Indenoxadiazine, indenopyrazole and spiro triazole derivatives from (substituted ylidene)-*N*-phenylhydrazine carbothioamides

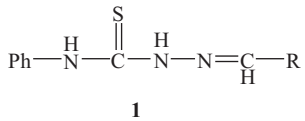
Alaa A. Hassan* and Hamdy S. Shehata

Chemistry Department, Faculty of Science, El-Minia University, 61519-El-Minia, A. R. Egypt

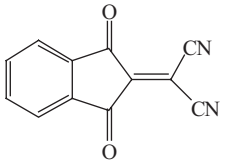
In a multistep reaction, indeno[2,1-*e*][1,3,4]oxadiazine-9-one, oxoindeno[1,2-*c*]- pyrazolecarbothioamide, (thioxo-1,2,4-triazaspiro[4.5]decadienylidene)malononitrile and spiro-(fluorine-9,3'-[1,2,4]triazoline)-5'-thione derivatives have been formed from a series of (substituted ylidene)-*N*-phenylhydrazinecarbothioamides **1a–e** with (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile, 7,7',8,8'-tetracyanoquinodimethane and (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile in aerated pyridine. Rationales of these conversions involving the nucleophilic reactions, condensation, dehydrogenation and oxidation are presented.

Keywords: (substituted ylidene)-*N*-phenylhydrazinecarbothioamides**,** indenoxadiazine**,** indeno-pyrazole and spiro triazole derivatives

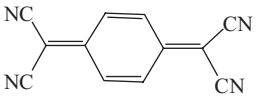
Azomethines constitute a densely populated class of compounds readily available by condensation of a carbonyl compound with ammonia derivative.[1, 2] Their widespread application in organic synthesis is based on the sensitivity of the C=N double bond towards attacks by nucleophiles and radicals, and an additional various possibilities offered by substituents on the nitrogen.[2-8]



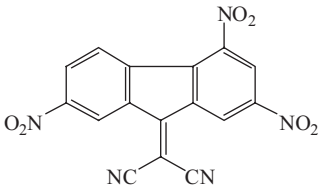
1



2



3



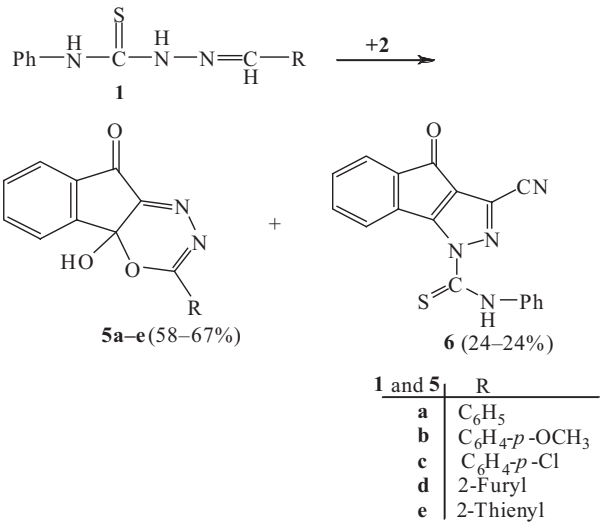
4

1	R
a	C_6H_5
b	C_6H_4-*p*-OCH_3
c	C_6H_4-*p*-Cl
d	2-Furyl
e	2-Thienyl

Fig 1

Aldehyde semicarbazones and thiosemicarbazones **(1)** are typical substrates that may undergo ring closure processes included by an oxidising agent to afford the corresponding 1,2,4-triazole and 1,2,4-oxa- or thiadiazole derivatives.[9-16] Selective combination of two or more different electron acceptors into one molecules leads to a series of new electron acceptors with unique properties. Such a composite acceptors are compounds **2-4**. (1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**2**), also referred to as 2-(dicyanomethylene)indane-1,3-dione readily adds *N*-nucleophiles such as secondary aliphatic[17] and primary aromatic amines[18] at the cyanomethylene carbon atom which release of hydrogen cyanide. Compound **2** is also able to generate imminium ions from the tertiary cyclic amines to generate α-cyanated amines.[19,20]

* Correspondent. E-mail: alaahasan2001@yahoo.com

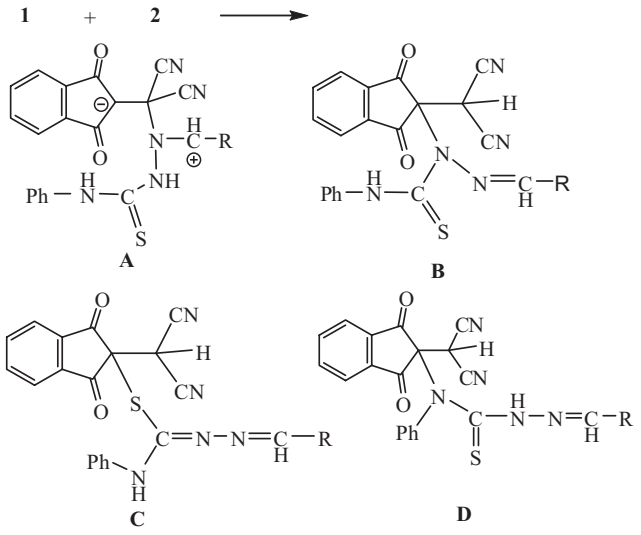


Scheme 1

Results and discussion

This paper focuses on the reactions of thiosemicarbazones **1a–e** with π-acceptors **2**–**4** (Fig. 1) to prepare fused and spiro heterocyclic compounds. We chose thiosemicarbazones **1a–e** having aryl groups with electron donating and withdrawing substituents on the benzene ring as well as heterocyclic rings, in order to examine their reactivity. Solutions of **1a–e** (1 mmol each) in dry pyridine were added to solutions of **2** (2 mmol). The mixtures were gently warmed to 80–100°C for 4 h with admission of air. Chromatographic separation of the residue afforded numerous zones, from which products **5** and **6** could be isolated (Scheme 1).

The structures of **5a–e** have been assigned on the basis of the elemental analyses and spectral data. The IR spectra showed strong absorption signals between 1725 and 1720 cm^{-1} for the carbonyl group, and between 3350–3335 cm^{-1} for hydroxyl group as well as 1080–1095 cm^{-1} for (C–O–C).[21] ^1H NMR spectra showed brood exchangeable signals with (D_2O) between 8.44 and 8.62 ppm due to hydroxyl group. The ^{13}C NMR decoupling showed signals between 94.26 and 94.96 ppm for aliphatic quaternary carbon atom bearing a hydroxyl group, between 164.12 and 164.76 for (*C*-3), and *C=N* attached to carbony group and adjacent to chiral carbon atom (*C*–9a) at 160.12–160.31 ppm, as well as carbonyl carbon at 193.42–193.74 ppm. The fragmentation patterns of the mass spectra of **5a–e** characterised by the loss of N_2 giving intense (M^+-28) ions and loss of RCO giving rise to the ion *m/z* = 145 common in the spectra of all compounds represents 1,3-dioxoindanyl fragments.



Scheme 2

Compound **6** shows a characteristic yellow colour. The gross formula $C_{18}H_{10}N_4OS$ of **6** was confirmed by the mass spectrum, which exhibited the molecular ion at *m/z* 330 (19%). The EI mass spectrum of **6** was characterised by molecular ion of low intensity and loss of 135 a.m.u. (representing Ph-N=C=S).

