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Trithia- and Dithiaselenapentalenes from Benzylidene-1,2-dithioles and Heterocumulenes

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ABSTRACT

*Deprotonation of the 5-aryl-3-benzyl-1λ⁴,2-dithiol-1-ylium iodides (**6a–6d**) obtained by reaction of the 1-aryl-4-phenylbutan-1,3-diones (**5a–5d**) with hydrogen sulfide and iodine in ethanol gave the stable 5-aryl-3-benzylidene-3H-1,2-dithioles (**3a–3d**), respectively. The dithioles (**3a–3d**) underwent thermal cycloaddition reactions with isoselenocyanates and isothiocyanates to give the 2-(substituted amino)-5-aryl-3-phenyl-6,6aλ⁴-dithia-1-selenapentalenes (**7a–7h**) and the 2-(substituted amino)-5-aryl-3-phenyl-1,6,6aλ⁴-trithiapentalenes (**8a–8l**), respectively. The dithioles (**3a–3d**) reacted with isocyanates to give the N-substituted-2-phenyl-2-(5-aryl-3H-1,2-dithiol-3-ylidene) acetamides (**11a–11h**). © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**: 233–244, 1997.*

INTRODUCTION

The cations in 1λ⁴,2-dithiol-1-ylium salts (**1**) possessing methyl, methylene, or methine groups at position 3(5) are readily deprotonated at these groups to give 3-methylene-3*H*-1,2-dithioles (**2**) [1,2]. The stability of the dithioles (**2**) varies, depending mainly on the nature of R^1 and R^2. 3-Alkylidene derivatives (**2**; R^1 = alkyl, R^2 = H, R^3, R^4 = H, alkyl) are transient species that decompose rapidly to give unidentified fragments [3]. 3-Methylene-5-phenyl-3*H*-1,2-dithiole (**2**; R^1 = R^2 = R^3 = H, R^4 = Ph) reacts immediately with its precursor salt (**1**; R^1 = R^2 = R^3 = H, R^4 = Ph, X = ClO_4) to give a 2*H*-thiopyran derivative [4]. Stable 3-methylene-3*H*-1,2-dithioles (**2**) have been obtained when R^1 and/or R^2 contain electron-acceptor groups (C=O, C≡N) or are part of hydrocarbon moieties (cyclopentadiene, fluorene) capable of stabilizing the negative charge on the exocyclic carbanion center [in (**2A**)] by delocalization [5,6]. It has been reported briefly without experimental details that deprotonation of 3-benzyl-5-phenyl-1λ⁴,2-dithiol-1-ylium salts (**1**; R^1 = R^4 = Ph, R^2 = R^3 = H) give 3-benzylidene-5-phenyl-3*H*-1,2-dithiole (**3a**) as a crystalline product [7]. 3-Methylene-3*H*-1,2-dithioles (**2**) are doubtless the participants in the reactions of 3-alkyl-1λ⁴,2-dithiol-1-ylium salts with electrophiles that lead directly or indirectly to 1,6,6aλ⁴-triheterapentalenes (**4**; Z = Se, S, O, NR) and their (poly)aza analogues [8,9]. In this article, we report a new type of synthesis of 1,6,6aλ⁴-triheterapentalenes (**4**; Z = Se, S, R^1 = NHR) and related compounds that consists of thermal [2 + 3]-cycloaddition reactions of 4π-electron component 3-methylene-3*H*-1,2-dithioles (**3**) with 2π-electron component heterocumulenes RNCZ (Z = Se, S, O).

RESULTS AND DISCUSSION

The report [7] of the isolation of 3-benzylidene-5-phenyl-3*H*-1,2-dithiole (**3a**) prompted us to synthe-

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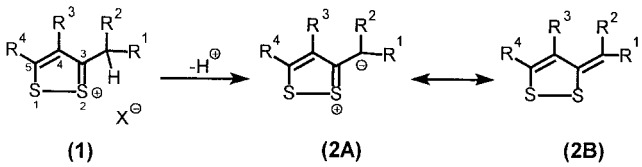
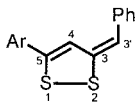
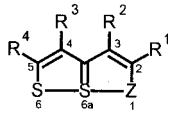


(1) **(2A)** **(2B)**

SCHEME 1



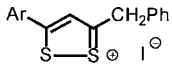
(3)



(4)

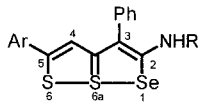
$ArCOCH_2COCH_2Ph$

(5)



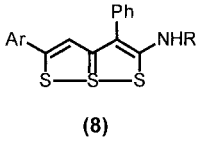
(6)

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



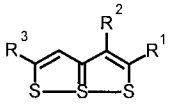
(7)

	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-$MeOC_6H_4$



(8)

	Ar	R
(8a)	Ph	$PhCH_2$
(8b)	Ph	Ph
(8c)	Ph	3-ClC_6H_4
(8d)	4-$MeOC_6H_4$	$PhCH_2$
(8e)	4-$MeOC_6H_4$	Ph
(8f)	4-$MeOC_6H_4$	3-ClC_6H_4
(8g)	4-ClC_6H_4	$PhCH_2$
(8h)	4-ClC_6H_4	Ph
(8i)	4-ClC_6H_4	3-ClC_6H_4
(8j)	2-Thienyl	$PhCH_2$
(8k)	2-Thienyl	Ph
(8l)	2-Thienyl	3-ClC_6H_4



(9)

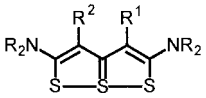
	R^1	R^2	R^3	Ref.
(9a)	NH_2	CN	Ph	[11-14]
(9b)	NH_2	CN	4-MeC_6H_4	[13]
(9c)	NH_2	CN	4-$MeOC_6H_4$	[13,14]
(9d)	NH_2	CN	4-ClC_6H_4	[14]
(9e)	NH_2	CN	4-BrC_6H_4	[14]
(9f)	NMe_2	H	Ph	[15,16]
(9g)	NMe_2	H	t-Bu	[16]
(9h)	NMe_2	Ph	Ph	[17]
(9i)		Me	H	[18]

size (**3a**) and the related dithioles (**3b–3d**) for use as the 4π-electron component in the cycloaddition reactions. This was achieved as follows. Passage of hydrogen sulfide into solutions containing the diketones (**5a–5d**) and iodine in ethanol, essentially according to a published procedure [10], gave the 3-benzyl-1λ^4,2-dithiol-1-ylium iodides (**6a–6d**) in workable yields (27–77%). Deprotonation of the iodides with aqueous sodium carbonate afforded the 3-benzylidene-3*H*-1,2-dithioles (**3a–3d**) in virtually quantitative yield as stable copper-colored crystals.

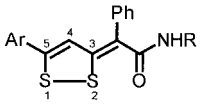
The dithioles (**3a–3d**) reacted rapidly with isoselenocyanates at 170°C to give the 6,6aλ^4-dithia-1-selenapentalenes (**7a–7h**) and with isothiocyanates at 220–230°C to give the 1,6,6aλ^4trithiapentalenes (**8a–8l**). Although very many 1,6,6aλ^4-trithiapentalenes (**4**; Z = S) are known [2], only a few amino derivatives have been reported, namely, compounds (**9a–9i**) and (**10**) [11–19]. Before the present work had been carried out, only one 6,6aλ^4-dithia-1-selenapentalene (**4**; $R^1 = R^3 = H$, $R^2 = R^4 = Ph$, Z = Se) had been prepared [20,21], and 2-amino derivatives of this system were unknown. The infrared spectra

of compounds (**7a–7h**) and (**8a–8l**) show sharp medium-intensity N–H stretching bands in the respective ranges 3304–3362 and 3313–3369 cm^{-1}.

The reactions of the dithioles (**3a–3d**) with isocyanates also gave in high yield 1:1 addition products. Infrared spectral data indicate that these compounds should be formulated as 3*H*-1,2-dithiol-3-ylideneacetamides (**11a–11h**) rather than 2-amino-1-oxa-6,6aλ^4-dithiapentalenes (**12**). The infrared spectra (KBr) of these compounds show a sharp medium-intensity N–H stretching band in the range 3398–3403 cm^{-1}, together with a strong band in the range 1607–1614 cm^{-1} arising from a polarized C=O group. Several compounds (**13a–13h**) structurally related to compounds (**11a–11h**) have previously been studied [12–14]. The two compounds (**13e**) and (**13f**) most closely similar to (**11a–11h**) show a strong infrared absorption band at 1615 and 1620 cm^{-1}, respectively, which has been attributed principally to the carbonyl group [13].

