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Reactions of 3-Benzylidene-3*H*-1,2-dithioles and 3-Alkyl-1λ^4,2-dithiol-1-ylium Salts with Isonitriles: A Synthesis of 1,6aλ^4-Dithia-6-azapentalenes*

Yunxiang Ding and David H. Reid**

Department of Chemistry, University of the Witwatersrand, Wits 2050, Johannesburg, South Africa

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ABSTRACT

*1,6aλ^4-Dithia-6-azapentalenes (**7a**)–(**7h**), (**12a**), and (**12b**) have been synthesized by the reaction of 5-aryl-3-benzylidene-3H-1,2-dithioles with isonitriles in the presence of phosphoryl chloride and by the reaction of 3-benzyl- and 3-methyl-1λ^4, 2-dithiol-1-ylium salts with isonitriles. Possible mechanisms for these reactions are discussed.* © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**: 479–485, 1997

INTRODUCTION

3-Methyl-and 3-(substituted methyl)-1λ^4,2-dithiol-1-ylium salts (**1**) are readily deprotonated by weak bases to give 3-methylene-3*H*-1,2-dithioles (**2**) whose stability depends mainly on the nature of R^1 and R^2 [1,2]. 3-Alkylidene derivatives (**2;** R^1, R^2 = H, alkyl) are transient species that decompose rapidly in solution and cannot be isolated [3]. The 3-methylene-3*H*-1,2-dithiole system is stabilized by conjugation with electron-acceptor groups (C=O, C≡N) in R^1 and R^2 [4]. We have shown recently that conjugation with a phenyl group is sufficient to stabilize the 3-methylene-3*H*-1,2-dithiole system. Thus deprotonation of the iodides (**3a**)–(**3d**) with aqueous sodium carbonate gave the 5-aryl-3-benzylidene-3*H*-1,2-dithioles (**4a**)–(**4d**), respectively, as stable crystalline compounds [5]. Dithiolylium salts (**1**; R^1 = R^2 = H or R^1 = H, R^2 = alkyl) react readily with a variety of electrophiles to give substitution products or substitution intermediates (**2**; R^1 = CHO, NO, ArN_2) that undergo electrocyclization in situ to give 1,6,6aλ^4-triheterapentalenes [6]. These reactions doubtless proceed via intermediate 3-methylene-3*H*-1,2-dithioles (**2**) that are in equilibrium with their conjugate acids (**1**) [7]. In this article, we describe a new general synthesis of 1,6aλ^4-dithia-6-azapentalenes involving the reaction of isonitriles with 3-benzyl-1λ^4,2-dithiol-1-ylium salts, 3-methyl-1λ^4,2-dithiol-1-ylium salts, and 3-methylene-3*H*-1,2-dithioles.

RESULTS AND DISCUSSION

A ^{1}H-NMR study confirmed that the dithioles (**4a**)–(**4d**) obtained by deprotonation of the iodides (**3a**)–(**3d**) react with acids to generate the respective 1,2-dithiolylium ions. The spectra of the dithioles (**4a**)–(**4d**) in CF_3COOH were identical in pattern with the spectra of the corresponding iodide precursors (**3a**)–(**3d**) in CF_3COOD [5], demonstrating that the dithioles (**4a**)–(**4d**) are protonated in CF_3COOH to give

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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**To whom correspondence should be addressed.

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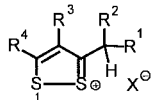
the trifluoroacetates (**5a**)–(**5d**). The spectra of the dithioles (**4a**)–(**4d**) in CF_3COOH show a 2H singlet arising from the CH_2 group, whereas the spectra of (**4a**)–(**4d**) in CF_3COOD show a 1H signal arising from the CHD group in the trifluoroacetates (**6a**)–(**6d**). The CHD signals of (**6a**) and (**6b**) were unresolved broadened triplets, and those of (**6c**) and (**6d**) were broadened singlets, due to geminal H-D coupling. The chemical shifts of the CH_2 group in (**3a**)–(**3d**) and (**5a**)–(**5d**) and the chemical shifts of the CHD group in (**6a**)–(**6d**) occur in the narrow range δ 4.64–4.80. The chemical shift of 4-H in (3a)–(3d), (**5a**)–(**5d**), and (**6a**)–(**6d**) correspondingly occur in a narrow range δ 8.35–8.73 (Table 1).