The resulting fragment ions undergo loss of 28 a.m.u (most likely dinitrogen) followed by loss of 27 (HCN). The IR spectrum of **6** showed strong absorption at 2225 due to cyano group, 1715 for the carbonyl group and bands characteristic of vibrational coupling of the C=S and C–N groups at 1360 and 995 cm^{-1}.[22] The ^1H NMR spectrum showed a broad signal at 9.91 ppm for NH attached to phenyl group besides the aromatic protons. Distinctive signals appeared in the ^{13}C NMR spectrum of **6** at δ = 194.16, 182.84 and 122.16, 118.26 corresponding to C=O, C=S, (C-3), and CN groups repectively. Next we have to accept that the nucleophilic attack at C=C of **2** theoretically from four positions of **1** (the three nitrogen atoms and the sulfur), thus giving rise to adducts **A–C** (Scheme **2**). **C** and **D** could be ruled out on the basis of the structures formed and the spectroscopic data. These results indicate that thiosemicarbazones **1a–e** react with **2** through a nucleophilic attack of **1a–e** to the C=C double bond of **2**, where the four electron-withdrawing groups (two nitrile and two carbonyl groups) facilitate this reaction to form the intermediates **A** and **B**. The hydrolysis of **A** followed by elimination of substituted aldehyde (RCHO) and loss of a molecule of HCN as well as H_2O afforded the indenopyrazole **6**. Elimination a molecule of Ph–N=C=S from the adduct **B**, followed by another molecule of malononitrile leads to the formation of **11** which, in turn, undergoes hydrolysis followed by dehydrogenation to give **13,** compound **13** exerts its nucleophilic character and attacking C-1 and forming compounds **5a–e** (Scheme 3). Many oxidised products have been isolated as a result of oxidative processes during the reaction of benzylidine compounds with π-deficient compounds.[23-25]

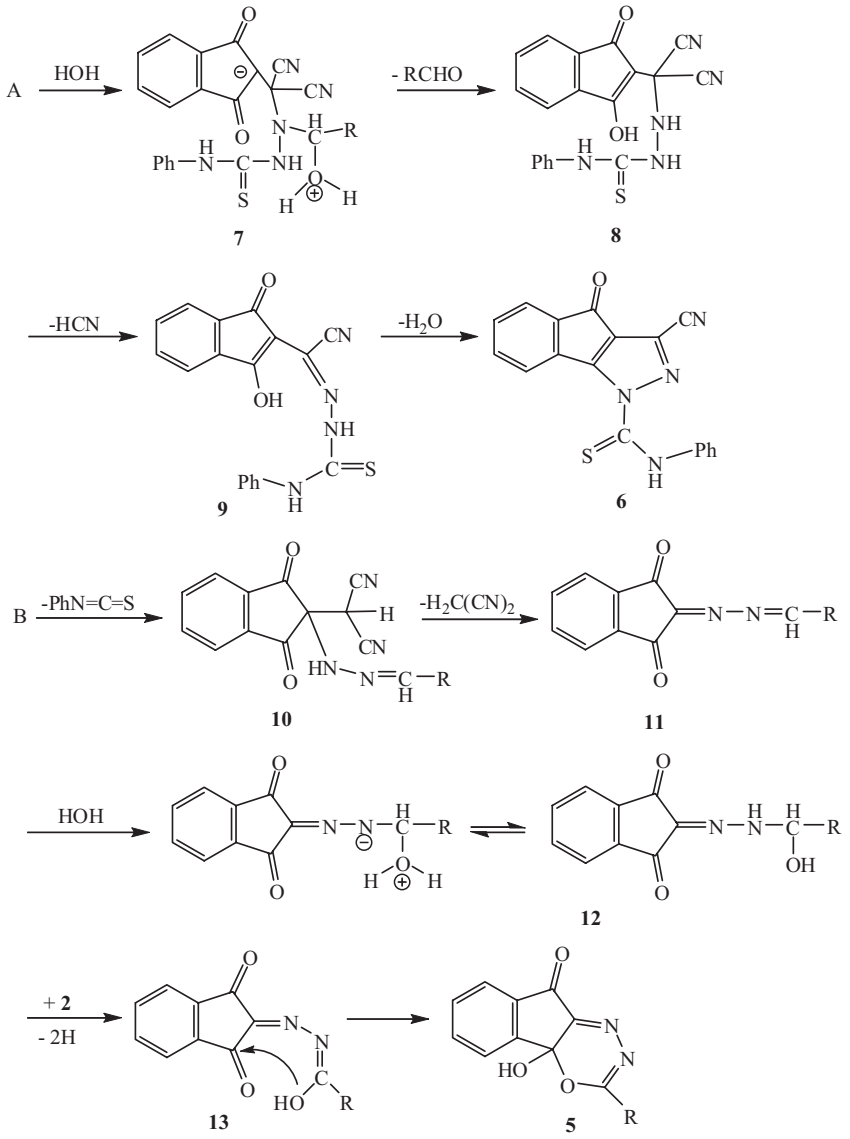
Much effort has been made so far to develop new electron acceptors whose structures would enhance the electrical conductivities of their charge transfer complexes. Such an attempts was made for the synthesis of 7,7',8,8'-tetracynoquinodimethane (**3**). The interest of **3** has focused on its potential applications on molecular rectifiers[26], non-linear optical materials[27] and electron accepting properties.[28] Mixture of two-fold molar amounts of **3** with one mole each of the donors **1a–e** in dry pyridine. The mixture was gently warmed with admission of air. The residue obtained from the concentration consisted of a complex mixture containing a deep blue main component **14a–e** and numerous coloured byproducts each in small quantities. From the gross composition and spectroscopic evidence the main products from **1a–e** were found to be formed from one molecule of **1a–e** and one of **3** in the presence of H_2O, by loss of 2H and one molecule of malononitrile.

The IR spectra (in KBr) of compounds **14a–e** show characteristic absorptions in the ranges of 3340–3325 (NH) and 1360–1350 as well as 995–1005 cm^{-1} to strong vibrational coupling of C=S and C–N entities. The IR spectra showed conjugated cyano groups at 2220–2225 cm^{-1} and carbonyl absorptions at 1700–1710 cm^{-1}. The ^1H NMR of **14b** clearly shows one broad signal at 8.10 for triazoline-NH, the expected signals for quinonoide-CH observed at δ = 6.69–6.82 ppm and singlet signal at 3.83 ppm due to OCH_3 signal besides the aromatic protons. Signals around 118.22 (CN), 172.28 (CO) and 183.55 ppm (C=S) in ^{13}C NMR spectrum further support for the structure assigned to **14b.** The molecular ions in EI-mass spectra of **14a–e** confirm the molecular masses and the gross compositions. Furthermore, the following common features of the fragmentation patterns also supports the assigned structures: Loss of Ph–N=C=S giving intense (M^+–135) and loss of RCO giving rise to the ion *m/z* 168 common in the spectra of all five compounds. The *a priori* possible isomeric structures **15a–d** (Scheme 4) were ruled out on the basis of the lowest field signals in the ^{13}C NMR spectra **14b** = 183.55, **14c** = 183.46, **14d** = 183.74 and **14e** = 183.34 ppm) which clearly support a C=S group and not an isothiourea carbon as in **15.** The formation of products **14a–e** may be rationalised by the mechanism shown in Scheme 5.

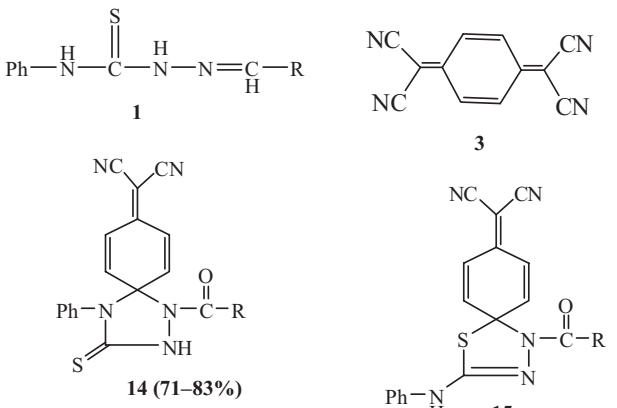
It has been reported earlier that (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**4**) and other 9-(dicyanomethylene) nitrofluorene derivatives react with secondary amines with subsequent substitution of cyano by amino groups to afford trinitrosubstituted-9-(aminomethylene)fluorenes, while we have reported the complex reaction of *N*-arylisoindolines (being tertiary amines) with **4**.[30] It has been found that the addition of N^2 of amidines to one of the cyano groups of **4** gives spiro[fluorene-9,4'-(1',2',3',4'-tetrahydropyridine)]-5'-carbonitriles.[31] Recently, it has been reported that 4-substituted thiosemicarbazides reacted with **4** to form spiro[fluorine-9,3'-[1,2,4]triazole]derivatives and (4-substituted thiosemicarbazone)propanedinitriles.[32] This fascinating versatility in the chemistry of **4** is intriguing and justifies further investigations of reactions of **4** with thiosemicarbazones **1a–e**.

