Synthesis of spiro-1,2,4-triazole-3-thiones from cycloalkanone thiosemicarbazones, and formation of a cyclic 1,2-dithione

Alaa A. Hassan,[a]* Shaaban K. Mohamed,[a,b] Nasr K. Mohamed,[a] Kamal M. A. El-Shaieb,[a] Ahmed T. Abdel-Aziz,[a] Joel T. Mague,[c] and Mehmet Akkurt [d]

[a] *Chemistry Department, Faculty of Science, Minia University, 61519 El-Minia, Egypt*
[b] *Chemistry Environmental Division, Manchester, Metropolitan University, Manchester M15GD, UK*
[c] *Department of Chemistry, Tulane University, New Orleans, LA 70118,USA*
[d] *Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey*
E-mail: alaahassan2001@mu.edu.eg

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Abstract
Substituted spiro-heterocycles containing 1,2,4-triazole-3-thione, were formed at room temperature *via* the reaction of *N*-cycloalkylidene hydrazinecarbothioamides **2** with benzo- as well as naphthoquinone derivatives. 2,3-Dithioxo-1,4-naphthalene-1,4-dione was synthesized upon heating compounds **2** with 2,3-dichloro-1,4-naphthoquinone. The synthesized compounds were characterized by using different spectroscopic methods and confirmed by single crystal X-ray analyses. Rationales for the role of benzo- and naphthoquinone derivatives as well as the conversions are also presented.

Keywords: *N*-Cycloalkylidene hydrazinecarbothioamides; benzoquinones, naphthoquinones, spiro-1,2,4-triazolethiones, 2,3-dithioxo-1,4-naphthalene-1,4-dione

Introduction

Certain spiro scaffold compounds containing sulfur and nitrogen are great interest molecules due to their physiological and biological activities.[1] Also, heterocyclic 1,2,4-triazoline-5-thione derivatives exhibited various biological properties such as analgesic,[2] anti-inflammatory,[3] bacteriostatic[4] and antimitotic[5] activities.

2,4-Diaryl-3-azabicyclo[3.3.1]nonane-9,3′-spiro-1,2,4-triazolidine-5′-thiones have been synthesized and studied for their *in vitro* antibacterial and antifungal activities.[6]

Oxidative cyclization of thiosemicarbazones by using MnO_2/H_2O_2 afforded the corresponding 7,9-diaryl-1,2,4-triaza-8-oxaspiro[4,5]decane-3-thiones.[7,8]

A series of trifluoromethyl substituted spiro-[3*H*-indole-3,3′-[3*H*-1,2,4]triazole-2(1*H*)]-ones has been synthesized *via* microwave (MW) one pot condensation of 3-arylamino-2*H*-indol-2-ones with thiosemicarbazide using montmorillonite as solid support.[9,10] Hydrazonyl halides reacted with cycloalkanones alkoxycarbonylhydrazones to give spiro-1,2,4-triazoles.[11,12]

Nitrilimines react with 4-piperidone oxime,[13] dipolarophiles containing (C=N),[14-17] and cycloalkanone hydrazones,[18,19] affording spiro-1,2,4-triazoles.

4-Substituted thiosemicarbazides reacted with (2,4,7-trinitrofluoren-9-ylidene)propane-dinitrile in pyridine to form spiro(fluorene-9,3′-[1,2,4]triazole) derivatives.[20] Three nucleophilic centers – two nitrogen atoms and one sulfur atom – within the thiosemicarbazone unit (which are affected by both substitution and available tautomerization) give rise to the possibility of several structural isomers.

Based on recent results,[21-25] we concluded that the thiosemicarbazone nitrogen atoms N^2 and N^4 can participate in product formation when reacted with dimethyl acetylenedicarboxylate,[22,23] dicyanomethylene-1,3-indanedione[24] or tetracyanoethylene.[25]

In this study, we describe the reaction of some *N*-cycloalkylidenehydrazine carbothioamides **2a-f** with benzo- and naphthoquinone derivatives (**4a,b**) to synthesize the corresponding cycloalkanespiro-5-[1,2,4]triazole-3-thione derivatives.