Isonitriles RN = C undergo α-addition reactions with a wide variety of reagents *X-Y* to give products of structure RN = C*XY* [8,9]. Relevant to the work described in this article are the addition reactions of isonitriles with hydrogen halides H*X* (*X* = Cl, Br, I) that give the highly reactive formimidoyl halides RN = CH*X* as the primary reaction products. The N = C carbon atom in isonitriles can behave as a nucleophilic or electrophilic center, depending on the reaction. We attempted first to bring about thermal cycloaddition reactions of the dithioles (**4**) with isonitriles to give 1,6aλ^4-dithia-6-azapentalenes (**7**) (Scheme 1), but none of the desired product was obtained even after prolonged heating of the reactants up to 150°C. In contrast, the dithioles (**4**) reacted readily with isonitriles in the presence of phosphoryl chloride in dichloromethane at room temperature to give the 1,6aλ^4-dithia-6-azapentalenes (**7a**)–(**7h**) in high yield. We think that the phosphoryl chloride functions by reacting with adventitious moisture in the air to form HCl, the actual catalyst in these re-



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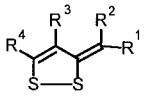

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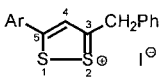

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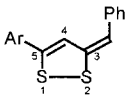

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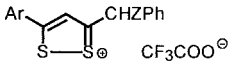
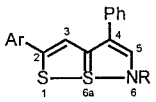


(5) Z = H

(6) Z = D

(3a), (4a), (5a), (6a)	Ar = Ph
(3b), (4b), (5b), (6b)	Ar = 4-$MeOC_6H_4$
(3c), (4c), (5c), (6c)	Ar = 4-ClC_6H_4
(3d), (4d), (5d), (6d)	Ar = 2-Thienyl



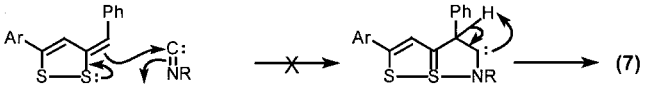
(7)

	Ar	R
(7a)	Ph	4-MeC_6H_4
(7b)	Ph	4-$MeOC_6H_4$
(7c)	4-$MeOC_6H_4$	4-MeC_6H_4
(7d)	4-$MeOC_6H_4$	4-$MeOC_6H_4$
(7e)	4-ClC_6H_4	4-MeC_6H_4
(7f)	4-ClC_6H_4	4-$MeOC_6H_4$
(7g)	2-Thienyl	4-MeC_6H_4
(7h)	2-Thienyl	4-$MeOC_6H_4$

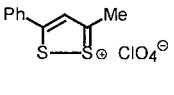
TABLE 1 ^{1}H-NMR Chemical Shifts (δ) of CH_2, CHD, and 4-H in the 1δ^4, 2-Dithiol-1-ylium Salts (**3**)[a], (**5**)[b] and (**6**)[a]

Compound	*CH_2*	*CHD*	*4-H*
(**3a**)[c]	4.80		8.73
(**5a**)	4.76		8.64
(**6a**)		4.73	8.63
(**3b**)[c]	4.72		8.59
(**5b**)	4.67		8.47
(**6b**)		4.66	8.47
(**3c**)[c]	4.79		8.72
(**5c**)	4.73		8.60
(**6c**)		4.74	8.63
(**3d**)[c]	4.70		8.46
(**5d**)	4.64		8.35
(**6d**)		4.64	8.37

[a]Solvent CF_3COOD.
[b]Solvent CF_3COOH.
[c]Data from Ref. [5].



SCHEME 1



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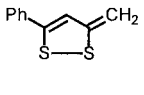
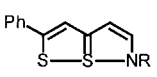
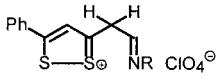


(11)



(12a) R = 4-MeC$_6$H$_4$

(12b) R = 4-MeOC$_6$H$_4$



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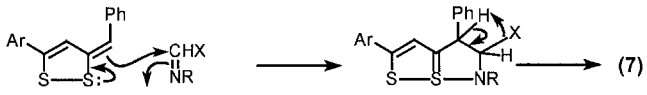
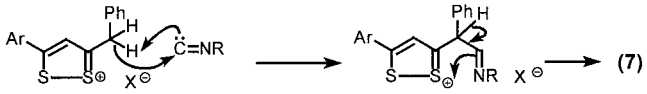