Pyridine solutions, 1.38 mmol each in **4** and thiosemicarbazones **1a–e**, respectively, were kept at 100°C for 3 hours with admission of air. Chromatographic separation of the residue obtained after concentration gave numerous coloured zones, from which the products **21a–e** and **25a–e** could be isolated (Scheme 6).

In addition compounds **22–24** were found in small quantities in all cases. Structure assignments of compounds **21a–e** were based on spectral data from combustion analysis. For **21a** the gross formula $C_{27}H_{18}N_6O_5S$ was confirmed by the mass spectrum which exhibited the molecular ion at *m/z* 538 (26%), which also shows fragments for loss of RCO and Ph–N=C=S. The IR spectrum showed absorption at 3420, 3375 (NH_2, NH) and 1360 as well as 1010 cm^{-1} to vibrational coupling of C=S and C–N. Two bands around 1530 and 1335 cm^{-1} have to be assigned to the nitro group. The ^1H NMR spectrum showed the presence of the two broad signals centred at 8.88 and 6.52 ppm due to triazole-NH and exocyclic NH_2, respectively, in addition to 15 aromatic protons. Also, the ^{13}C NMR thiocarbonyl and carbonyl resonances (in DMSO-d_6) are formed at 183.84 and 169.36 ppm, respectively.



Scheme 3

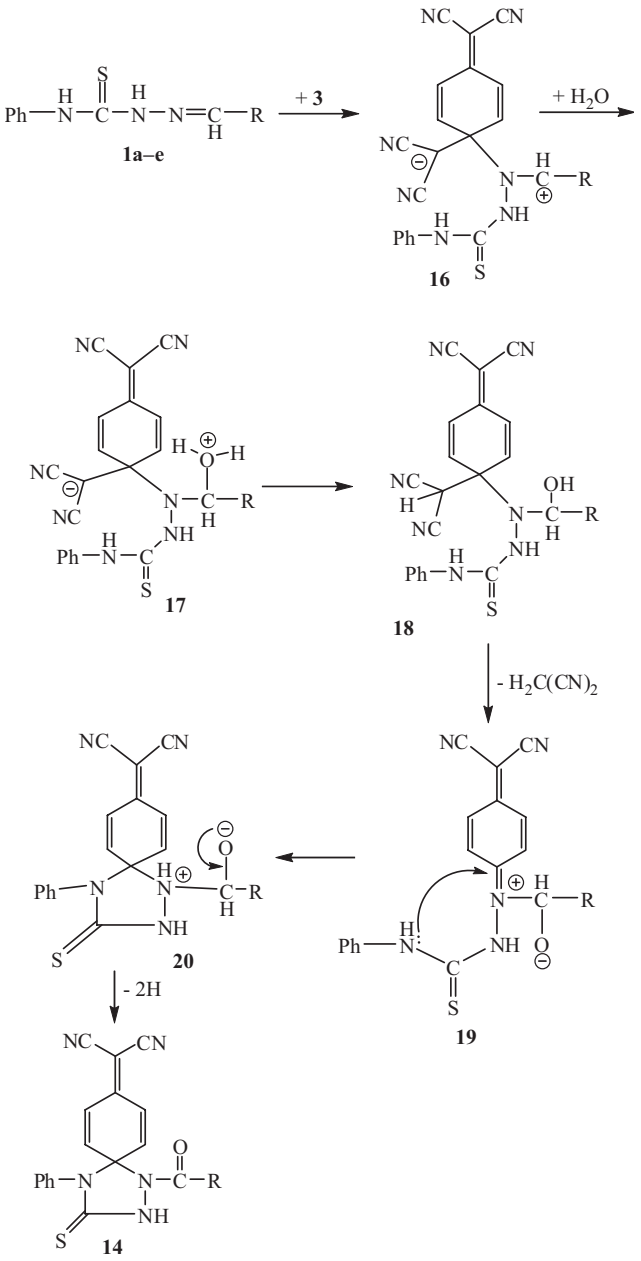


1 and 14	R
a	C_6H_5
b	C_6H_4-*p*-OCH_3
c	C_6H_4-*p*-Cl
d	2-Furyl
e	2-Thienyl

Scheme 4

The isolation of reduction products **23** and **24** derived from **4** posed a special problem. The results of combustion analysis and spectral data suggested that one of the three nitro groups in both cases had been reduced, but it was difficult decide on the basis of IR and ^{1}H NMR spectra which one of the three nitro groups had been replaced by an amino group. Acetylation of **23** gave a product showing a UV/Vis spectrum very similar to that of 2,7-dinitrofluorenone. On this basis it is suggested that compound **23** is 4-amino-2,7-dinitro-9-fluorenone. When the latter was treated with malononitrile in methanol in the presence of piperidine, a product identical in its m.p., IR and ^{1}H NMR spectra with the sample of **24** as isolated before was obtained.[30] The identity of reduction products **23** and **24** as well as 2,4,7-trinitro-9-fluorenone **22** derived from **4** was also demonstrated by comparison with authentic samples.[30]

The reaction conditions provide an overall dehydrogenating and oxygenating environment. The most likely introductory steps have been outlined in scheme 7. Starting materials **1a–e** form, *via* a CT-complex followed by a radical ion pair and the radical pair **1**$^{\cdot+}$ **4-H**$^{\cdot}$ as intermediates, the (4-amino-2,7-dinitro-9*H*-fluoren-9-ylidene)propanedinitrile **24**. Compounds **1a–e** may attack a molecule of **24** followed by elimination a molecule of malononitrile and another of hydrogen to give spiro compounds **21a–e**. On the other hand, **1a–e** may react



Scheme 5

with another molecule of **4** to give the adduct **27** which, in turn, may break down to malononitrile, thiadiazoles (**25**) and compound **28**, being a precursor to 2,4,7-trinitro-9-fluorenone (**22**). Reduction product **24** may react similarly to generate **23**.

Conclusion

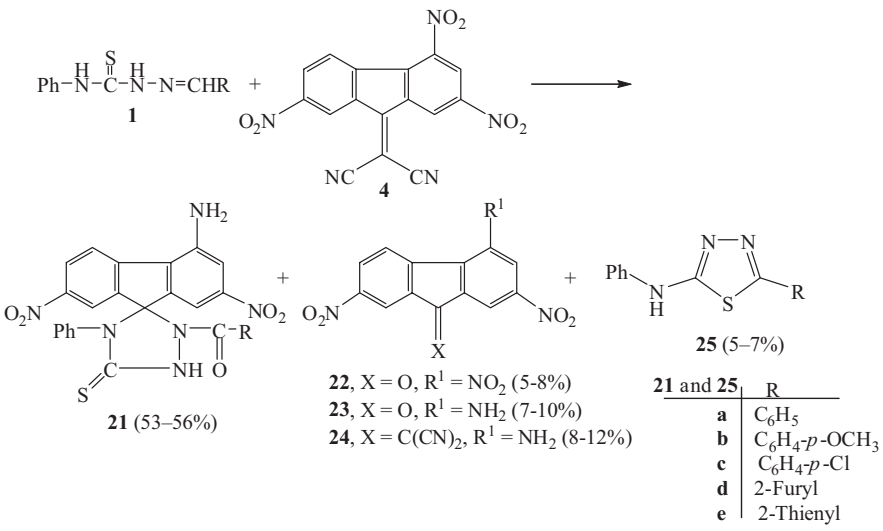
Different interesting fused and spiro heterocyclic structures have been obtained from the interaction of electron rich thiosemicarbazones **1a–e** with the TCNE-analogous acceptors (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (**2**), 7,7',8,8'-tetracyanoquinodimethane (**3**) and (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**4**). The reactions and products presented here provide insight into the spontaneous reactions between electron donors **1a–e** and some electron acceptors **2**–**4.** The results reported also indicate that thiosemicarbazones **1a–e** react like amines with compounds **2**–**4** that is by nucleophilic addition–elimination mechanism, through C=C double bond of **2**, **3** and **4.**