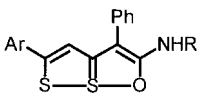


(10) R = Me; R,R = $[CH_2]_5$
R^1 = H, Me
R^2 = H, Ph
Ref. [19]



(11)

	Ar	R
(11a)	Ph	Ph
(11b)	Ph	4-ClC_6H_4
(11c)	4-$MeOC_6H_4$	Ph
(11d)	4-$MeOC_6H_4$	4-ClC_6H_4
(11e)	4-ClC_6H_4	Ph
(11f)	4-ClC_6H_4	4-ClC_6H_4
(11g)	2-Thienyl	Ph
(11h)	2-Thienyl	4-ClC_6H_4

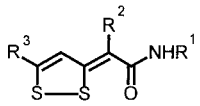


(12)

We propose that the (cyclo)addition reactions take place according to Scheme 2 in which a zwitterionic addition product (**14**) is first formed. Conversion of (**4**; Z = Se, S) into the triheterapentalene (**16**; Z = Se, S) [≡(**7**) or (**8**)] takes place by path (a) by a successive proton-transfer and ring-closure sequence (**14**) → (**15**; Z = Se, S) → (**16**; Z = Se, S), or by path (b) involving a 2,3-dihydro triheterapentalene intermediate (≡**17**) that tautomerizes to give (**16**; Z = Se, S). Proton transfer in (**14**; Z = O) gives the 3*H*-1,2-dithiol-3-ylideneacetamides (**15**; Z = O) [≡(**11a–11h**)].

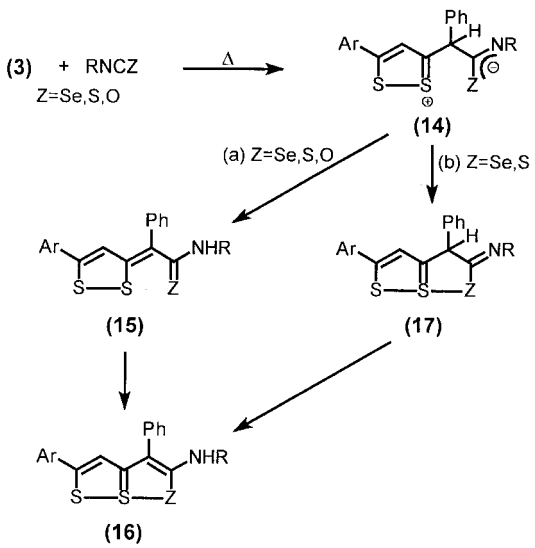
EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spec-



(13)

	R^1	R^2	R^3	Ref.
(13a)	NH_2	CN	Ph	[12-14]
(13b)	NH_2	CN	4-$MeOC_6H_4$	[13, 14]
(13c)	NH_2	CN	4-ClC_6H_4	[14]
(13d)	NH_2	CN	4-BrC_6H_4	[14]
(13e)	NHPh	CN	4-MeC_6H_4	[13]
(13f)	NHPh	CN	4-$MeOC_6H_4$	[13]
(13g)	NHPh	CONHPh	4-MeC_6H_4	[13]
(13h)	NHPh	CONHPh	4-$MeOC_6H_4$	[13]



SCHEME 2

tra were obtained from solids dispersed in KBr discs. ^{1}H NMR spectra were determined at 200.13 or 400.13 MHz, and ^{13}C NMR spectra were determined at 50.32 MHz or 100.62 MHz with Bruker AC 200 and Bruker DRX 400 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 the *p*-substituted phenyl groups in compounds (**3b**), (**5b**), (**5c**), (**6b**), (**6c**), (**7b**), (**7c**), (**7d**), (**7f**), (**7h**), (**8d**), (**8e**), (**8f**), (**11c**), and (**11d**) correspond to the midpoint 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 δ = 77.0 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. Ether denotes diethyl ether. Petroleum ether denotes an alkane mixture consisting mainly of hexane, of boiling range 60–80°C. Acetonitrile, benzene, dichloromethane, ethanol, hexane, and petroleum ether were dried by standard procedures and distilled before use. Solvent mixtures are described in ratios by volume. Isoselenocyanates were prepared as previously described [25]. Column chromatography was carried out with silica (85–200 mesh).

Preparation of 1-Aryl-4-phenylbutan-1,3-diones (*by Beate G Rose*)

1,4-Diphenylbutan-1,3-dione (**5a**). This diketone was prepared as in the references cited [22–24]. Enol-keto ratio [^{1}H NMR ($CDCl_3$)], 12:1. ^{1}H NMR ($CDCl_3$): enol, δ 3.70 (2H, 4-CH_2), 6.11 (1H, 2-CH), 7.18–7.46 (8H, m, 5H of 4-Ph + *m*- + *p*-protons of 1-Ph), 7.76–7.82 (2H, m, *o*-protons of 1-Ph), 16.11 (1H, OH); keto, δ 3.84 (2H) and 4.05 (2H) (2-CH_2, 4-CH_2). ^{13}C NMR ($CDCl_3$): enol, δ 45.9 (C-4), 96.1 (C-2), 126.9, 127.0, 128.5, 128.7, 129.3, 132.3, 134.5, 135.0 [C-1, C-4, C-2(6), C-3(5) of 1-Ph and 4-Ph]

1-(4-Methoxyphenyl)-4-phenylbutan-1,3-dione (**5b**). This diketone was prepared according to the method cited [22,23], using 4-methoxyacetophenone (30.0 g, 200 mmol), ethyl phenylacetate (47.8 mL, 300 mmol), sodium (9.2 g, 400 mmol), liquid ammonia (200 mL), and ether (200 mL). After purification via its copper complex, using copper(II) acetate (24 g, 120 mmol) in water (300 mL), followed by crystallization from hexane, the diketone (**5b**) (43.5 g, 81%) was obtained as pale yellow needles, mp 79–80°C. Enol-keto ratio [^{1}H NMR ($CDCl_3$)], 10:1. ^{1}H NMR ($CDCl_3$): enol, δ 3.69 (2H, 4-CH_2), 3.81 (3H, OMe), 6.05 (1H, 2-CH), 6.89 (2H, *m*-protons of 1-Ar), 7.23–7.35 (5H, m, 4-Ph), 7.78 (2H, *o*-protons of 1-Ar), 16.27 (1H, OH); keto, δ 3.82 (3H, OMe), 3.85 (2H), and 4.02 (2H) (2-CH_2, 4-CH_2). ^{13}C NMR ($CDCl_3$): enol δ 45.4 (C-4), 55.3 (OMe), 95.3 (C-2), 113.8 (C-3, C-5 of 1-Ar), 127.0, 128.6, 129.1, 129.3, 130.9, 135.3 [C-1, C-2(6) of 1-Ar, C-1, C-4, C-2(6), C-3(5) of 4-Ph], 163.1 (C-4 of 1-Ar), 184.1, 192.7 (C-1, C-3); keto, δ 50.2, 52.3, (C-2, C-4), 55.4 (OMe). Anal. calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.22; H, 5.98%.

1-(4-Chlorophenyl)-4-phenylbutan-1,3-dione (**5c**). The procedure was identical with that of the preceding experiment, with 4-chloroacetophenone (25.9 mL, 200 mmol) in place of 4-methoxyacetophenone. Crystallization of the product from ethanol (charcoal) gave the diketone (**5c**) (30.2 g, 55%) as white crystals, mp 75–76°C. Enol-keto ratio [^{1}H NMR ($CDCl_3$)], 14:1. ^{1}H NMR ($CDCl_3$): enol, δ 3.72 (2H, 4-CH_2), 6.07 (1H, 2-CH), 7.23–7.40 (7H, m, *m*-protons of 1-Ar, 5 protons of 4-Ph), 7.72 (*o*-protons of 1-Ar), 16.02 (1H, OH); keto, δ 3.85 (2H) and 4.04 (2H) (2-CH_2, 4-CH_2). ^{13}C NMR ($CDCl_3$): enol, δ 45.9 (C-4). 96.0 (C-2), 127.1, 128.3, 128.7, 128.8, 129.3, 133.1, 134.9, 138.5 [C-1, C-4, C-2(6), C-3(5) of 1-Ar and 4-Ph], 182.1, 194.8 (C-1, C-3); keto, δ 50.4, 52.3 (C-2, C-4). Anal. calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found C, 70.81; H, 4.85%.