SCHEME 2



(8) **(9)**

SCHEME 3

actions. Two possible mechanisms could account for the catalytic effect of HCl on the reactions of the dithioles (**4**) with isonitriles. In the first mechanism, the isonitrile reacts with HCl to form the electrophilic formimidoyl chloride RN=CHCl, which reacts with the dithiole (**4**) to give eventually the product (**7**) in an overall cycloaddition process (Scheme 2, X = Cl). In the second mechanism, the HCl protonates the dithiole (**4**) to give the corresponding dithiolylium chloride (**8**; X = Cl). The isonitrile then undergoes an α-addition reaction of the dithiolylium cation in (**8**) at the CH_2 group to give the intermediate salt (**9**; X = Cl) that loses HCl to form the product (**7**) (Scheme 3).

Consideration of the foregoing mechanisms led us to carry out reactions of dithiolylium salts with isonitriles. We have found that the iodide (**3b**) reacts with 4-methylphenyl isonitrile and 4-methoxyphenyl isonitrile in dichloromethane at room temperature to give the dithiaazapentalenes (**7c**) and (**7d**), respectively, nearly quantitatively. The dithiolylium perchlorate (**10**), whose deprotonation product (**11**) is unstable [3,10], reacted with 4-methylphenyl isonitrile and 4-methoxyphenyl isonitrile to give the dithiaazapentalenes (**12a**) and (**12b**), albeit in low yield. This direct route from 1,2,-dithiol-1-ylium salts to 1,6aλ^4-dithia-6-azapentalenes has the merit of being short, and it can be applied to those 1,2-dithiol-1-ylium salts from which stable 3-methylene-3*H*-1,2-dithioles cannot be isolated [11].

The reactions of the iodide (**3b**) with isonitriles to give (**7c**) and (**7d**) is in accord with the α-addition mechanism (Scheme 3, X = 1). The mechanism in Scheme 2 might also be valid because exchange of HI between the iodide (**3b**) and the isonitrile RN=C would give the dithiole (**4b**) together with the formimidoyl iodide RN=CHI. Cycloadditon of the formimidoyl iodide to the dithiole (**4b**) would give the product (**7**) according to Scheme 2 (X = I).

In the reactions of the perchlorate (**10**) with isonitriles, the α-addition mechanism (Scheme 3, X = ClO_4) could operate. Alternatively, exchange of $HClO_4$ between (**10**) and the isonitrile would give the transient unstable dithiole (**11**) together with a formimidoyl perchlorate. Due to the low nucleophilicity of the perchlorate ion, the isonitrile might instead form the formonitrilium perchlorate ion pair $RN^+{\equiv}CH\ ClO_4^-$. Electrophilic attack of the dithiole (**11**) by the formonitrilium ion would produce the intermediate dithiolylium salt (**13**) that, on being deprotonated, would give the product (**12**).

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H-NMR spectra were determined at 200.13 or 400.13 MHz and ^{13}C-NMR spectra were determined at 50.32 or 100.62 MHz with Bruker AC200 and DRX400 spectrometers, respectively. ^{1}H- and ^{13}C-NMR spectra were obtained using solutions in $CDCl_3$, unless otherwise stated. ^{1}H-NMR chemical shifts are given in parts per million downfield from tetramethylsilane as internal reference. Unless otherwise stated, δ values refer to singlet absorptions. Data are given in the following order: δ value, number of protons, multiplicity (d, doublet; dd, double doublet; t, triplet; m, multiplet; br, broad), J (Hz), and assignment. ^{1}H-NMR signals assigned to the pairs of *o*-and *m*-protons of *p*-substituted phenyl groups correspond to the midpoints between the two most intense signals in the AA′ and BB′ multiplets. ^{13}C-NMR chemical shifts are given relative to the central deuteriochloroform peak taken as δ77.0 and are proton-decoupled values.

Extracts were dried over sodium sulfate. Solvents were removed from extracts and chromatographic eluates at reduced pressure with a rotary evaporator. Petroleum ether denotes an alkane mixture consisting mainly of hexane, of boiling

range 60–80°C. Benzene, dichloromethane, and hexane were dried by standard procedures and distilled before use. Solvent mixtures are described in ratios by volume. 4-Methylphenyl isonitrile and 4-methoxyphenyl isonitrile were prepared according to the literature method [12] and were redistilled immediately before use. The dithiolylium perchlorate (**10**) was prepared according to the literature method [13]. Column chromatography was carried out with silica (85–200 mesh).