Experimental

The uncorrected melting points were determined on a Gallenkamp melting point apparatus; IR spectra were recorded using KBr disks on Shimadzu 408 instruments. ^{1}H NMR 500 MHz and 125 MHz ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer. Chemical shifts are expressed as δ [ppm] with reference to the tetramethylsilane as an internal standard, s = singlet, m = multiplet, d = doublet, br = broad. The ^{13}C signals were assigned on the basis of DEPT 135/90 spectra. The mass spectra (70 ev, electron impact mode) were recorded on a Varian MAT 311 instrument. Combustion analyses were run at the microanalytical centre, Cairo University, Egypt. Preparative layer chromatography (PLC) was carried out using air dried 1.0 mm thick layers of slurry of silica gel (Merck Pf_{254}) applied on 48 cm wide and 20 cm high glass plates using toluene/ethyl acetate as developing solvent. Zones were detected by their colour or by quenching of indicator fluorescence upon exposure to 254 nm light and extracted out with acetone.

Starting materials

2-(Substituted benzylidene)-*N*-phenylhydrazinecarbothioamides **1a–e** were prepared according to the literatures.[34-38] The ^{1}H NMR spectra of 2-benzylidene-*N*-phenyhydrazine-carbothioamide (**1a**),[34] 2-(4-methoxy-benzylidene)-*N*-phenylhydrazinecarbothioamide (**1b**),[35] 2-(4-chlorobenzylidene)-*N*-phenylhydrazinecarbothioamide (**1c**),[36] *N*-pheny-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamide (**1d**)[37] and 2-(furan-2-ylmethylene)-*N*-phenylhydrazinecarbothioamide (**1e**)[38] were in full accord with the published data. 2-(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile (dicyanomethyleneindane-1,3-dione) (**2**) was prepared according to Chatterjee.[39] 7,7',8,8'-Tetra-cyano-quinodimethane (**3**) (Aldrich). (2,4,7-Trinitro-9*H*-fluoren-9-ylidene) propanedinitrile (**4**) was prepared from 2,4,7-trinitro-9-fluorenone and malononitrile according to Mukherjee.[40]



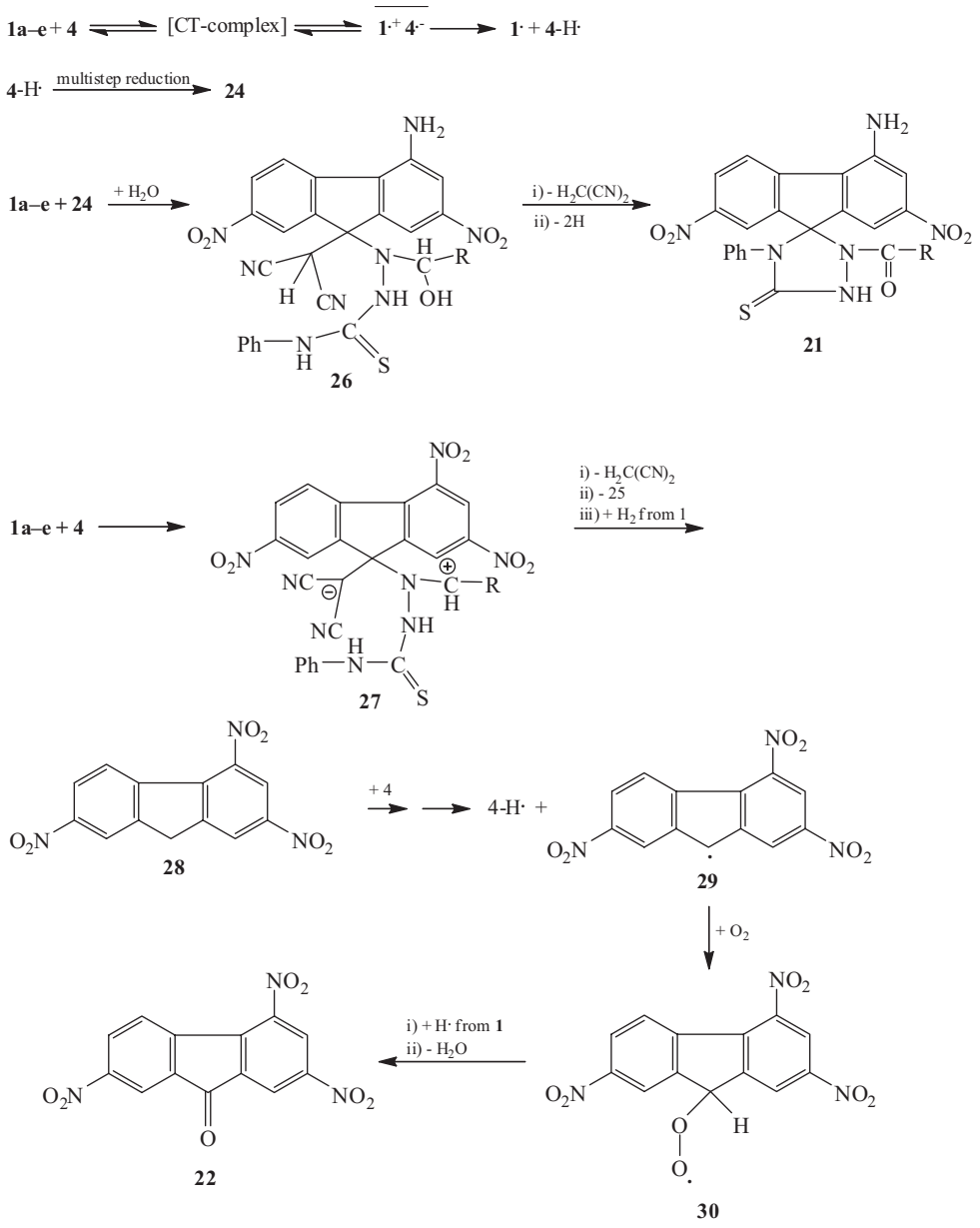
21 (53–56%)

22, X = O, R^1 = NO_2 (5-8%)
23, X = O, R^1 = NH_2 (7-10%)
24, X = $C(CN)_2$, R^1 = NH_2 (8-12%)

25 (5–7%)

21 and **25**	R
a	C_6H_5
b	C_6H_4-*p*-OCH_3
c	C_6H_4-*p*-Cl
d	2-Furyl
e	2-Thienyl

Scheme 6



Scheme 7

Reactions of (1,3-dioxo-2,3-dihydro-1H-indene-2-ylidene)propanedinitrile (**2**) *with* **1a–e**

To a solution of 2 (416 mg, 2.0 mmol) in dry pyridine (10 ml) a solution of **1a–e** (1.0 mmol each) in 10 ml of pyridine was added dropwise over 5 min at room temperature with stirring and admission of air. The mixture was warmed gently to 80–100°C and kept at this temperature with stirring and admission of air for 4 h and concentrated to dryness. The residue was taken up several times with cold ethanol (15 ml) at the slurry was concentrated again to remove any residue pyridine. The solid was then taken up in hot methanol, and solution was filtrated. This operation was repeated four times. Filtrates and extracts were combined and concentrated to dryness and the residue was dissolved in acetone (5 ml). The solution in each case was applied to 5 PLC-plates and developed with toluene/ethyl acetate (3 : 1) for the run with **1a–c** and toluene/ethyl acetate (4 : 1) for the run with **1d**,**e**. Two intense main zones were extracted. The fastest migrating zone contained 4a-hydroxy-3-aryl indeno[2,1-*e*][1,3,4]oxadiazine-9(4a*H*)-one (**5a–e**), whereas the second zone contained 3-cyano-4-oxo-*N*-substituted[1,2-*c*]pyrazole-1(4*H*)-carbothioamide **6**. Extraction of the zones with acetone and recrystallisation from suitable solvents afforded compounds **5a–e** and **6**.