4-Phenyl-1-(2-thienyl)butan-1,3-dione (**5d**). This diketone was prepared according to the method cited [22,23], using 2-acetylthiophene (5.4 mL, 50 mmol), ethyl phenylacetate (12 mL, 75 mmol), sodium (2.3 g, 100 mmol), liquid ammonia (50 mL), and ether (50 mL). The diketone was purified via its copper complex that was obtained by addition of a solution of the impure diketone in its own volume of methanol to a solution of copper(II) acetate (6 g, 30 mmol) in water (100 mL). Crystallization of the diketone from ethanol (charcoal) gave white needles (5.33 g, 44%), mp 46.5–47.5°C. Enol-keto ratio [^{1}H NMR ($CDCl_3$)], 6:1. ^{1}H NMR ($CDCl_3$): enol, δ 3.65 (2H, 4-CH_2), 5.96 (1H, 2-CH), 7.04–7.09 (1H, m, 4-H of thienyl), 7.18–7.39 (5H, m, 4-Ph), 7.53–7.65 (2H, m, 3-H + 5-H of thienyl), 15.63 (1H, OH); keto, δ 3.87 (2H) and 4.00 (2H) (2-CH_2, 4-CH_2). ^{13}C NMR ($CDCl_3$): enol, δ 43.9 (C-4), 96.0 (C-2), 127.1, 128.1,

128.6, 129.2, 130.3, 132.5, 135.0, 141.4 [C-1, C-4, C-2(6), C-3(5) of 4-Ph, C-2, C-3, C-4, C-5 of thienyl], 181.8, 188.3 (C-1, C-3). Anal. calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.97; H, 4.97%.

Preparation of 5-Aryl-3-benzyl-1λ⁴,2-dithiol-1-ylium Iodides (**6a–6d**)

3-Benzyl-5-phenyl-1λ⁴,2-dithiol-1-ylium Iodide (**6a**). Hydrogen sulfide was bubbled slowly (glass frit) through a solution of the dione (**5a**) (11.9 g, 50 mmol) in ethanol (100 mL) at ambient temperature for 2 hours. A green solid precipitated from the brown solution. The solution was heated to 40–50°C and kept in this temperature range for 6 hours, while hydrogen sulfide was slowly passed into the solution. The green solid redissolved, the solution became red, and red crystals of the iodide (**6a**) separated from the solution. The red solid (13.1 g) was filtered off and washed successively with ethanol, carbon disulfide, and ether. Iodine (4.4 g, 17.3 mmol) was dissolved in the reaction filtrate, and hydrogen sulfide was bubbled through the resulting solution, kept at 40–50°C, for 6 hours. Addition of ether to the cooled solution precipitated more (2.1 g) of the iodide (**6a**), giving a total yield of 15.2 g (76.7%). Recrystallization of the iodide from acetonitrile gave red crystals, mp 149–150°C; ^{1}H NMR (CF_3COOD): δ 4.80 (2H, CH_2), 7.49 (5H, CH_2*Ph*), 7.62–7.90 (3H, m, *m*- + *p*-protons of 5-Ph), 7.99 (2H, d, *J* 8.0, *o*-protons of 5-Ph), 8.73 (1H, 4-H). ^{13}C NMR (CF_3COOD): δ 42.8 (CH_2), 130.7, 131.2, 131.9, 132.5 [C-2(6), C-3(5) of CH_2Ph and 5-Ph], 131.3 (C-4), 132.1 (C-1 of 5-Ph), 136.4 (C-1 of CH_2Ph), 136.7 (C-4 of CH_2Ph), 137.9 (C-4 of 5-Ph), 193.4 (C-5), 200.6 (C-3). Anal. calcd for $C_{16}H_{13}IS_2$: C, 48.49; H, 3.31. Found: C, 48.60; H, 3.25%.

3-Benzyl-5-(4-methoxyphenyl)-1λ⁴,2-dithiol-2-ylium Iodide (**6b**). Hydrogen sulfide was bubbled slowly through a solution of the dione (**5b**) (13.4 g, 50 mmol) and iodine (19 g, 75 mmol) in ethanol (100 mL) kept at 40–50°C. The solution became orange and after 9 hours the yellow iodide (4.3 g) that had crystallized was filtered off and washed successively with ethanol, carbon disulfide, and ether. Iodine (8 g, 31.5 mmol) was dissolved in the reaction filtrate and hydrogen sulfide was passed slowly into the resulting solution at 40–50°C for 9 hours to give a further quantity (1.5 g) of the iodide (**6b**) and thereby a total yield of 5.8 g (27.2%). Recrystallization of the iodide from acetonitrile gave yellow crystals, mp 178–179°C; ^{1}H NMR (CF_3COOD): δ 4.03 (3H, OMe), 4.72 (2H, CH_2), 7.21 (2H, *m*-protons of 5-Ar), 7.48 (5H, CH_2Ph), 8.03 (2H, *o*-protons of 5-Ar), 8.59 (4-H); ^{13}C NMR (CF_3COOD): δ 42.5 (CH_2), 57.4 (OMe), 118.3 [C-3(5) of 5-Ar], 125.6 (C-1 of 5-Ar), 131.1, 131.9 [C-2(6), C-3(5) of CH_2Ph], 131.3 (C-4), 133.5 [C-2(6) of 5-Ar], 134.7 (C-4 of CH_2Ph)], 136.5 (C-1 of CH_2Ph), 168.8 (C-4 of 5-Ar), 192.9 (C-5), 198.5 (C-3). Anal. calcd for $C_{17}H_{15}IOS_2$: C, 47.89; H, 3.55. Found: C, 47.58; H, 3.35%.

3-Benzyl-5-(4-chlorophenyl)-1λ⁴,2-dithiol-1-ylium Iodide (**6c**). The procedure was identical with that for the preparation of (**6b**), with the dione (**5c**) (13.6 g, 50 mmol) in place of (**5b**). The red iodide (**6c**) (7.21 g) that had crystallized after 6 hours was filtered off and washed in succession with ethanol, carbon disulfide, and ether. Solvent was removed at reduced pressure from the reaction mother liquor, the residue was redissolved together with iodine (8 g, 31.5 mmol) in ethanol (50 mL), and hydrogen sulfide was bubbled through the solution for 6 hours. A further quantity (3.48 g) of the iodide (**6c**) was thereby obtained, giving a total yield of 10.69 g (49.6%). Recrystallization of the iodide from acetonitrile gave red crystals, mp 187–188°C; ^{1}H NMR (CF_3COOD): δ 4.79 (2H, CH_2). 7.49 (5H, CH_2*Ph*), 7.64 (2H, *m*-protons of 5-Ar), 7.96 (2H, *o*-protons of 5-Ar), 8.72 (1H, 4-H); ^{13}C NMR (CF_3COOD): δ 42.9 (CH_2), 130.5 (C-1 of 5-Ar), 131.2, 131.9 [C-2(6), C-3(5) of CH_2Ph], 131.5 (C-4), 132.0, 133.0 [C-2(6), C-3(5) of 5-Ar], 136.3 (C-1 of CH_2Ph), 136.9 (C-4 of CH_2Ph), 145.7 (C-4 of 5-Ar), 191.9 (C-5), 201.6 (C-3). Anal. calcd for $C_{16}H_{12}ClIS_2$: C, 44.61; H, 2.81. Found: C, 44.47; H, 2.67%.

3-Benzyl-5-(2-thienyl)-1λ⁴,2-dithiol-1-ylium Iodide (**6d**). The procedure was identical with that for the preparation of (**6c**), with the dione (**5d**) (12.2 g, 50 mmol) in place of (**5c**). Two crops of crystals of the red iodide (**6d**) amounting to 10.20 g (50.7%) were obtained. Recrystallization from acetonitrile gave the iodide as red crystals, mp 169–170°C; ^{1}H NMR (CF_3COOD): δ 4.70 (2H, CH_2), 7.36–7.43 (1H, dd, 4-H of thienyl) 7.48 (5H, CH_2*Ph*), 8.07–8.12 (2H, m, 3-H + 5-H of thienyl), 8.46 (4-H); ^{13}C NMR (CF_3COOD): δ 42.4 (CH_2), 131.1, 131.9 [C-2(6), C-3(5) of CH_2Ph], 131.4 (C-4), 133.2, 137.9, 141.0 (C-3, C-4, C-5 of thienyl), 134.8 (C-4 of CH_2Ph), 135.1 (C-2 of thienyl), 136.4 (C-1 of CH_2Ph), 184.2 (C-5), 198.6 (C-3). Anal. calcd for $C_{14}H_{11}IS_3$: C, 41.79; H, 2.76. Found: C, 41.51; H, 2.56%.