Reactions of the 5-Aryl-3-benzylidene-3H-1,2-dithioles (**4a**)–(**4d**) *with Isonitriles and Phosphoryl Chloride: Synthesis of the 1,6aλ^4-Dithia-6-azapentalenes* (**7a**)–(**7h**)

General Procedure. The dithiole (**4**) (1 mmol), the isonitrile (1.1 mmol), and phosphoryl chloride (1.1 mmol) were dissolved in dichloromethane (30 mL) in that order, and the solution was allowed to stand overnight at room temperature. A solution of sodium carbonate (583 mg, 5.5 mmol) in water was added to the solution (effervescence), and the mixture was extracted with benzene (3 × 100 mL). The combined extracts were dried, the solvent was removed, and the residue was chromatographed on silica (35 × 1.9 cm) with benzene-petroleum ether (1:1) for elution. The colored fractions were collected, the solvent was removed, and the residue was recrystallized from CH_2Cl_2-hexane to give the dithiaazapentalene (**7**). Experimental details, physical properties, and analytical data are given in Table 2.

Synthesis of 1,6aλ^4-Dithia-6-azapentalenes by the Reaction of 3-Alkyl-1λ^4,2-dithiol-1-ylium Salts with Isonitriles

2-(4-Methoxyphenyl)-6-(4-methylphenyl)-4-phenyl-1,6aλ^4-dithia-6-azapentalene (**7c**). The iodide (**3b**) (426 mg, 1 mmol) and 4-methylphenyl isonitrile (129 mg, 1.1 mmol) were dissolved in dichloromethane (30 mL), and the solution was kept at room temperature overnight. A solution of sodium carbonate (530 mg, 5 mmol) in water was added to the solution, and the mixture was extracted with benzene (3 × 100 mL). Solvent was removed from the dried combined extracts, and the residue was chromatographed on silica (35 × 1.9 cm) with benzene-petroleum ether for elution. The orange fraction was collected, the solvent was removed, and the remaining solid was recrystallized from dichloromethane-hexane to give the dithiaazapentalene (**7c**) (380 mg, 91%) as orange-red crystals, mp 178–179°C, identical with the product from the reaction of the dithiole (**4b**) with 4-methylphenyl isonitrile and phosphoryl chloride.

2,6-Bis-(4-methoxyphenyl)-4-phenyl-1,6aλ^4-dithia-6-azapentalene (**7d**). The procedure was identical with that of the preceding experiment, with 4-methoxyphenyl isonitrile (147 mg, 1.1 mmol) in place of 4-methylphenyl isonitrile. The dithiaazapentalene (**7d**) (405 mg, 94%) was obtained as orange-red needles, mp 186–187°C, identical with the product from the reaction of the dithiole (**4b**) with 4-methoxyphenyl isonitrile and phosphoryl chloride.

6-(4-Methylphenyl)-2-phenyl-1,6aλ^4-dithia-6-aza-

TABLE 2 Preparation, Physical Properties, and Analytical Data of Compounds (**7a**)–(**7h**)

						Found (%) (Required)		
Compound	*Dithiole (**4**)*	*RNC*	*Yield (%)*	*Mp (°C)*	*Formula*	*C*	*H*	*N*
(**7a**)	(**4a**)	4-MeC_6H_4NC	96	215–216	$C_{24}H_{19}NS_2$	74.67 (74.77)	4.85 (4.97)	3.63 (3.63)
(**7b**)	(**4a**)	4-MeOC_6H_4NC	95	155–156	$C_{24}H_{19}NOS_2$	71.58 (71.79)	4.66 (4.77)	3.47 (3.49)
(**7c**)	(**4b**)	4-MeC_6H_4NC	90	178–179	$C_{25}H_{21}NOS_2$	72.49 (72.25)	5.15 (5.09)	3.33 (3.37)
(**7d**)	(**4b**)	4-MeOC_6H_4NC	96	186–187	$C_{25}H_{21}NO_2S_2$	69.63 (69.58)	4.83 (4.90)	3.25 (3.25)
(**7e**)	(**4c**)	4-MeC_6H_4NC	94	224–225	$C_{24}H_{18}ClNS_2$	67.98 (68.63)	4.30 (4.32)	3.30 (3.33)
(**7f**)	(**4c**)	4-MeOC_6H_4NC	95	214–215	$C_{24}H_{18}ClNOS_2$	66.06 (66.12)	4.04 (4.16)	3.37 (3.21)
(**7g**)	(**4d**)	4-MeC_6H_4NC	62	191–193	$C_{22}H_{17}NS_3$	66.90 (67.48)	4.26 (4.38)	3.45 (3.58)
(**7h**)	(**4d**)	4-MeOC_6H_4NC	67	150–151	$C_{22}N_{17}NOS_3$	64.55 (64.83)	4.17 (4.20)	3.41 (3.44)