4a-Hydroxy-3-phenylindeno[2,1-e][1,3,4]oxadiazin-9(4aH)-one (**5a**): Pale orange crystals (0.175 g, 63%), m.p. 212–214°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.44 (br, 1H, OH), 7.46–7.98 (m, 9H, aryl H). ^{13}C NMR: δ = 193.66 (*C*-9), 164.28 (*C*-3), 160.19 (*C*-9a), 147.66, 143.35, 134.64 (aryl-*C*), 131.28, 130.12, 128.86, 128.41, 127.83, (aryl-*C*H), 93.27 (*C*-4a). IR (KBr): 3445 (OH), 1720 (CO), 1635 (C=N), 1095 (C–O–C). MS (*m/z*,%): 278 (M^+, 42), 250 (61), 145 (32), 105 (10), 77 (86). $C_{16}H_{10}N_2O_3$ (278.26): Calcd; C, 69.06; H, 3.62; N, 10.07. Found C, 68.79; H, 3.81; N, 9.84.

4a-Hydroxy-3-(4-methoxypheny)indeno[2,1-e][1,3,4]oxadiazin-9(4aH)-one (**5b**): Orange crystals (0.206 g, 67%), m.p. 241–243°C (methanol). ^{1}H NMR (DMSO-d_6): δ = 8.51 (br, 1H, OH), 7.10–8.00 (m, 8H, aryl H), 3.86 (s, 3H, OCH_3). ^{13}C NMR: δ = 193.42 (*C*-9), 164.37 (*C*-3), 160.13 (*C*-9a), 147.53, 142.16, 130.46 (aryl-*C*), 130.22, 128.19, 127.78, 126.91 (aryl-*C*H), 94.46 (*C*-4a), 56.12 (*C*H_3O). IR (KBr): 3450 (OH), 1725 (CO), 1630 (C=N), 1080 (C–O–C). MS (*m/z*,%): 308 (M^+, 24), 277 (29), 249 (26), 145 (46), 135 (76), 104 (82), 77 (100). $C_{17}H_{12}N_2O_4$ (308.29): Calcd; C, 66.23; H, 3.92; N, 9.09. Found: C, 66.46; H, 4.11; N, 8.82.

3-(4-Chloropheny)-4a-hydroxyindeno[2,1-e][1,3,4]oxadiazin-9(4aH)-one (**5c**): Yellow crystals (0.161 g, 58%), m.p. 253–255°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.62 (br, 1H, OH), 7.51–7.82 (m, 8H, aryl H). ^{13}C NMR: δ = 193.58 (*C*-9), 164.78 (*C*-3), 160.21 (*C*-9a), 147.39, 142.18, 136.86, 132.26 (aryl-*C*), 129.34, 128.98, 127.74 (aryl-*C*H), 94.96(*C*-4a). IR (KBr): 3440(OH), 1725 (CO), 1640 (C=N), 1085 (C–O–C). MS (*m/z*,%): 314/312 (M^+, 46), 284 (34), 248 (19), 145 (39), 140 (62), 105 (74), 77 (100). $C_{16}H_9ClN_2O_3$ (312.71): Calcd; C, 61.45; H, 2.90; Cl, 11.34; N, 8.96. Found: C, 61.67; H, 3.06; Cl, 11.19; N, 9.12.

3-(Furan-2-yl)-4a-hydroxyindeno[2,1-e][1,3,4]oxadiazin-9(4aH)-one (**5d**): Yellow crystals (0.161 g, 60%), m.p. 192–194°C (ethanol). ^{1}H NMR (DMSO-d_6): δ = 8.58 (br, 1H, OH), 6.67–7.80 (m, 7H, aryl and furan-H). ^{13}C NMR: δ = 193.52 (*C*-9), 164.76 (*C*-3), 160.31 (*C*-9a), 147.41, 143.33, 142.26, (aryl and furan-*C*), 140.18 (furan-*C*H-5), 128.26, 127.86 (aryl-*C*H), 112.74, 112.16 (furan-*C*H-3,4), 94.84 (*C*-4a). IR (KBr): 3435 (OH), 1725 (CO), 1635 (C=N), 1075, 1090 (C–O–C). MS (*m/z*,*%*): 268(M$^+$, 36), 240 (17), 145 (56), 105 (83), 95 (100), 67 (64). $C_{14}H_8N_2O_4$ (268.22): Calcd; C, 62.69; H, 3.01; N, 10.44. Found: C, 62.86; H, 2.89; N, 10.65.

4a-Hydroxy-3-(thiophene-2-yl)indeno[2,1-e][1,3,4]oxadiazine-9(4aH)-one (**5e**): Yellow crystals (0.185 g, 65%), m.p. 227–229°C (ethanol). ^{1}H NMR (DMSO-d_6): δ = 8.62 (br, 1H, OH), 7.21–7.90 (m, 7H, aryl and thiophen-H). ^{13}C NMR: δ = 193.74 (*C*-9), 164.12 (*C*-3), 160.23 (*C*-9a), 147.46, 142.33, 130.19 (thiophenyl and aryl-*C*), 94.26 (*C*-4a). IR (KBr): 3445 (OH), 1720 (CO), 1640 C=N), 1090, 1090 (C–O–C). MS (*m/z*,*%*): 284 (M$^+$, 46), 256 (18), 145 (61), 139 (92), 105 (100), 77 (65). $C_{14}H_8N_2O_3S$ (284.29): Calcd; C, 59.15; H, 2.84; N, 9.85; S, 11.28. Found: C, 58.96; H, 2.97; N, 10.07; S, 11.46.

3-Cyano-4-oxo-N-phenylindeno[1,2-c]pyrazole-1(4H)-carbothioamide (**6**): Yellow crystals (0.079–0.092 g, 24–28%), m.p. 276–278°C (methanol). ^{1}H NMR (DMSO-d_6): δ = 9.91 (br, 1H, NH), 6.94–7.78 (m, 9H, aryl H). ^{13}C NMR: δ = 194.16 (*C*=*O*), 182.84 (*C*=*S*), 152.23 (*C*-8b), 140.29, 137.63, 135.18 (aryl-*C*), 130.14, 129.54, 128.62, 127.43, 126.87 (aryl-*C*H), xxxx (*C*-3), 106.14 (*C*-3a). IR (KBr): 3335 and 3280 (NH), 2225 (CN), (OH), 1715 (CO), 1625 (C=N), 1575 (NH def. and C–N str.), 1360, 995 (C=S, C-N). MS (*m/z*,*%*): 330 (M$^+$, 19), 195 (29), 167 (48), 105 (69), 77 (87), 65 (100). $C_{18}H_{10}N_4OS$ (330.36): Calcd; C, 65.44; H, 3.05; N, 16.96; S, 9.71.Found: C, 65.21; H, 2.89; N, 17.14; S, 9.54.

Reaction of 7,7',8,8'-tetracyanoquinodimethane (**3**) *with* **1a–e.** A solution of 2-(substituted ylidene)-*N*-phenyhydrazine-carbothioamides **1a–e** (1.0 mmol) in 10 ml of dry pyridine was added dropwise to a solution of **3** (2.0 mmol) in 15 ml of dry pyridine with stirring. The mixture was warmed gently to 60–70°C and kept at this temperature with stirring and admission of air for 3 h, then warmed to maximum 100°C for few minutes and concentrated to dryness at 60°C. The residue was washed several times with ethanol to remove residual pyridine. The residue was dissolved in acetone and separated by preparative layer chromatography using toluene/ethyl acetate (5:3) as eluent. Intense blue main zones were extracted and the residue subjected to repeated plc with the same solvents. Crystallisation from acetonitrile afforded pure samples of **14a–e,** all appearing black, but giving blue solutions in acetonitrile, ethyl acetate or methanol. Numerous other mostly coloured zones were observed but it always contained too little materials to allow for isolation and significant amounts and had to be discarded as well as the tarry materials remaining at the start line.