Preparation of 5-Aryl-3-benzylidene-3H-1,2-dithioles (**3a–3d**)

General Procedure. A solution of sodium carbonate (10.6 g, 100 mmol) and sodium thiosulfate pentahydrate (24.8 g, 100 mmol) in water (1 L) was added to a suspension of the iodide (**6**) (50 mmol) in

benzene (500 mL), and the resulting mixture was stirred until all the iodide had reacted (ca. 24 h). The benzene layer was collected, and the aqueous layer was extracted with more benzene (3 × 200 mL). The combined benzene extracts and benzene layer were washed with water and dried, and solvent was removed. The residual solid was recrystallized from benzene–hexane (1:1) unless otherwise stated.

3-Benzylidene-5-phenyl-3H-1,2-dithiole (**3a**). The dithiole (**3a**) (12.68 g, 94.5%) was obtained as orange plates, mp 180–181°C; ^{1}H NMR: δ 6.68 (1H, 3-PhC*H*), 6.85 (1H, 4-H), 7.25–7.52 (10H, m, 2 × Ph); ^{13}C NMR δ 117.1 (3-Ph*C*H), 124.9 (C-4), 125.9, 129.4 (C-4 of 3-PhCH and C-4 of 5-Ph), 126.5, 126.9, 128.6, 128.9 [C-2(6), C-3(5) of 3-PhCH and 5-Ph], 132.8, 137.1 (C-1 of 3-PhCH and C-1 of 5-Ph), 145.6, 145.8 (C-3, C-5). Anal. calcd for $C_{16}H_{12}S_2$: C, 71.60; H, 4.51. Found: C, 71.50; H, 4.29%.

3-Benzylidene-5-(4-methoxyphenyl)-3H-1,2-dithiole (**3b**). The dithiole (**3b**) (14.50 g, 97%) was obtained as orange plates, mp 211–212°C; ^{1}H NMR: δ 3.84 (3H, OMe), 6.64 (1H, 3-PhC*H*), 6.76 (1H, 4-H), 6.92 (2H, *m*-protons of 5-Ar), 7.18 (1H, t, *p*-proton of 3-PhCH), 7.36–7.41 (4H, m, *o*- + *m*-protons of 3-PhCH), 7.46 (2H, *o*-protons of 5-Ar); ^{13}C NMR: δ 55.4 (OMe), 114.3 [C-3(5) of 5-Ar], 116.4 (3-Ph*C*H), 123.4 (C-4), 125.7 (C-4 of PhCH), 125.4, 137.2 (C-1 of 3-PhCH and C-1 of 5-Ar), 126.8, 128.0, 128.6 [C-2(6), C-3(5) of 3-PhCH, C-2(6) of 5-Ar], 145.4, 146.0 (C-3, C-5), 160.6 (C-4 of 5-Ar). Anal. calcd for $C_{17}H_{14}OS_2$: C, 68.42: H, 4.73. Found: C, 68.29; H, 4.61%.

3-Benzylidene-5-(4-chlorophenyl)-3H-1,2-dithiole (**3c**). The dithiole (**3c**) (15.0 g, 99%) was obtained as golden yellow crystals, mp 204–205°C; ^{1}H NMR: δ 6.68 (1H, 3-PhC*H*), 6.83 (1H, 4-H), 7.20–7.27 (1H, m, 4-H of 3-PhCH), 7.35–7.48 (8H, m, *o*- and *m*-protons of 3-PhCH and 5-Ar); ^{13}C NMR: δ 117.6 (3-Ph*C*H), 125.5 (C-4), 126.1 (C-4 of 3-PhCH), 127.0, 127.7, 128.6, 129.1 [C-2(6), C-3(5) of 3-PhCH and 5-Ar], 131.3, 135.3, 137.0 (C-1 of 3-PhCH and 5-Ar, C-4 of 5-Ar), 144.2, 145.5 (C-3, C-5). Anal. calcd for $C_{16}H_{11}ClS_2$: C, 63.46; H, 3.66. Found: C, 63.21; H, 3.61%.

3-Benzylidene-5-(2-thienyl)-3H-1,2-dithiole (**3d**). The dithiole (**3d**) (13.50 g, 98%) was obtained as orange crystals, mp 147–148°C after recrystallization from dichloromethane-hexane (1:3); ^{1}H NMR: δ 6.63 (1H, 3-Ph*C*H), 6.74 (1H, 4-H), 7.00–7.03 (1H, dd, 4-H of thienyl), 7.11–7.38 (7H, m, Ph + 3-H and 5-H of thienyl); ^{13}C NMR [$CDCl_3$-CH_2Cl_2 (3:1)]: δ 117.2 (3-PhCH), 124.6 (C-4), 125.8 (C-4 of 3-PhCH), 126.6, 126.7, 127.9 (C-3, C-4, C-5 of thienyl), 126.8, 128.4 [C-2(6), C-3(5) of 3-PhCH], 135.0 136.8, 138.0 (C-5, C-1 of 3-PhCH, C-2 of thienyl), 144.9 (C-3). Anal. calcd for $C_{14}H_{10}S_3$: C, 61.27; H, 3.67. Found: C, 61.01; H, 3.61%.

Reactions of the 5-Aryl-3-benzylidene-3H-1,2-dithioles (**3a–3d**) *with Isoselenocyanates: Synthesis of the 2-Substituted Amino-6,6aλ^4-dithia-1-selenapentalenes* (**7a–7h**).

General Procedure. A mixture of the dithiole (**3**) (1 mmol) and the isoselenocyanate (4 mmol) was heated at 170°C (oil bath) for 4 minutes. The cooled mixture was dissolved in benzene-petroleum ether (1:1, 10 mL) and chromatographed on silica (35 × 1.9 cm). Elution with benzene-petroleum ether (1:1) brought through red eluates that yielded the product (**7**). Recrystallization from dichloromethane-petroleum ether gave compounds (**7a–7h**) as red needles. Experimental details, physical properties, and analytical data are given in Table 1.

Reactions of the 5-Aryl-3-benzylidene-3H-1,2-dithioles (**3a–3d**) *with Isothiocyanates: Synthesis of the 2-Substituted Amino-1,6,6aλ^4-trithiapentalenes* (**8a–8l**)

The following general procedures A and B were used. Experimental details, physical properties, and analytical data are given in Table 2.

Procedure A. A mixture of the dithiole (**3**) (1 mmol) and the isothiocyanate (20 mmol) was heated at 220–230°C (oil bath) for 10 minutes. Hexane was added to the cooled mixture to precipitate completely the product (**8**) that had partly crystallized. The solid was filtered off, washed with hexane, and recrystallized from dichloromethane-hexane (1:5).

Procedure B. A mixture of the dithiole (**3**) (1 mmol) and benzylisothiocyanate (20 mmol) was heated at 220–230°C (oil bath) for 15 minutes. The cooled mixture was chromatographed on silica (24 × 2.5 cm). Elution was carried out with hexane-benzene (H-B) mixtures and finally with benzene (B), giving the fractions indicated (Table 2, footnotes). The residue from the combined, colored product-bearing fractions was recrystallized from dichloromethane-hexane (1:5).

Reactions of the 5-Aryl-3-benzylidene-3H-1,2-dithioles (**3a–3d**) *with Isocyanates: Synthesis of the 3H-1,2-Dithiol-3-ylideneacetamides* (**11a–11h**)

General Procedure. A mixture of the dithiole (**3**) (1 mmol) and the isocyanate (20 mmol) was heated

TABLE 1 Preparation, Physical Properties, and Analytical Data of Compounds (**7a**–**7h**)

Compound	*Dithiole* (**3**)	*RNCSe*	*Yield* (%)	*Mp* (°C)	*Formula*	*Found* (%) (*Required*)		
						C	*H*	*N*
(**7a**)	(**3a**)	4-MeC_6H_4NCSe	72	240–241	$C_{24}H_{19}NS_2Se$	61.98 (62.06)	3.96 (4.12)	3.24 (3.02)
(**7b**)	(**3a**)	4-$MeOC_6H_4NCSe$	66	214–216	$C_{24}H_{19}NOS_2Se$	59.75 (59.99)	3.90 (3.99)	2.73 (2.91)
(**7c**)	(**3b**)	4-MeC_6H_4NCSe	74	225–226	$C_{25}H_{21}NOS_2Se$	60.74 (60.72)	4.19 (4.28)	2.99 (2.83)
(**7d**)	(**3b**)	4-$MeOC_6H_4NCSe$	72	214–216	$C_{25}H_{21}NO_2S_2Se$	58.76 (58.82)	4.01 (4.15)	2.84 (2.74)
(**7e**)	(**3c**)	4-MeC_6H_4NCSe	74	243–245	$C_{24}H_{18}ClNS_2Se$	57.98 (57.77)	3.57 (3.64)	2.98 (2.81)
(**7f**)	(**3c**)	4-$MeOC_6H_4NCSe$	66	213–215	$C_{24}H_{18}ClNOS_2Se$	55.79 (55.98)	3.36 (3.52)	2.94 (2.72)
(**7g**)	(**3d**)	4-MeC_6H_4NCSe	75	207–210	$C_{22}H_{17}NS_3Se$	55.98 (56.16)	3.49 (3.64)	3.12 (2.98)
(**7h**)	(**3d**)	4-$MeOC_6H_4NCSe$	78	194–196	$C_{22}H_{17}NOS_3Se$	54.02 (54.31)	3.35 (3.52)	2.85 (2.82)