pentalene (**12a**). 4-Methylphenyl isonitrile (1.29 g, 11 mmol) was added to a solution of the perchlorate (**10**) (2.93 g, 10 mmol) in dichloromethane (30 ml), and the resulting solution was allowed to stand at room temperature overnight. A solution of sodium carbonate (5.3 g, 50 mmol) in water was added to the solution, and the mixture was extracted with benzene (3 × 100 mL). Solvent was removed from the dried extracts, and the residue was chromatographed on silica (35 × 1.9 cm) with benzene-petroleum ether for elution. The organic eluates were collected, the solvent was removed, and the remaining solid was recrystallized from dichloromethane-hexane to give the dithiaazapentalene (**12a**) (330 mg, 10.7%) as orange-red crystals, mp 181–182°C. Anal. calcd for $C_{18}H_{15}NS_2$: C, 69.86; H, 4.88; N, 4.53. Found: C, 69.57; H, 4.84; N, 4.71%.

6-(4-Methoxyphenyl)-2-phenyl-1,6aλ^4-dithia-6-azapentalene (**12b**). The procedure was identical with that of the preceding experiment, with 4-methoxyphenyl isonitrile (1.47 g, 11 mmol) in place of 4-methylphenyl isonitrile. The dithiaazapentalene (**12b**) (363 mg, 11.2%) was obtained as orange-red needles, mp 187–188°C. Anal. calcd for $C_{18}H_{15}NOS_3$: C, 66.43; H, 4.65; N, 4.30. Found: C, 66.20; H, 4.63; N, 4.50%.

^{1}H-NMR Spectral Data for the 1λ^4,2-Dithiol-1-ylium Trifluoroacetates (**5a**)–(**5d**) *and* (**6a**)–(**6d**)

The ^{1}H-NMR spectra of (**5a**)–(**5d**) and (**6a**)–(**6d**) were obtained from solutions of the corresponding dithioles (**4a**)–(**4d**) in CF_3COOH and CF_3COOD, respectively.

3-Benzyl-5-phenyl-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**5a**). ^{1}H NMR: δ 4.76 (2H, CH_2), 7.46–7.90 (8H, m, *Ph*CH_2 and 2*m*- + *p*-protons of 5-Ph), 7.99 (2H, d, *o*-protons of 5-Ph), 8.64 (4-H).

3-(α-Deuteriobenzyl)-5-phenyl-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**6a**). ^{1}H NMR: δ 4.73 (1H, unresolved t, CHD), 7.44–7.89 (8H, m, *Ph*CHD + 2*m*- + *p*-protons of 5-Ph), 7.98 (2H, d, *o*-protons of 5-Ph), 8.63 (1H, 4-H).

3-Benzyl-5-(4-methoxyphenyl)-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**5b**). ^{1}H NMR: δ 4.04 (3H, OMe), 4.67 (2H, CH_2), 7.21 (2H, d, *m*-protons of 5-Ar), 7.42–7.51 (5H, m, Ph), 7.99 (2H, d, *o*-protons of 5-Ar), 8.47 (1H, 4-H).

3-(α-Deuteriobenzyl)-5-(4-methoxyphenyl)-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**6b**). ^{1}H NMR: δ 4.04 (3H, OMe), 4.66 (1H, unresolved t, CHD), 7.22 (2H, d, *m*-protons of 5-Ar), 7.42–7.53 (5H, m, Ph), 8.00 (2H, d, *o*-protons of 5-Ar), 8.47 (1H, 4-H).