(1-Benzoyl-4-phenyl-3-thioxo-1,2,4-triazaspiro[4.5]deca-6,9-dien-8-ylidene)malononitrile (**14a**): Blue crystals (0.323 g, 79%), m.p. 285–287°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.10 (br, 1H, NH), 7.60–7.82 (m, 10H, aryl H), 6.72–6.86 (dd, dd, 4H, cyclohexadiene-H). ^{13}C NMR: δ = 183.67 (*C*=*S*), 172.44 (*C*O), 169.84 (*C*-δ), 140.74, 137.96 (aryl-*C*), 120.64 (cyclohexadiene-*C*H-3',5'), 118.34 (*C*N), 76.33 (*C*-5), 71.33 (*C*-2). IR (KBr): 3340 (NH), 2225 (CN), 1705 (CO), 1570 (NH def. and C–N str.), 1355, 1005 (C=S, C–N). MS (*m/z*,*%*): 409 (M$^+$, l29), 274 (49), 169 (51), 141 (26), 135 (64), 106 (47), 105 (100), 77 (69), 65 (53). $C_{23}H_{15}N_5OS$ (409.46): Calcd; C, 67.47; H, 3.69; N, 17.10; S, 7.83. Found: C, 67.24; H, 3.84; N, 16.88; S, 8.06.

1-[(4-Methoxybenzoyl)-4-phenyl-3-thioxo-1,2,4-triazaspiro[4.5]deca-6,9-dien-8-ylidene]malononitrile (**14b**): Blue crystals (0.364 g, 83%), m.p. 310–312°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.10 (br, 1H, NH), 7.54–7.76 (m, 9H, aryl H), 6.69–6.82 (dd, dd, 4H, cyclohexadien-H), 3.83 (S, 3H, OCH_3). ^{13}C NMR: δ = 183.55 (*C*=*S*), 172.28 (*C*O), 170.14 (*C*-δ), 162.18, 140.76, 134.23 (aryl-*C*), 132.48, 129.82, 128.96, 128.22, 127.93, 127.68, 127.56 (cyclohexadiene-*C*H-6,10 and aryl-*C*H), 120.53 (cyclohexadiene-*C*H-7,9), 118.22 (*C*N), 76.22 (*C*-5), 72.11 (*C*-2), 56.12 (CH_3O). IR (KBr): 3330 (NH), 2220 (CN), 1710 (CO), 1565 (NH def. and C–N str.), 1360, 995 (C=S, C–N). MS (*m/z*,*%*): 439 (M$^+$, 27), 408 (12), 304 (42), 168 (56), 140 (29), 136 (87), 135 (100), 105 (61), 77 (42), 65 (59). $C_{24}H_{17}N_5O_2S$ (439.49): Calcd; C, 65.59; H, 3.90; N, 15.94; S, 7.30.Found: C, 65.36; H, 4.02; N, 16.18; S, 7.55.

[1-(4-Chlorobenzoyl)-4-phenyl-3-thioxo-1,2,4-triazaspiro[4.5]deca-6,9-dien-ylidene]malononitrile (**14c**): Blue crystals (0.315 g, 71%), m.p. 318–320°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.16 (br, 1H, NH), 7.76–7.94 (m, 9H, aryl H), 6.75–6.88 (dd, dd, 4H, cyclohexadien-H). ^{13}C NMR: δ = 183.46 (*C*=*S*), 172.45 (*C*O), 169.88 (*C*-δ), 140.33, 136.24, (aryl-*C*), 132.14, 130.16, 129.52, 128.96, 128.44, 127.84 (aryl-*C*H), 120.74 (cyclohexadiene-*C*H-7,9), 118.68 (*C*N), 76.39 (*C*-5), 72.89 (*C*-2). IR (KBr): 3325 (NH), 2225 (CN), 1700 (CO), 1575 (NH def. and C–N str.), 1350, 1005 (C=S, C–N). MS (*m/z*,*%*): 445/443 (M$^+$, 46), 407 (33), 308 (41), 168 (21), 140 (64), 135 (76), 105 (37), 77 (100), 65 (68). $C_{23}H_{14}ClN_5OS$ (443.91): Calcd; C, 62.23; H, 3.18; Cl, 7.9 N, 15.78; S, 7.22. Found: C, 62.46; H, 3.27; Cl, 8.19; N, 15.51; S, 7.45.

[1-(Furan-2-carbonyl)-4-phenyl-3-thioxo-1,2,4-triazaspiro[4.5]deca-6,9-dien-ylidene]malononitrile (**14d**): Blue crystals (0.295 g, 74%), m.p. 271–273°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.14 (br, 1H, NH), 7.27–7.85 (m, 8H, furan and aryl-H) 6.72–6.84 (dd, dd, 4H, cyclohexadien-H). ^{13}C NMR: δ = 183.12 (*C*=*S*), 170.34 (*C*-δ), 168.12 (*C*O), 147.18, 140.46, (aryl-*C* and furan-*C*-2), 144.12 (furan-*C*H-5), 132.31, 129.43, 128.62 (aryl-*C*H), 120.62, 120.41, 119.74 (furan-*C*H and cyclohexadiene-*C*H-7,9), 118.34 (*C*N), 75.96 (*C*-5), 73.23 (*C*-2). IR (KBr): 3340 (NH), 2225 (CN), 1705 (CO), 1570 (NH def. and C–N str.), 1350, 1000 (C=S, C–N). MS (*m/z*,*%*): 399 (57), 264 (38), 168 (41), 135 (82), 95 (44), 77 (100), 65 (59). $C_{21}H_{13}N_5O_2S$ (399.43): Calcd; C, 63.15; H, 3.28; N, 17.53; S, 8.03. Found: C, 62.94; H, 3.41; N, 17.76; S, 7.86.

[4-Phenyl-1-(thiophen-2-carbonyl)-3-thioxo-1,2,4-triazaspiro[4.5]deca-6,9-dien-8-ylidene)malononitrile (**14e**): Blue crystals (0.320 g, 77%), m.p. 301–303°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.19 (br, 1H, NH), 7.23–7.89 (m, 8H, thiophen and aryl H), 6.74–6.87 (dd, dd, 4H, cyclohexadien-H).^{13}C NMR: δ = 183.34 (*C*=*S*), 179.12 (*C*-δ), 166.86 (*C*O), 140.65, 137.92 (thiophen-*C*-2 and aryl-*C*), 132.78, 132.46, 130.56, 129.16, 129.35, 128.46, 127.86 (cyclohexadien 6,10, thiophen and aryl-*C*H), 120.26 (cyclohexadiene-*C*H-7,9), 118.16 (*C*N), 76.18 (*C*-5), 72.67 (*C*-2). IR (KBr): 3335 (NH), 2220 (CN), 1710 (CO), 1565 (NH def. and C–N str.), 1360, 995 (C=S, C–N). MS (*m/z*,*%*): 415 (M$^+$, 51), 288 (48), 168 (34), 140 (28), 135 (49), 112 (37), 111 (74), 77 (100), 65 (78). $C_{21}H_{13}N_5OS_2$ (415.49): Calcd; C, 60.71; H, 3.15; N, 16.86; S, 15.43. Found: C, 60.94; H, 3.24; N, 17.15; S, 15.66.