TABLE 2 Preparation, Physical Properties, and Analytical Data of Compounds (**8a**–**8l**)

Compound[a]	*Dithiole* (**3**)	*RNCS*	*Procedure*	*Yield* (%)	*Mp* (°C)	*Formula*	*Found* (%) (*Required*)		
							C	*H*	*N*
(**8a**)	(**3a**)	$PhCH_2NCS$	B[b]	41	148–149	$C_{24}H_{19}NS_3$	68.81 (69.03)	4.48 (4.59)	3.57 (3.35)
(**8b**)	(**3a**)	PhNCS	A	95	215–216	$C_{23}H_{17}NS_3$	68.22 (68.45)	4.18 (4.25)	3.48 (3.47)
(**8c**)	(**3a**)	3-ClC_6H_4NCS	A	83	184–185	$C_{23}H_{16}ClNS_3$	63.07 (63.07)	3.66 (3.68)	3.21 (3.20)
(**8d**)	(**3b**)	$PhCH_2NCS$	B[c]	45	164–165	$C_{25}H_{21}NOS_3$	67.39 (67.08)	4.76 (4.73)	3.18 (3.13)
(**8e**)	(**3b**)	PhNCS	A	93	205–206	$C_{24}H_{19}NOS_3$	66.25 (66.48)	4.33 (4.42)	3.21 (3.23)
(**8f**)	(**3b**)	3-ClC_6H_4NCS	A	93	206–207	$C_{24}H_{18}ClNOS_3$	61.26 (61.59)	3.87 (3.88)	3.00 (3.00)
(**8g**)	(**3c**)	$PhCH_2NCS$	B[d]	59	175–176	$C_{24}H_{18}ClNS_3$	63.75 (63.77)	3.97 (4.01)	3.14 (3.10)
(**8h**)	(**3c**)	PhNCS	A	88	220–221	$C_{23}H_{16}ClNS_3$	63.01 (63.31)	3.64 (3.68)	3.22 (3.20)
(**8i**)	(**3c**)	3-ClC_6H_4NCS	A	93	229–230	$C_{23}H_{15}Cl_2NS_3$	58.36 (58.47)	3.19 (3.20)	2.96 (2.96)
(**8j**)	(**3d**)	$PhCH_2NCS$	B[e]	45	144–145	$C_{22}H_{17}NS_4$	62.16 (62.37)	3.99 (4.04)	3.35 (3.31)
(**8k**)	(**3d**)	PhNCS	A	83	178–179	$C_{21}H_{15}NS_4$	61.35 (61.58)	3.63 (3.69)	3.41 (3.42)
(**8l**)	(**3d**)	3-ClC_6H_4NCS	A	72	170–171	$C_{21}H_{14}ClNS_4$	56.58 (56.80)	3.15 (3.18)	3.18 (3.15)

[a]Compounds (**8a**–**8c**) and (**8h**–**8l**) were obtained as red crystals, and (**8d**–**8g**) were obtained as orange crystals.
[b]Chromatographic eluates: H-B (3:1), 240 mL, discarded; H-B (1:1), 100 mL and B, 150 mL contained (**8a**).
[c]Chromatographic eluates: H-B (3:1), 300 mL and H-B (2:1), 240 mL, discarded; H-B (1:1), 200 mL and B, 200 mL contained (**8d**).
[d]H-B (3:1), 240 mL and H-B (2:1), 100 mL, discarded; H-B (1:1), 100 mL and B, 250 mL contained (**8g**).
[e]H-B (3:1), 240 mL, discarded. H-B (1:1), 100 mL and B_1 150 mL contained (**8j**).

(oil bath) in a nitrogen atmosphere for 1 hour at the temperature indicated (Table 3). Hexane was added to the cooled mixture to precipitate completely the product that had partly crystallized. The solid was filtered off, washed with hexane, and recrystallized from dichloromethane-hexane to give the acetamide (**11**) as yellow crystals. Experimental details, physical properties, and analytical data are given in Table 3.

Spectral Data for the 6,6aλ⁴-Dithia-1-selenapentalenes (**7**) *and the 1,6,6aλ⁴-Trithiapentalenes* (**8**)

2-(4-Methylphenylamino)-3,5-diphenyl-6,6aλ⁴-dithia-1-selenapentalene (**7a**). IR: υ (N–H) 3344 cm^{-1}. ^1H NMR: δ 2.32 (3H, Me), 7.02 (1H, 4-H), 7.10–7.65 (15H, m, ArN + 3-Ph + 5-Ph + NH). ^{13}C NMR: δ 21.1 (Me), 123.5, 127.0, 128.7, 129.6, 130.4, 131.1 [C-2(6), C-3(5) of ArN, 3-Ph, 5-Ph], 124.7 (C-4), 129.0, 129.5, 129.6 (C-3, C-4 of 3-Ph, C-4 of 5-Ph), 136.3, 136.7, 137.5, 138.0 (C-1, C-4 of ArN, C-1 of 3-Ph, C-1 of 5-Ph), 166.8 (C-2), 176.4 (C-5), 179.0 (C-3a).

2-(4-Methoxyphenylamino)-3,5-diphenyl-6,6aλ⁴-dithia-1-selenapentalene (**7b**). IR: υ (N–H) 3362 cm^{-1}. ^1H NMR: δ 3.78 (3H, OMe), 6.85 (2H, *m*-protons of ArN), 7.00 (1H, 4-H), 7.22 (2H, *o*-protons of ArN), 7.28–7.64 (11H, m, 3-Ph + 5-Ph + NH). ^{13}C NMR: δ 55.4 (OMe), 114.2 [C-3(5) of ArN], 124.6 (C-4), 125.8, 127.0, 128.6, 130.4, 131.0 [C-2(6) of ArN, C-2(6), C-3(5) of 3-Ph and 5-Ph], 128.9, 129.6 (C-4 of 3-Ph and 5-Ph), 129.0, 133.6, 136.6, 137.4 (C-1 of ArN, 3-Ph, and 5-Ph, C-3), 158.0 (C-4 of ArN), 166.5 (C-2), 176.3 (C-5), 180.1 (C-3a).

5-(4-Methoxyphenyl)-2-(4-methylphenylamino)-3-phenyl-6,6aλ⁴-dithia-1-selenapentalene (**7c**). IR: υ (N–H) 3348 cm^{-1}. ^1H NMR: δ 2.32 (3H, Me), 3.78 (3H, OMe), 6.82 (2H, *m*-protons of 5-Ar), 6.97 (1H, 4-H), 7.12 (2H, *m*-protons of ArN), 7.21–7.62 (10H, m, *o*-protons of ArN and 5-Ph, 3-Ph, NH). ^{13}C NMR: δ 21.1 (Me), 55.3 (OMe), 114.0 [C-3(5) of 5-Ar], 123.5, 128.4, 129.6, 130.4, 131.1 [C-2(6), C-3(5) of ArN and 3-Ph, C-2(6) of 5-Ar], 123.8 (C-4), 128.9, 129.2, 136.1, 137.6, 138.1 (C-1, C-4 of ArN, C-1 of 3-Ph and 5-Ar, C-3), 160.9 (C-4 of 5-Ar), 166.7 (C-2), 176.5 (C-5), 178.5 (C-3a).