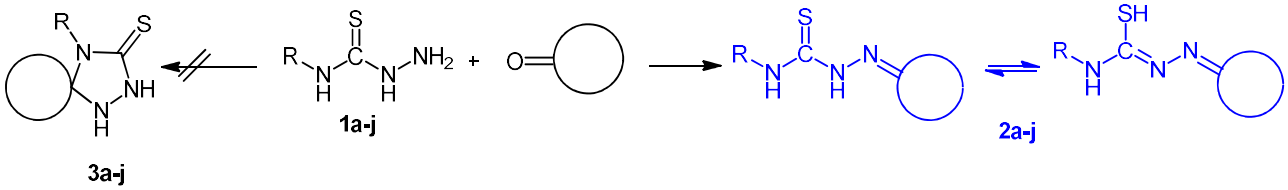
Results and Discussion

N-Cycloalkylidene hydrazinecarbothioamides (cyclic ketone *N(4)*-phenylthiosemicarbazones) **2a-j** were prepared according to published procedures.[26-30] The structures of **2a-j** were confirmed by IR, ^{1}H NMR and ^{13}C NMR spectra. The IR spectrum of **2j** (as an example) contained absorption bands belonging to C=S and C-N stretching at 1352 and 954 cm^{-1}, sharp band at 1618 for C=N and broad bands at 3332-3261 cm^{-1} due to NH. The ^{1}H NMR spectrum of **2j** showed two NH proton signals, each one at 8.59 and 7.68 ppm due to the hydrazine-NH and NH-attached to cyclohexyl, respectively. Multiplets at 1.40-1.48, 1.69-1.78, 2.28-2.36 and 2.42-2.67 were observed and attributed to the CH_2 and CH of the cyclohexyl and cycloheptyl substituents. ^{13}C NMR of **2j**, clearly showed downfield signals at 178.71 and 159.89 ppm due to C=S and C=N, respectively, whereas DEPT-^{13}C NMR exhibited negative signals at 24.45, 25.32, 25.55, 26.20, 27.68, 27.79, 32.40 and 36.90 due to the cycloheptyl and cyclohexyl CH_2 groups.

Differentiation between the linear structure **2** and alternative isomeric triazolidinethione **3** (Scheme 1) by simple ^{1}H-and ^{13}C-NMR is not easy.

We have previously confirmed the structure of 2-cyclopentylidene-*N*-phenyl(hydrazine-carbothioamide) **2a,**[28] 2-cycloheptylidene-*N*-phenyl(hydrazinecarbothioamides) **2c**[29] and *N*-allyl 2-cyclohexylidene(hydrazinecarbothioamides) **2h**[30] *via* single X-ray structural determination.

From these findings, it is clear that the structures of **2a-j** exist in an open-chain, linear configuration **2** rather than the cyclic triazolidinethione forms **3** (Scheme 1).



1,2	a	b	c	d	e	f	g	h	i	j
R	Ph	Ph	Ph	Ph	Ph-CH$_2$	Ph-CH$_2$				

Scheme 1. Putative linear (**2a-j**) and triazolidine-3-thione (**3a-j**) structures.

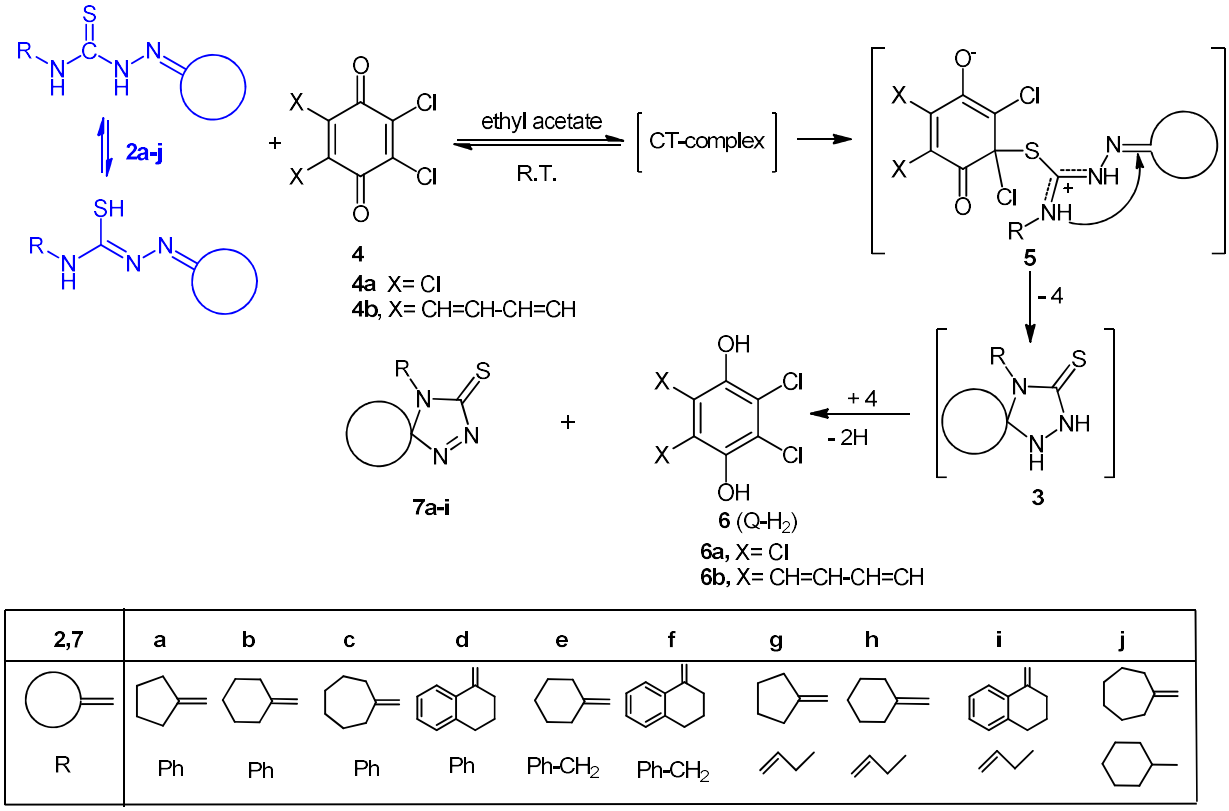
We chose (cycloalkylidene)hydrazinecarbothioamides **2a-j** having *N*-phenyl, *N*-allyl, *N*-benzyl and *N*-cyclohexyl as well as different alicyclic rings such as cyclopentyl, cyclohexyl, cycloheptyl and dihydronaphthalene, in order to examine their reactivity towards cyclization and formation of different spiro-triazole ring system.