3-Benzyl-5-(4-chlorophenyl)-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**5c**). ^{1}H NMR: δ 4.73 (2H, CH_2), 7.41–7.54 (5H, m, Ph), 7.67 (2H, d, *m*-protons of 5-Ar), 7.91 (2H, d, *o*-protons of 5-Ar), 8.60 (1H, 4-H).

5-(4-Chlorophenyl)-3-(α-deuteriobenzyl)-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**6c**). ^{1}H NMR: δ 4.74 (1H, brs, CHD), 7.44–7.55 (5H, m, Ph), 7.69 (2H, d, *m*-protons of 5-Ar), 7.93 (2H, d, *o*-protons of 5-Ar), 8.63 (1H, 4-H).

3-Benzyl-5-(2-thienyl)-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**5d**). ^{1}H NMR: δ 4.64 (2H, CH_2), 7.40–7.51 (6H, m, Ph + 4-H of thienyl), 8.07 (1H, dd), 8.12 (1H, dd) (3-H, 5-H of thienyl), 8.35 (1H, 4-H).

3-(α-Deuteriobenzyl)-5-(2-thienyl)-1λ^4,2-dithiol-1-ylium Trifluoroacetate (**6d**). ^{1}H NMR: δ 4.64 (1H, brs, CHD), 7.41–7.53 (6H, m, Ph + 4-H of thienyl), 8.08 (1H, dd), 8.13 (1H, dd) (3-H, 5-H of thienyl), 8.37 (1H, 4-H).

^{1}H and ^{13}C-NMR Spectral Data for the 1,6aλ^4-Dithia-6-azapentalenes (**7a**)–(**7h**), (**12a**), *and* (**12b**)

*6-(4-Methylphenyl)-2,4-diphenyl-1,6aλ^4-dithia-6-azapentalene (**7a**).* ^{1}H NMR: δ 2.38 (3H, Me), 7.24 (2H, *m*-protons of 6-Ar), 7.32–7.53 (10H, m, 2*m*- + *p*-protons of 2-Ph; 4-Ph, *o*-protons of 6-Ar), 7.73 (2H, *o*-protons of 2-Ph), 7.95 (1H, 3-H), 8.26 (1H, 5-H). ^{13}C NMR: δ 21.0 (Me), 117.4 (C-3), 122.0, 127.5, 128.5, 129.0, 129.1, 130.3 [C-2(6), C-3(5) of 2-Ph, 4-Ph, 6-Ar], 126.6, 127.5, 129.1, 136.1, 136.3, 139.1, 139.4 (C-4; C-1, C-4 of 2-Ph, 4-Ph, 6-Ar), 143.3 (C-5), 166.4 (C-2), 170.6 (C-3a).

6-(4-Methoxyphenyl)-2,4-diphenyl-1,6aλ^4-dithia-6-azapentalene (**7b**). ^{1}H NMR: δ 3.83 (3H, OMe), 6.96 (2H, *m*-protons of 6-Ar), 7.32–7.52 (10H, m, 2*m*- + *p*-protons of 2-Ph; 4-Ph, *o*-protons of 6-Ar), 7.73 (2H, *o*-protons of 2-Ph), 7.94 (1H, 3-H), 8.22 (1H, 5-H). ^{13}C NMR: δ 55.6 (OMe), 114.9 [C-3(5) of 6-Ar], 117.3 (C-3), 123.4, 127.4, 128.5, 128.95, 129.0 [C-2(6), C-3(5) of 2-Ph, 4-Ph; C-2(6) of 6-Ar], 126.5, 127.5, 129.1, 135.1, 136.1, 139.0 (C-4; C-1, C-4 of 2-Ph, 4-Ph; C-1 of 6-Ar), 143.4 (C-5), 158.3 (C-4 of 6-Ar), 166.0 (C-2), 170.1 (C-3a).