5-(4-Methoxyphenyl)-2-(4-methoxyphenylamino)-3-phenyl-6,6aλ⁴-dithia-1-selenapentalene (**7d**). IR: υ (N–H) 3350 cm^{-1}. ^1H NMR: δ 3.78 (6H, 2 × OMe), 6.81 (2H, *m*-protons of ArN), 6.84 (2H, *m*-protons of 5-Ar), 6.95 (1H, 4-H), 7.23 (2H, *o*-protons of ArN), 7.25 (1H, t, *p*-proton of 3-Ph), 7.40–7.60 (7H, m, *o*-protons of 3-Ph and 5-Ar, *m*-protons of 3-Ph, NH). ^{13}C NMR: δ 55.36, 55.45 (2 × OMe), 114.0, 114.2 [C-3(5) of ArN and 5-Ar], 123.7 (C-4), 125.8, 128.5, 130.4, 131.1 [C-2(6) of ArN, 3-Ph, 5-Ar, C-3(5) of 3-Ph], 128.9 (C-4 of 3-Ph), 128.5, 129.2, 133.8, 137.7 (C-1 of ArN, 3-Ph, 5-Ph; C-3), 158.1 (C-4 of ArN), 160.9 (C-4 of 5-Ar), 166.5 (C-2), 176.5 (C-5), 179.7 (C-3a).

5-(4-Chlorophenyl)-2-(4-methylphenylamino)-3-phenyl-6,6aλ⁴-dithia-1-selenapentalene (**7e**). IR: υ

TABLE 3 Preparation, Physical Properties, and Analytical Data of Compounds (**11a**–**11h**)

Compound	*Dithiole* (**3**)	*RNCO*	*Reaction Temperature* (°*C*)	*Yield* (%)	*Mp* (°*C*)	*Formula*	*Found* (%) (*Required*) *C*	*H*	*N*
(**11a**)	(**3a**)	PhNCO	160–170	96	217–218	$C_{23}H_{17}NOS_2$	71.22 (71.29)	4.33 (4.42)	3.70 (3.61)
(**11b**)	(**3a**)	4-ClC_6H_4NCO	190–200	97	218–219	$C_{23}H_{16}ClNOS_2$	63.72 (65.47)	3.78 (3.82)	3.43 (3.32)
(**11c**)	(**3b**)	PhNCO	160–170	88	148–150	$C_{24}H_{19}NO_2S_2$	68.87 (68.97)	4.54 (4.58)	3.41 (3.35)
(**11d**)	(**3b**)	4-ClC_6H_4NCO	190–200	86	214–215	$C_{24}H_{18}ClNOS_2$	63.62 (63.78)	3.94 (4.01)	3.10 (3.10)
(**11e**)	(**3c**)	PhNCO	160–170	98	227–228	$C_{23}H_{16}ClNOS_2$	65.30 (65.47)	3.78 (3.82)	3.34 (3.32)
(**11f**)	(**3c**)	4-ClC_6H_4NCO	190–200	97	250–251	$C_{23}H_{15}Cl_2NOS_2$	60.25 (60.53)	3.27 (3.32)	3.08 (3.07)
(**11g**)	(**3d**)	PhNCO	160–170	81	171–172	$C_{21}H_{15}NOS_3$	64.10 (64.10)	3.81 (3.84)	3.59 (3.56)
(**11h**)	(**3d**)	4-ClC_6H_4NCO	190–200	98	180–181	$C_{21}H_{14}ClNOS_3$	58.94 (58.93)	3.23 (3.30)	3.31 (3.27)

(N–H) 3346 cm^{-1}. ^1H NMR: δ 2.32 (3H, Me), 6.98 (1H, 4-H), 7.12–7.63 (14H, m, ArN + 3-Ph + 5-Ar + NH). ^{13}C NMR: δ 21.1 (Me), 123.4, 128.2, 128.8, 129.1, 129.7, 129.8, 130.4, 131.0, 135.5, 136.4, 137.2, 137.9 [C-1, C-2(6), C-3(5), C-4 of ArN, 3-Ph, 5-Ar], 124.5 (C-4), 166.0 (C-2), 176.4 (C-5), 178.8 (C-3a). The signal from C-3 or one ring carbon in one of the substituents ArN, 3-Ph, or 5-Ar was missing due to overlap or low intensity.

5-(4-Chlorophenyl)-2-(4-methoxyphenylamino)-3-phenyl-6,6aλ^4-dithia-1-selenapentalene (**7f**). IR: υ (N–H) 3304 cm^{-1}. ^1H NMR: δ 3.80 (3H, OMe), 6.86 (2H, *m*-protons of ArN), 6.97 (1H, 4-H), 7.23 (*o*-protons of ArN), 7.24–7.62 (10H, m, 3-Ph + *o*- and *m*-protons of 5-Ar, NH). ^{13}C NMR: δ 55.5 (OMe), 114.4 [C-3(5) of ArN], 124.5 (C-4), 125.8, 128.2, 128.8, 130.5, 131.1 [C-2(6) of ArN, 3-Ph, 5-Ar, C-3(5) of 3-Ph and 5-Ar], 128.6, 129.4, 133.6, 135.5, 137.3 (C-3; C-1 of ArN, 3-Ph, 5-Ar; C-4 of 5-Ar), 129.1 (C-4 of 3-Ph), 158.3 (C-4 of ArN), 165.8 (C-2), 176.4 (C-5), 180.1 (C-3a).

2-(4-Methylphenylamino)-3-phenyl-5-(2-thienyl)-6,6aλ^4-dithia-1-selenapentalene (**7g**). IR: υ (N–H) 3340 cm^{-1}. ^1H NMR: δ 2.33 (3H, Me), 6.94–7.66 (13H, m, ArN + 3-Ph + 5-thienyl + NH), 7.00 (1H, 4-H). ^{13}C NMR: δ 21.1 (Me), 123.3, 129.8, 130.3, 131.1 [C-2(6), C-3(5) of ArN and 3-Ph], 123.3 (C-4), 126.9, 128.1, 128.2, 129.0 (C-4 of 3-Ph, C-3, C-4, C-5 of thienyl), 129.3, 136.4, 136.9, 138.0, 141.9 (C-1, C-4 of ArN, C-1 of 3-Ph, C-2 of thienyl, C-3), 161.6 (C-2), 176.3 (C-5), 177.2 (C-3a).

2-(4-Methoxyphenylamino)-3-phenyl-5-(2-thienyl)-6,6aλ^4-dithia-1-selenapentalene (**7h**). IR: υ (N–H) 3348 cm^{-1}. ^1H NMR: δ 3.79 (3H, OMe), 6.85 (2H, *m*-protons of ArN), 6.95 (1H, dd, 4-H of thienyl), 7.00 (1H, 4-H), 7.21 (2H, *o*-protons of ArN), 7.25–7.64 (8H, m, 3-Ph + 3-H and 5-H of thienyl, NH). ^{13}C NMR: δ 55.4 (OMe), 114.3 C-3(5) of ArN], 123.1 (C-4), 125.6, 130.3, 131.1 [C-2(6) of 2-ArN and 3-Ph, C-3(5) of 3-Ph], 126.8, 128.1, 128.2, 129.0 (C-4 of 3-Ph, C-3, C-4, C-5 of thienyl), 128.7, 133.6, 136.8, 141.8 (C-1 of ArN, 3-Ph, C-2 of thienyl, C-3), 158.1 (C-4 of ArN), 161.2 (C-2), 176.2 (C-5), 178.4 (C-3a).

2-Benzylamino-3,5-diphenyl-1,6,6aλ^4-trithiapentalene (**8a**). IR: υ (N–H) 3356 cm^{-1}. ^1H NMR: δ 4.69 (2H, d, $J_{CH_2,NH}$ 5.7, CH_2), 6.17 (1H, t, NH), 6.86 (1H, 4-H), 7.17–7.57 (15H, m, 3 × Ph). ^{13}C NMR: δ 49.8 (CH_2), 123.6 (C-4), 124.8, 127.5, 129.7, 135.2, 137.27, 137.29 (one signal missing due to overlap or low intensity) (C-1, C-4 of $PhCH_2N$, 3-Ph, 5-Ph; C-3), 127.1, 127.3, 128.68, 128.70, 130.2, 130.9 [C-2(6), C-3(5) of $PhCH_2N$, 3-Ph, 5-Ph], 161.1 (C-2), 171.8 (C-5), 183.5 (C-3a).

3,5-Diphenyl-2-phenylamino-1,6,6aλ^4-trithiapentalene (**8b**). IR: υ (N–H) 3360 cm^{-1}. ^1H NMR: δ 7.00 (1H, 4-H), 7.11–7.65 (16H, m, 3 × Ph + NH). ^{13}C NMR: δ 122.5, 127.1, 128.7, 128.8, 130.3, 131.1 [C-2(6), C-3(5) of PhN, 3-Ph, 5-Ph], 123.8 (C-4), 125.5, 126.4, 129.0, 129.8, 135.7, 137.0, 139.4 (C-1, C-4 of PhN, 3-Ph, 5-Ph; C-3), 163.9 (C-2), 173.4 (C-5), 178.6 (C-3a).