Dry ethyl acetate solutions of (alkylidene)hydrazinecarbothioamides **2a-j** and benzo- or naphthoquinone derivatives (Q, **4a,b**) in a molar ratio (1:1) were stirred for 2h, with admission of air, the pink coloration of the reaction mixture solutions (maybe with initial formation of CT complexes) became quickly reddish brown. The mixture was left standing for 72 hours at room temperature, during which time a precipitate of hydroquinone (**6a,b**) separated. The filtrate was concentrated and processed by chromatographic plates (plc) to give reddish brown or yellowish orange crystals of **7a-j**. The product structures **7a-j** were assigned based on elemental analysis, mass spectrometry, IR, ^{1}H-and ^{13}C-NMR spectral data. The mass spectrum of **7h** (as an example) shows the [M$^+$] peak at *m/z* 209 in agreement with the molecular formula $C_{10}H_{15}N_3S$. ^{1}H NMR spectrum of 4-allyl 1,2,4-triazaspiro[4.5]dec-1-ene-3-thione **7h** displayed CH_2 protons of the cyclohexylidene ring at 1.56-1.63 (2H), 2.24-2.28 (4H) and 2.39-2.41 (4H), in addition to the allyl protons which resonate as three multiplets at 4.13-4.18 (allyl CH_2N), 5.07-5.12 (allyl CH_2=) and 5.88-5.94 (allyl CH=). The ^{13}C-NMR spectrum of **7h** showed one downfield and another upfield peak at 186.7 and 112.5 due to C=S and spiro-C, respectively. The presence of cyclohexylidene-CH_2 was also evident from the ^{13}C-DEPT-NMR spectrum, exhibiting negative signals at 25.6, 26.3, 27.85 and 33.5 ppm, while the allyl group shows two negative signals in the ^{13}C-DEPT-NMR spectrum at 46.3, 116.2 due to (allyl CH_2N) and (allyl CH_2=) respectively, and a positive signal at 135.8 due to (allyl CH=).

The EI-mass spectra of **7a-j** are characterized by molecular ions of low to moderate-intensity and the loss of 28 a.m.u (representing CH_2=CH_2 or N_2). The resulting fragment ions

undergo loss of R-N=C=S.

In addition, the structures of **7a-j** are strongly supported by the single X-ray structure analysis of 4-allyl-1,2,4-triazaspiro[4.5]dec-1-ene-3-thione (**7h**) (Fig. 1).



Scheme 2. Reaction of **2a-j** with **4a,b**.

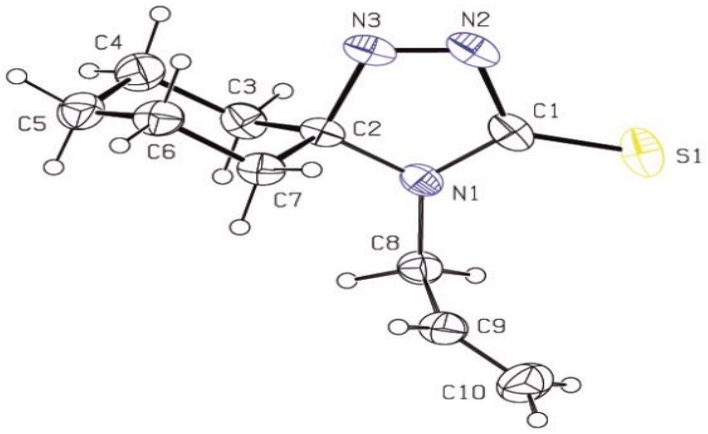


Figure 1. Molecular structure of **7h** with labeling scheme and 50% probability ellipsoids.

