.61; H, 5.28; N, 9.13.

*6-tert-Butyl-3-cyano-2-methoxy-5-(methylthio)-1-oxa-6aλ⁴-thia-4,6-diazapentalene (***16d***).* m.p. 240°C ($MeOH/CH_2Cl_2$) (58% yield). IR 2200, 1630, 1495 cm^{-1}. ^1H NMR δ 1.74 (s, 9H), 2.82, 3.85 (2s, 6H). MS calcd. for $C_{11}H_{15}N_3O_2S_2$ *m/z*: 285.0606 $[M]^+$, found 285.0609; *m/z* (rel. int.): 285 (12), 229 (74), 197 (22), 105 (17), 57 (100). Anal. calcd. C, 46.31; H, 5.26; N, 14.73; S, 22.45. Found: C, 46.43; H, 5.23; N, 14.72; S, 22.20.

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