2-(3-Chlorophenylamino)-3,5-diphenyl-1,6,6aλ^4-trithiapentalene (**8c**). IR: υ (N–H) 3357 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 6.96 (1H, 4-H), 7.21–7.64 (14H, m, ArN + 3-Ph + 5-Ph), 9.04 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 122.5 (C-4), 122.8, 124.1, 125.3, 127.6, 128.6, 130.0, 130.1, 132.5, 135.6, 135.9, 141.7 (C-1–C-6 of ArN; C-1, C-4 of 3-Ph, 5-Ph; C-3), 126.5, 129.1, 129.8, 131.0 [C-2(6), C-3(5) of 3-Ph, 5-Ph], 164.4 (C-2), 173.3 (C-5), 178.5 (C-3a).

2-Benzylamino-5-(4-methoxyphenyl)-3-phenyl-1,6,6aλ^4-trithiapentalene (**8d**). IR: υ (N–H) 3351 cm^{-1}. ^1H NMR [$(CD_3)_2$)SO]: δ 3.75 (3H, OMe), 4.58 (2H, d, $J_{CH_2,NH}$ 6.0, CH_2), 6.68 (1H, 4-H), 6.95 (2H, *m*-protons of 5-Ar), 7.17–7.39 (9H, m) and 7.48–7.65 (3H, m) (2 × Ph + *o*-protons of 5-Ar), 8.00 (1H, t, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 48.8 (CH_2), 55.2 (OMe), 114.4 [C-3(5) of 5-Ar], 120.9 (C-4), 125.1, 126.7, 127.3, 128.4, 136.6, 137.9 (C-1 of 5-Ar; C-1, C-4 of $PhCH_2N$, 3-Ph; C-3), 126.8, 128.8, 129.1, 129.9, 130.7 [C-2(6), C-3(5) of $PhCH_2N$, 3-Ph; C-2(6) of 5-Ar], 160.2 (C-2), 160.6 (C-4 of 5-Ar), 170.3 (C-5), 182.3 (C-3a).

5-(4-Methoxyphenyl)-3-phenyl-2-phenylamino-1,6,6aλ^4-trithiapentalene (**8e**). IR: υ (N–H) 3313 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 3.76 (3H, OMe), 6.87 (1H, 4-H), 6.96 (2H, *m*-protons of 5-Ar), 7.16–7.66 (12H, m, 2 × Ph + *o*-protons of 5-Ar), 8.89 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 55.2 (OMe), 114.3 [C-3(5) of 5-Ar], 121.0 (C-4), 124.3, 127.9, 128.4, 129.7, 130.9 [C-2(6), C-3(5) of PhN, 3-Ph; C-2(6) of 5-Ar], 125.6, 126.5, 128.2, 129.5, 136.1, 140.2 (C-1, C-4 of PhN, 3-Ph; C-1 of 5-Ar; C-3), 160.7 (C-4 of 5-Ar), 164.2 (C-2), 173.0 (C-5), 178.4 (C-3a).

2-(3-Chlorophenylamino)-5-(4-methoxyphenyl)-3-phenyl-1,6,6aλ^4-trithiapentalene (**8f**). IR: υ (N–H) 3343 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 3.76 (3H, OMe), 6.90 (1H, 4-H), 6.97 (2H, *m*-protons of 5-Ar), 7.20–7.65 (11H, m, ArN + 3-Ph + *o*-protons of 5-Ar), 8.96 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 55.2 (OMe), 114.4 [C-3(5) of 5-Ar], 121.4 (C-4), 122.7, 123.9, 125.1,

126.9, 127.8, 128.5, 129.9, 132.5, 136.0, 141.7 (C-1–C-6 of ArN; C-1, C-4 of 3-Ph; C-1 of 5-Ar; C-3), 128.0, 129.7, 130.9 [C-2(6), C-3(5) of 3-Ph; C-2 (6) of 5-Ar]. 160.8 (C-4 of 5-Ar), 164.3 (C-2), 173.5 (C-5), 178.0 (C-3a).

2-Benzylamino-5-(4-chlorophenyl)-3-phenyl-1,6,6aλ⁴-trithiapentalene (**8g**). IR: υ (N–H) 3369 cm^{-1}. ^1H NMR: δ 4.67 (2H, d, $J_{CH_2,NH}$ 5.7, CH_2), 6.17 (1H, t, NH), 6.83 (1H, 4-H), 7.16–7.57 (14H, m,*Ph*CH_2N + 3-Ph + 5-Ar). ^{13}C NMR: δ 49.8 (CH_2), 123.5 (C-4), 125.0, 127.6, 128.8, 133.9, 135.6, 137.0, 137.1 (C-1, C-4 of $PhCH_2N$, 3-Ph, 5-Ar; C-3), 127.2, 128.3, 128.7, 128.8, 130.2, 130.9 [C-2(6), C-3(5) of $PhCH_2N$, 3-Ph, 5-Ar], 159.9 (C-2), 171.7 (C-5), 183.3 (C-3a).

5-(4-Chlorophenyl)-2-phenyl-2-phenylamino-1,6,6aλ⁴-trithiapentalene (**8h**). IR: υ (N–H) 3363 cm^{-1}. ^1H NMR: δ 6.96 (1H, 4-H), 7.11–7.66 (15H, m, 2 × Ph + 5-Ar + NH). ^{13}C NMR: δ 122.5, 128.3, 128.9, 129.1, 130.3, 131.0 [C-2(6), C-3(5) of ArN, 3-Ph, 5-Ar], 123.7 (C-4), 125.6, 126.6, 129.5, 134.4, 135.7, 136.7, 139.3 (C-1, C-4 of PhN, 3-Ph, 5-Ar; C-3), 162.8 (C-2), 173.3 (C-5), 178.3 (C-3a).

5-(4-Chlorophenyl)-2-(3-Chlorophenylamino)-3-phenyl-1,6,6aλ⁴-trithiapentalene (**8i**). IR: υ (N–H) 3364 cm^{-1}. ^1H NMR: δ 6.97 (1H, 4-H), 7.10–7.64 (14H, m, ArN + 3-Ph + 5-Ar + NH). ^{13}C NMR: δ 120.4, 124.1, 125.4, 126.7, 129.3, 129.8, 134.2, 134.5, 135.9, 136.6, 140.6 (C-1–C-6 of ArN; C-1, C-4 of 3-Ph, 5-Ar; C-3), 122.3 (C-4), 128.4, 129.0, 130.5, 131.0 [C-2(6), C-3(5) of 3-Ph, 5-Ar], 163.0 (C-2), 173.8 (C-5), 177.9 (C-3a).

2-Benzylamino-3-phenyl-5-(2-thienyl)-1,6,6aλ⁴-trithiapentalene (**8j**). IR: υ (N–H) 3355 cm^{-1}. ^1H NMR: δ 4.66 (2H, d, $J_{CH_2,NH}$ 5.8, CH_2), 6.12 (1H, t, NH), 6.81 (1H, 4-H), 6.97 (1H, dd, 4-H of thienyl), 7.18–7.54 (12H, m, 2 × Ph + 3-H and 5-H of thienyl). ^{13}C NMR: δ 50.0 (CH_2), 122.6 (C-4), 124.6, 127.3, 127.6, 127.9, 128.1, 128.8, 136.8, 137.1, 139.2 (C-1, C-4 of $PhCH_2N$, 3-Ph; C-3; C-2, C-3, C-4, C-5 of thienyl), 127.3, 128.7, 130.1, 130.9 [C-2(6), C-3(5) of $PhCH_2N$, 3-Ph], 154.4 (C-2), 171.7 (C-5), 182.6 (C-3a).

3-Phenyl-2-phenylamino-5-(2-thienyl)-1,6,6aλ⁴-trithiapentalene (**8k**). IR: υ (N–H) 3359 cm^{-1}. ^1H NMR: δ 6.95 (1H, 4-H), 6.97 (1H, dd, 4-H of thienyl), 7.10–7.64 (13H, m, 2 × Ph + 3-H and 5-H of thienyl + NH). ^{13}C NMR: δ 122.4, 128.9, 130.2, 131.0 [C-2(6), C-3(5) of PhN, 3-Ph), 122.5 (C-4), 125.6, 127.3, 128.1, 128.2, 129.1, (C-4 of PhN, 3-Ph; C-3, C-4, C-5 of thienyl), 126.2, 136.4, 139.4, 140.2 (C-1 of PhN, 3-Ph; C-3; C-2 of thienyl), 157.7 (C-2), 173.4 (C-5), 177.1 (C-3a).