2-(4-Methoxyphenyl)-6-(4-methylphenyl)-4-phenyl-1,6aλ^4-dithia-6-azapentalene (**7c**). ^{1}H

NMR: δ 2.37 (3H, Me), 3.80 (3H, OMe), 6.87 (2H, *m*-protons of 2-Ar), 7.20–7.50 (9H, m, 4-Ph, *o*- + *m*-protons of 6-Ar), 7.69 (2H, *o*-protons of 2-Ar), 7.89 (1H, 3-H), 8.23 (1H, 5-H). ^{13}C NMR: δ 21.0 (Me), 55.3 (OMe), 113.8 [C-3(5) of 2-Ar], 116.2 (C-3), 121.8, 128.8, 128.9, 129.0, 130.2 [C-2(6) of 2-Ar, C-2(6), C-3(5) of 4-Ph, 6-Ar], 126.0, 127.4, 131.8, 136.1, 136.3, 139.4 (C-4; C-1 of 2-Ar; C-1, C-4 of 6-Ar), 143.2 (C-5), 160.6 (C-4 of 2-Ar), 166.5 (C-2), 170.4 (C-3a).

2,6-Bis-(*4-methoxyphenyl*)*-4-phenyl-1,6a*λ^4*-dithia-6-azapentalene* (**7d**). ^{1}H NMR: δ 3.80 (3H), 3.82 (3H) (2 $\times$ OMe), 6.87 (2H, *m*-protons of 6-Ar), 6.95 (2H, *m*-protons of 2-Ar), 7.34–7.51 (7H, m, 4-Ph, *o*-protons of 6-Ar), 7.69 (2H, *o*-protons of 2-Ar), 7.88 (1H, 3-H), 8.19 (1H, 5-H). ^{13}C NMR: δ 55.3, 55.5 (2 $\times$ OMe), 113.8 [C-3(5) of 6-Ar], 114.9 [C-3(5) of 2-Ar], 116.2 (C-3), 123.2 [C-2(6) of 6-Ar], 125.9, 127.4, 131.8, 135.3, 136.3 (C-4: C-1 of 2-Ar, 6-Ar; C-1, C-4 of 4-Ph), 128.8, 128.9, 129.0 [C-2(6) of 2-Ar; C-2(6), C-3(5) of 4-Ph], 143.3 (C-5), 158.2 (C-4 of 6-Ar), 160.6 (C-4 of 2-Ar), 166.2 (C-2), 169.9 (C-3a).

2-(*4-Chlorophenyl*)*-6-*(*4-methylphenyl*)*-4-phenyl-1,6a*λ^4*-dithia-6-azapentalene* (**7e**). ^{1}H NMR: δ 2.40 (3H, Me), 7.25–7.52 (11H, m, *m*-protons of 2-Ar, 4-Ph, *o*- and *m*-protons of 6-Ar), 7.67–7.69 (2H, m, *o*-protons of 2-Ar), 7.92 (1H, 3-H), 8.28 (1H, 5-H). ^{13}C NMR: δ 21.1 (Me), 117.1 (C-3), 122.1, 128.6, 128.7, 127.06, 129.09, 130.4 [C-2(6), C-3(5) of 2-Ar, 4-Ph, 6-Ar], 127.1, 127.7, 135.1, 135.8, 136.6, 137.8, 138.9 (C-4; C-1, C-4 of 2-Ar, 4-Ph, 6-Ar), 143.0 (C-5), 166.6 (C-2), 169.8 (C-3a).

2-(*4-Chlorophenyl*)*-6-4-*(*methoxyphenyl*)*-4-phenyl-1,6a*λ^4*-dithia-6-azapentalene* (**7f**). ^{1}H NMR: δ 3.86 (3H, OMe), 7.00 (2H, *m*-protons of 6-Ar), 7.33 (2H, *o*-protons of 6-Ar), 7.39–7.52 (7H, m, *m*-protons of 2-Ar; 4-Ph), 7.68 (2H, *o*-protons of 2-Ar), 7.92 (3-H), 8.25 (5-H). ^{13}C NMR: δ 55.6 (OMe), 115.0 [C-3(5) of 6-Ar], 117.1 (C-3), 123.6, 128.6, 128.7, 129.05, 129.07 [C-2(6), C-3(5) of 2-Ar, 4-Ph; C-2(6) of 6-Ar], 127.0, 134.6, 135.1, 135.8, 137.9 (C-4; C-1, C-4 of 2-Ar; C-1 of 4-Ph, 6-Ar), 127.7 (C-4 of 4-Ph), 143.1 (C-5), 158.6 (C-4 of 6-Ar), 166.3 (C-2), 169.4 (C-3a).