Reactions of (2,4,7-trinitro-9H-fluoren-9-ylidene)propanedinitrile (**4**) *with* **1a–e.** To 1.38 mmol of **4** in dry pyridine (20 ml) equimolar amounts of **1a–e** in 10 ml of dry pyridine were added with stirring. The mixture was heated gently without increasing the temperature about 100°C for 5 hours. The solvent was removed by concentration and the residue was washed several times with ethanol to remove residual pyridine. The residue was dissolved in acetone and separated by preparative layer chromatography using toluene/ethyl acetate (2 : 1) as eluent into numerous zones, three of which were extracted. The fastest migrating zone contained 2,4,7-trinitro-9-fluorenone (**22**), the second zone which quenched all indicator fluorescence upon exposure to 254 nm UV-light contained the thiadiazoles **25a–e** the third zone which is always characterised by reddish orange colour, contained compounds **21a–e**. The material confirmed to the start was rechromatographed using toluene/ethyl acetate (1:1) to give another two zones, the faster migrating are of which contained 4-amino-2,7-dinitro-9-fluorenone (**23**) whereas the second zone (deep blue colour) contained (4-amino-2,7-dinitro-9*H*-fluorene-9-ylidene)propanedinitrile (**24**). Extraction of the zones with acetone and recrystallisation from suitable solvents afforded pure compounds.

4-Amino-1-benzoyl-2,7-dinitro-4'-phenylspiro(fluoren-9,3'-[1,2,4]triazolidine)-5'-thione (**21a**): Reddish orange crystals (0.290 g, 54%), m.p. 323–325°C (methanol). ^{1}H NMR (DMSO-d_6): δ = 8.88 (m, 15H, aryl H), 6.52 (br, 2H, NH_2). ^{13}C NMR: δ = 183.84 (*C*=*S*), 169.23 (*C*O), 148.19, 147.33 (*C*-7, *C*-2), 146.23 (*C*-4), 140.67, 138.12 (aryl-*C*), 131.44, 129.72, 129.26, 128.89, 128.38, 127.76, 127.45, 127.21, 126.36, 126.24, 125.83 (aryl-*C*H), and 78.46 (*C*-9 = *C*-3'). (KBr): 3420, 3375 (NH_2, NH), 1710 (CO), 1610 (aryl), 1530, 1335 (NO_2), 1360, 1010 (C=S, C–N). MS (*m/z*,*%*): 538 (M$^+$, 26), 433 (39), 432 (16), 298 (62), 270 (48), 294 (29), 135 (54), 105 (79), 105 (100), 77 (83), 65 (66). $C_{27}H_{18}N_6O_5S$ (538.53): Calcd; C, 60.22; H, 3.37; N, 15.61; S, 5.95. Found: C, 60.44; H, 3.51; N, 15.39; S, 6.12.

4-Amino-1-(4-methoxybenzoyl)-2,7-dinitro-4'-phenylspiro(fluoren-9,3'-[1,2,4]triazolidine)-5'-thione (**21b**): Reddish orange crystals (0.318 g, 56%), m.p. 339–341°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.90 (br, 1H, NH), 7.96–7.12 (m, 14H, aryl H), 6.48 (br, 2H, NH_2), 3.87 (S, 3H, OCH_3). ^{13}C NMR: δ = 183.59 (*C*=*S*), 170.14 (*C*O), 162.66 (aryl-*C*-OCH_3), 148.05, 147.12 (*C*-7, C-2), 146.57 (*C*-4), 140.46, 130.17 (aryl-*C*), 129.88, 128.22, 127.69, 127.23, 127.16, 126.84, 126.41, 126.19, 125.93, 125.36 (aryl-*C*H), 77.93 (*C*-9 = C-3'), 55.42 (CH_3O). IR (KBr): 3430, 3360 (NH_2, NH), 1705 (CO), 1600 (aryl), 1525, 1340 (NO_2), 1360, 990 (C=S, C–N). MS (*m/z*,*%*): 568 (M$^+$, 33), 433 (40), 298 (52), 270 (35), 224 (27), 178

(22), 135 (100), 77 (89), 65 (61). $C_{28}H_{20}N_6O_6S$ (568.56): Calcd; C, 59.15; H, 3.55; N, 14.78; S, 5.64. Found C, 58.92; H, 3.71; N, 15.03; S, 5.39.

4-Amino-1-(4-chlorobenzoyl)-2,7-dinitro-4'-phenylspiro(fluoren-9,3'-[1,2,4]triazolidine)-5'-thione (**21c**): Blue crystals (0.306 g, 53%), m.p. 347–49°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.88 (br, 1H, NH), 7.97–7.26 (m, 14H, aryl H), 6.54 (br, 2H, NH_2), 7.26–7.51. ^{13}C NMR: δ = 183.33 (*C*=*S*), 170.41 (*C*O), 148.21, 147.33 (*C*-7, *C*-2), 146.76 (*C*-4), 140.24, 136.14 (aryl-*C*), 138.22 (aryl-*C*-Cl), 130.14, 129.57, 128.88, 128.33, 127.94, 127.87 127.33, 126.96, 126.57, 126.26 (aryl-*C*H), 77.91 (*C*-9 = *C*-3'). IR (KBr): 3425, 3370 (NH_2, NH), 1720 (CO), 1615 (aryl), 1530, 1335 (NO2), 1355, 1005 (C=S, C–N). MS (*m/z,%*): 574/572 (M^+, 37), 536 (22), 432 (44), 298 (54), 270 (36), 178 (23), 140 (31), 135 (64), 77 (100), 65 (46). $C_{27}H_{17}ClN_6O_5S$ (577.48): Calcd; C, 56.60; H, 2.99; Cl, 6.19; N, 14.67; S, 5.60. Found: C, 56.81; H, 3.11; Cl, 5.97; N, 14.43; S, 5.81.

4-Amino-1-(furan-2-carbonyl)-2,7-dinitro-4'-phenylspiro(fluoren-9,3'-[1,2,4]triazolidine)-5'-thione (**21d**): Orange crystals (0.280 g, 53%), m.p. 316–318°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.91 (br, 1H, NH), 7.16–7.94 (m, 13H, aryl H), δ 6.51 (br, 2H, NH_2). ^{13}C NMR: δ = 183.26 (*C*=*S*), 168.72 (*C*O), 148.25, 147.41 (*C*-7, *C*-2), 147.10 (furan-*C*-2), 146.61 (*C*-4), 144.12 (furan-*C*H-5), 140.37, (aryl-*C*), 129.54, 128.77, 128.14, 127.84, 127.53, 127.15, 126.81, 126.66, 125.74, 125.26 (furan-and aryl-*C*H), 77.84 (*C*-9 = *C*-3'). IR (KBr): 3430, 3375 (NH_2, NH), 1705 (CO), 1600 (aryl), 1525, 1340 (NO2), 1360, 1010 (C=S, C–N). MS (*m/z,%*): 528 (M^+, 28), 433 (17), 433 (17), 298 (36), 270 (27), 178 (42), 135 (76), 95 (64), 77 (100), 65 (78). $C_{25}H_{16}N_6O6S$ (528.50): Calcd; C, 56.82; H, 3.05; N, 15.90; S, 6.07. Found: C, 56.61; H, 2.94; N, 16.12; S, 5.87.

4-Amino-2,7-dinitro-4'-phenylspiro(fluoren-9,3'-[1,2,4]triazolidine)-5'-thione-1-(thiophen-2-carbonyl) (**21e**): Reddish orange crystals (0.300 g, 55%), m.p. 334–336°C (acetonitrile). ^{1}H NMR (DMSO-d_6): δ = 8.90 (br, 1H, NH), 7.22–7.95 (m, 13H, thiophen and aryl-H), 6.56 (br, 2H, NH_2). ^{13}C NMR: δ = 183.42 (*C*=*S*), 168.84 (*C*O), 148.17, 147.29 (*C*-7, *C*-2), 146.61 (*C*-4), 140.38, 137.61 (thiophen and aryl-*C*), 131.16, 130.36, 129.57, 129.20, 128.67, 128.22, 127.91, 127.44, 127.16, 126.74, 126.23 (thiophen- and aryl-*C*H), 77.81 (*C*-9 = *C*-3'). IR (KBr): 3420, 3380 (NH_2, NH), 1710 (*C*O), 1595 (aryl), 1535, 1330 (NO2), 1360, 995 (*C*=*S*, *C*–N). MS (*m/z,%*): 544 (M^+, 46), 433 (31), 298 (19), 270 (37), 224 (18), 135 (100), 77 (94), 65 (36). $C_{25}H_{16}N_6O_5S_2$ (544.56): Calcd; C, 55.14; H, 2.96; N, 15.43; S, 11.78. Found: C, 54.91; H, 3.09; N, 15.65; S, 11.55.