2-(3-Chlorophenylamino)-3-phenyl-5-(2-thienyl)-1,6,6aλ⁴-trithiapentalene (**8l**). IR: υ (N–H) 3356 cm^{-1}. ^1H NMR: δ 6.94–7.63 (13H, m, ArN + 3-Ph + 5-thienyl + NH), 6.95 (1H, 4-H). ^{13}C NMR: δ 120.2, 122.1, 125.3, 126.3, 127.5, 128.2, 128.4, 129.2, 129.8, 134.4, 136.3, 139.8, 140.6 (C-1–C-6 of ArN; C-3; C-1, C-4 of 3-Ph; C-2, C-3, C-4, C-5 of thienyl), 123.0 (C-4), 130.3, 131.0 [C-2(6), C-3(5) of 3-Ph], 157.8 (C-2), 173.8 (C-5), 176.6 (C-3a).

Spectral Data for the 3H-1,2-Dithiol-3-ylideneacetamides (**11**)

N,2-Diphenyl-2-(5-phenyl-3H-1,2-dithiol-3-ylidene)acetamide (**11a**). IR: υ (N–H) 3403 cm^{-1}; υ (C=O) 1614 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 6.77 (1H, 4-H); 7.04–7.08 (1H, t), 7.24–7.31 (2H, t), 7.40–7.60 (12H, m) (3 × Ph); 8.29 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 117.8 (C-2), 120.7 (C-4), 120.5, 126.5, 128.3, 129.2, 129.4, 130.7 [C-2(6), C-3(5) of PhN, 3-Ph, 5-Ph], 123.3, 128.2, 130.3, 132.4, 135.5, 138.6 (C-1, C-4 of PhN, 3-Ph, 5-Ph), 156.4 (C-1), 162.9 (C-5), 166.1 (C-3).

N-(4-Chlorophenyl)-2-phenyl-2-(5-phenyl-3H-1,2-dithiol-3-ylidene)acetamide (**11b**). IR: υ (N–H) 3402 cm^{-1}; υ (C=O) 1612 cm^{-1}. ^1H NMR [$(CD_3)_2SO$]: δ 6.76 (1H, 4-H), 7.30–7.64 (14H, m, ArN + 3-Ph + 5-Ph), 8.50 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 117.6 (C-2), 120.8 (C-4), 122.1, 122.6, 128.1, 129.3, 129.4, 130.8 [C-2(6), C-3(5) of ArN, 2-Ph, 5-Ph], 126.9, 128.2, 130.4, 132.4, 135.4, 137.7 (C-1, C-4 of ArN, 3-Ph, 5-Ph), 156.7 (C-1), 163.4 (C-5), 166.1 (C-3).

N,2-Diphenyl-2-[5-(4-methoxyphenyl)-3H-1,2-dithiol-3-ylidene]acetamide (**11c**). IR: υ (N–H) 3402 cm^{-1}; υ (C=O) 1610 cm^{-1}. ^1H NMR: δ 3.79 (3H, OMe), 6.68 (1H, 4-H), 6.84 (2H, *m*-protons of 5-Ar), 6.96–7.55 (13H, ArN + 2-Ph + *o*-protons of 5-Ar + NH). ^{13}C NMR: δ 55.3 (OMe), 114.2 [C-3(5) of 5-Ar], 115.9 (C-2), 119.4, 128.4, 128.8, 129.8, 130.9 [C-2(6), C-3(5) of PhN, 2-Ph; C-2(6) of 5-Ar], 120.0 (C-4), 123.6 (C-4 of PhN), 125.8, 136.8, 138.2 (C-1 of PhN, 2-Ph, 5-Ar), 128.5 (C-4 of 2-Ph), 157.7 (C-1), 161.1 (C-4 of 5-Ar), 164.6 (C-5), 166.1 (C-3).

N-(4-Chlorophenyl)-2-[5-(4-methoxyphenyl)-3H-1,2-dithiol-3-ylidene]-2-phenylacetamide (**11d**). IR: υ (N–H) 3399 cm^{-1}; υ (C=O) 1607 cm^{-1}. ^1H NMR: δ 3.80 (3H, OMe), 6.67 (1H, 4-H), 6.85 (2H, *m*-protons

of 5-Ar), 6.94 (1H, s), 7.35–7.59 (9H, m) (ArN + 2-Ph + NH), 7.21 (2H, *o*-protons of 5-Ar). ^{13}C NMR: δ 55.4 (OMe), 114.2 [C-3(5) of 5-Ar], 115.6 (C-2), 120.0 (C-4), 120.6, 128.5, 128.8, 129.9, 130.9 [C-2(6), C-3(5) of ArN, 2-Ph; C-2(6) of 5-Ar], 125.7, 128.4, 136.6, 136.9 (C-1, C-4 of 2-ArN, C-1 of 2-Ph and 5-Ar), 128.6 (C-4 of 2-Ph), 158.1 (C-1), 161.2 (C-4 of 5-Ar), 165.1 (C-5), 166.0 (C-3).

2-[5-(4-Chlorophenyl)-3H-1,2-dithiol-3-ylidene]-N,2-diphenylacetamide (**11e**). IR: υ (N–H) 3399 cm^{-1}; υ (C=O) 1614 cm^{-1}. ^{1}H NMR: δ 6.72 (1H, 4-H), 6.98–7.59 (15H, m, PhN + 2-Ph + 5-Ar + NH). ^{13}C NMR: δ 117.0 (C-2), 119.5, 128.2, 128.9, 129.0, 129.9, 130.8, [C-2(6), C-3(5) of PhN, 2-Ph, 5-Ar], 121.7 (C-4), 123.8 (C-4 of PhN), 128.7 (C-4 of 2-Ph), 131.7, 136.1, 136.5, 138.0 (C-1 of PhN, 2-Ph, 5-Ph; C-4 of 5-Ph), 156.1 (C-1), 164.0 (C-5), 166.1 (C-3).

N-(4-Chlorophenyl)-2-[5-(4-chlorophenyl)-3H-1,2-dithiol-3-ylidene]-2-phenylacetamide (**11f**). IR: υ (N–H) 3398 cm^{-1}; υ (C=O) 1610 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 6.77 (1H, 4-H), 7.29–7.63 (13H, m, ArN + 2-Ph + 5-Ar), 8.52 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 117.9 (C-2), 121.3 (C-4), 122.2, 128.1, 128.3, 129.2, 129.4, 130.7 [C-2(6), C-3(5) of ArN, 2-Ph, 5-Ar], 128.2 (C-4 of 2-Ph), 128.5, 131.2, 134.9, 135.3, 137.6 (C-1 of 2-Ph; C-1, C-4 of ArN, 5-Ar), 155.1 (C-1), 163.2 (C-5), 166.1 (C-3).

N,2-Diphenyl-2-[5-(2-thienyl)-3H-1,2-dithiol-3-ylidene]acetamide (**11g**). IR: υ (N–H) 3399 cm^{-1}; ν (C=O) 1610 cm^{-1}. ^{1}H NMR: δ 6.66 (1H, 4-H) 6.97–7.59 (14H, m, PhN + 2-Ph + 5-thienyl + NH). ^{13}C NMR: δ 116.6 (C-2), 119.4, 128.9, 129.8, 130.8 [C-2(6) C-3(5) of PhN and 2-Ph], 120.8 (C-4), 123.7, 127.8, 127.9, 128.1, 128.7, 135.9, 136.4, 138.1 (C-1, C-4 of PhN, 2-Ph; C-2, C-3, C-4, C-5 of 5-thienyl), 150.0 (C-1), 163.6 (C-5), 166.1 (C-3).

N-(4-Chlorophenyl)-2-phenyl-2-[5-(2-thienyl)-3H-1,2-dithiol-3-ylidene]acetamide (**11h**). IR: υ (N–H) 3400 cm^{-1}; υ (C=O) 1610 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 6.62 1(1H, 4-H), 7.12 (1H, dd, 4-H of thienyl), 7.29–7.72 (11H, m, ArN + 2-Ph + 3-H and 5-H of thienyl), 8.55 (1H, NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 117.4 (C-2), 120.0 (C-4), 122.2, 128.1, 129.3, 130.7 [C-2(6), C-3(5) of ArN and 2-Ph], 126.9, 128.2, 128.5, 128.8, 129.5, 134.8, 135.2, 137.6 (C-1, C-4 of ArN, 2-Ph; C-2, C-3, C-4, C-5 of 5-thienyl), 149.1 (C-1), 162.7 (C-5), 166.1 (C-3).

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