6-(*4-Methylphenyl*)*-4-phenyl-2-*(*2-thienyl*)*-1,6a*λ^4*-dithia-6-azapentalene* (**7g**). ^{1}H NMR: δ 2.38 (3H, Me), 7.01 (1H, dd, 4-H of thienyl), 7.24–7.51 (11H, m, 3-H, 5-H of thienyl; 4-Ph; *o*- and *m*-protons of 6-Ar), 7.89 (3-H), 8.20 (5-H). ^{13}C NMR: δ 21.0 (Me), 115.4 (C-3), 122.1 [C-2(6) of 6-Ar], 126.3, 126.9, 127.7, 128.0, 135.4, 136.7, 138.4, 145.0 (one signal missing due to overlap or low intensity) (C-4; C-2, C-3, C-4, C-5 of thienyl; C-1, C-4 of 4-Ph, 6-Ar), 129.0, 129.1, 130.3 [C-2(6), C-3(5) of 4-Ph, C-3(5) of 6-Ar], 142.1 (C-5), 165.0 (C-2), 166.3 (C-3a).

6-(*4-Methoxyphenyl*)*-4-phenyl-2-*(*2-thienyl*)*-1,6a*λ^4*-dithia-6-azapentalene* (**7h**). ^{1}H NMR: δ 3.82 (3H, OMe), 6.96 (2H, *m*-protons of 6-Ar), 6.99 (1H, dd, 4-H of thienyl), 7.30–7.50 (9H, m, 3-H, 5-H of thienyl; 4-Ph; *o*-protons of 6-Ar), 7.88 (1H, 3-H), 8.14 (1H, 5-H). ^{13}C NMR: δ 55.6 (OMe), 115.0 [C-3(5) of 6-Ar], 115.3 (C-3), 123.5 [C-2(6) of 6-Ar], 126.2, 126.8, 127.6, 127.9, 128.0, 134.0, 135.3, 145.0 [C-2, C-3, C-4, C-5 of thienyl; C-4; C-1, C-4 of 4-Ph; C-2(6) of 6-Ar], 128.96, 129.0 [C-2(6), C-3(5) of 4-Ph], 142.3 (C-5), 158.5 (C-4 of 6-Ar), 164.5 (C-2), 166.0 (C-3a).

6-(*4-Methylphenyl*)*-2-phenyl-1,6a*λ^4*-dithia-6-azapentalene* (**12a**). ^{1}H NMR: δ 2.38 (3H, Me), 7.11 (1H, d, $J_{4,5}$ 3.7, 4-H), 7.21–7.44 (7H, m, 2*m*- + *p*-protons of 2-Ph, *o*- and *m*-protons of 6-Ar), 7.75 (1H, 3-H), 7.78–7.83 (2H, m, *o*-protons of 2-Ph), 8.27 (1H, d, $J_{5,4}$ 3.7, 5-H). ^{13}C NMR: δ 21.0 (Me), 111.2 (C-4), 118.6 (C-3), 121.8, 127.4, 128.6, 130.2 [C-2(6), C-3(5) of 2-Ph, 6-Ar], 129.2 (C-4 of 2-Ph), 136.0, 138.3, 140.5 (C-1 of 2-Ph, C-1, C-4 of 6-Ar), 143.6 (C-5), 168.83, 168.86 (C-2, C-3a).

6-(*4-Methoxyphenyl*)*-2-phenyl-1,6a*λ^4*-dithia-6-azapentalene* (**12b**). ^{1}H NMR: δ 3.84 (3H, OMe), 6.97 (2H, *m*-protons of 6-Ar), 7.10 (1H, d, $J_{4,5}$ 3.5, 4-H), 7.32–7.43 (5H, m, 2*m*- + *p*-protons of 2-Ph, *o*-protons of 6-Ar), 7.73 (1H, 3-H), 7.80 (2H, *o*-protons of 2-Ar), 8.24 (1H, d, $J_{5,4}$ 3.5, 5-H). ^{13}C NMR: δ 55.6 (OMe), 111.1 (4-H), 114.9 [C-3(5) of 6-Ar], 118.6 (C-3), 123.2 [C-2(6) of 6-Ar], 127.4, 128.6 [C-2(6), C-3(5) of 2-Ph], 129.2 (C-4 of 2-Ph), 136.3, 138.3 (C-1 of 2-Ph, 6-Ar), 143.6 (C-5), 158.2 (C-4 of 6-Ar), 168.37, 168.56 (C-2, C-3a).

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