2,4,7-Trinitro-9-fluorenone (**22**): M.p. 174–176°C (Lit.[33], 175°C) (5–8%).

4-Amino-2,7-dinitro-9-fluorenone (**23**): M.p. 311–313°C (Lit.[30], 310–312°C) (7–10%).

(4-Amino-2,7-dinitro-9H-fluoren-9-ylidene)propane dinitrile (**24**): M.p. 340–342°C (Lit.[30], 340–342°C) (8–15%).

Phenyl-(5-phenyl-3H-[1,3,4]thiadiazole-2-ylidene)amine (**25a**): M.p. 137–139°C (Lit.[41,42]139°C) (6%).

Phenyl-(5-(4-methoxyphenyl)-3-H-[1,3,4]thiadiazole-2-ylidene) amine (**25b**): M.p. 141–143°C (Lit.[42] 141°C) (7%).

Phenyl-(5-(4-chlorophenyl)-3-H-[1,3,4]thiadiazole-2-ylidene) amine (**25c**): M.p. 174–176°C (Lit.[42] 175°C) (5%).

5-(Furan-2-yl)-N-phenyl-1,3,4-thiadiazole-2-amine (**24d**): M.p. 174–176°C (Lit. [43] 175°C) (5%).

N-Phenyl-5-(thiophen-2-yl)-1,3,4-thiadiazole-2-amine (**25e**): M.p. 174–176°C (Lit.[43] 175°C) (6%).

Received 28 August 2007; accepted 9 November 2007
Paper 07/4857 doi: 10.3184/030823407X262472

References

1 D. Klamann and H. Hagemann *Organische Stickstoff-Verbindungen mitviner C, N, Doppol bindung* Thieme: Stuttgart 1990, Vol. E146.
2 G. Tennat, In *Comprehensive Organic Chemistry*, I.O., Sutherland, (ed.) Imines, nitrones, nitriles and isocyanides, Vol.2, Pergamon Press, Oxford, 1979; pp 385-443.
3 D. Enders and U. Reinhold, *Tetrahedron Asym*. 1997, **8**, 1895.
4 R. Bloch, *Chem. Rev.*, 1998, **98**, 1407.
5 A.G. Steining and D.M. Spero, *Org. Prep. Proc. Int*., 2000, **32**, 205.
6 E. Ãbele and E. Lukevies, *Org. Prep. Proc. Int.*, 2000, **32**, 235
7 J.P. Adams, *J. Chem. Soc. Perkin Trans. I*, 2000, 125.
8 G.K. Friestad, *Tetrahedron,* 2001, **57**, 5461.
9 P. Lo Meo, C. Aprile, F. D'Anna, M. Gruttadauria, S. Rieta and R. Noto, *Res. Adv. Inorg. Chem.,* 2000, **1**, 107.
10 M.S. Gibson, *Tetrahedron,* 1962, **18**, 1377.
11 G. Werber, F. Buccheri and M.L. Marino, *Ann. Chim*., 1972, **62**, 11.
12 R. Noto, F. Buccheri, G. Cusmano, M. Gruttadauria and G. Werber, *J. Heterocyc. Chem*., 1991, **28**, 1421.
13 M. Gruttadauria, F. Buccheri, G. Cusmano, P. Lo Meo, R. Noto and G. Weber, *J. Heterocyc. Chem*., 1993, **30**, 765.
14 R. Noto, P. Lo Meo, M. Gruttadauria and G. Weber, *J. Heterocyc. Chem*., 1996, **33**, 863.
15 M. Gruttadauria, P. Lo Meo, R. Noto and G. Weber, *Gazz. Chim It*., 1997, **127**, 277.
16 R. Noto, P. Lo Meo, M. Gruttadauria and G. Weber, *J. Heterocyc. Chem*., 1999, **36**, 667.
17 H. Fischer-Colbrie, H. Aigner and H. Junek, *Monatsch. Chem*., 1975, **106**, 743.
18 A. Boila-Göckel, W.M.F. Fabian and H. Junk, *Liebigs Ann. Chem*., 1996, 397.
19 D. Döpp, S. Jüschke and G. Henkel, *Z. Naturfarsch,* 2002, **57b**, 460.
20 D.D. Döpp, A.A. Hassan, A.M. Nour El-Din, A.E. Mourad, C.W. Lehmann and J. Rust, *Tetrahedron*, 2006, **62**, 11618.
21 D.A. Christos, G.V. Vagenas, L.C. Tzavellas, C.A. Tsoleridis and N.A. Rodios, *J. Heterocyc. Chem*., 1994, **31**, 1593.
22 G. Socrates, *Infrared Characteristic Group Frequencies*, Chichester, Wiley&Sons, 1980, pp. 116-117.
23 M.A.-M. Gomaa, A.A. Hassan and H.S. Shehatta, *Heteroatom Chem*., 2006, **17**, 261.
24 A.A. Hassan, N.K. Mohamed, A.A. Ali and A.E. Mourad, *Monatsh Chem*., 1997, **128**, 61.
25 A.A. Aly, E.K. Ahmed and K.M. El-Mokadam, *J. Sulf. Chem*., 2007, **28**, 285.
26 R.M. Metzger, R.R. Shumaker, M.P. Cara, R.K. Laidlow, L.A. Panetta and E. Torres, *Langmuir,* 1988, **4**, 298.
27 G.J. Ashwell, E. Je. Downay, A.P. Kuczynski, M. Szablewski, I.M. Sandy, M.R. Bryce, A.M. Grainger and M. Hasan, *J. Chem. Soc. Faraday Trans*., 1990, **86**, 1117.
28 N.A. Zaidi, M.R. Bryce and G.H. Cross, *Tetrahedron Lett*., 2000, **41**, 4645.
29 I.F. Perepichka, M.R. Bryle, A.S. Batsanov, J.A.K. Howard and J.C. Megson, *J. Chem. Soc., Perkin Trans. II*, 1995, 3.
30 A.A. Hassan, D. Döpp and G. Henkel, *J. Heterocyc. Chem*., 1998, **35**, 121.
31 M.A. Gomaa and D. Döpp, *J. Heterocyc. Chem.,* 1998, **35**, 339.
32 A.A. Hassan, Y.R. Ibrahim, A.M. Shawky and D. Döpp, *J. Heterocyc. Chem*., 2006, **43**, 849.
33 F. Bell. *J. Chem. Soc.,* 1928, 1990.
34 N.M. Koushik and A.K. Mishra, *Indian J. Chem.,* 2003, **42A**, 2762.
35 K.M.M.S. Prakash, L.D. Prabhakar and D.V. Reddy, *Analyt. Lett*., 1987, **20**, 959.
36 R. Beckert, M.G. Gruner, I. Seidel and R. Kuban, *Monatsh Chemie*., 1989, **120**, 1125.
37 J. El Mostapha, A. Magali, A.K. Mustayeen and M.B. Gilles, *J. Mol. Struct.,* 2002, **604**, 205.
38 G.M. Lima, J.L. Neto, H. Benaldo, H.G.L. Siebald and D.J. Duncalf, *J. Mol. Struct.,* 2002, **604**, 287.
39 S. Chatterjee, *J. Chem. Soc. (B),* 1969, 725.
40 K. Mukherjee and L. Levasseur, *J. Org. Chem*., 1965, **30**, 644.
41 V.R. Srinivasan and G. Ramachander, *Indian J Chem*., 1963, **1**, 234.
42 M. Dobosz, M. Pitucha and M. Wajec, *Acta Pol. Phar*., 1996, **53**, 31.
43 A. Martvon, S. Stankovsky and M. Uher, *Chem. Zvesti.,* 1980, **34**, 118.