As seen in fig. 1, the C2—C7 cyclohexane ring of **7h** adopts a chair conformation with the puckering parameters[31] of Q_T = 0.556 (2) Å, θ = 3.0 (2) ° and φ = 207 (3)°. The mean plane of the N1—N3/C1/C2 triazinethione ring (r.m.s. deviation = 0.001 Å) is almost perpendicular, with a dihedral angle of 89.91(8)° to the mean plane formed by the C3,C4, C6 and C7 atoms of the cyclohexane ring. The bond lengths[32] and bond angles in table 2 (see supplementary file) are within the expected values as those of the similar compound 4-phenyl-1,2,4-triazaspiro[4.6]undec-1-ene-3-thione (**7c**).[33] No specific intermolecular interactions are discerned in the crystal packing. The crystal packing of the compound is shown in fig. 2.

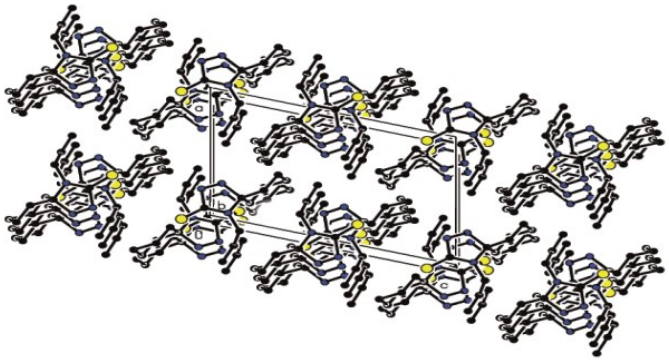


Figure 2. Packing view of **7h** down the *b* axis with hydrogen atoms omitted for clarity.

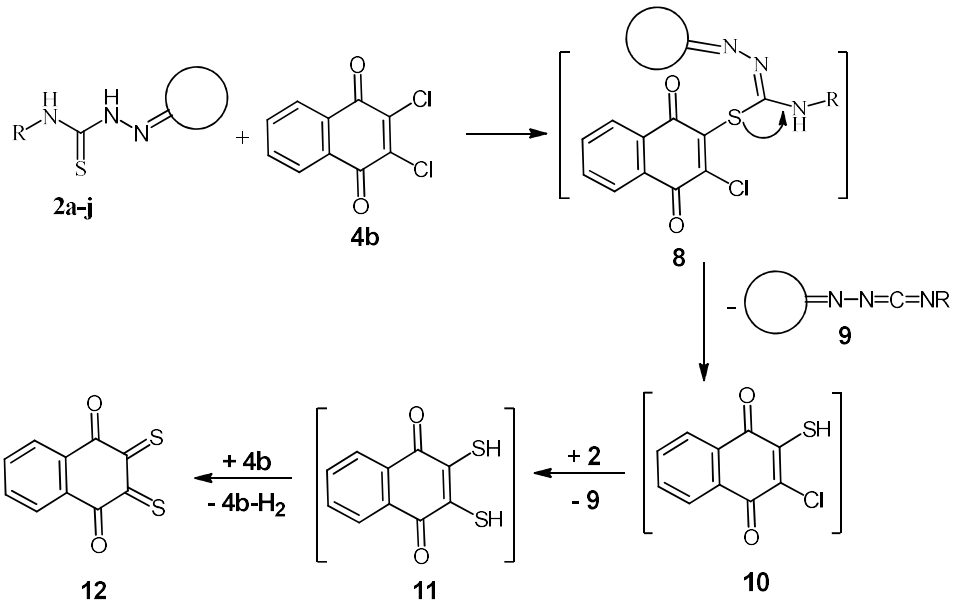
H-atoms in **7h** were placed in calculated positions (C—H = 0.95 − 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 times those of the attached carbon atoms. The allyl group is disordered over two sites in a 75/25 ratio. The components of the disorder were refined with restraints that their geometries be approximately the same. N1 and N1A were included on the same sites as dummy disordered atoms (using the EXYZ and EADP constraints) to allow for the disorder of the H atoms bonded to C8 and C8A. The crystal data and experimental details are listed in table 1, whereas selected bond lengths and bond angles are given in table 2. (for Tables see supplementary file).

The structure of the spiro compounds **7a,**[34] **7b,**[35] **7c**[33] and **7d**[36] have been determined by their single crystal X-ray diffractions.

Since the aforementioned reactions do not take place when none of the quinone **4** is added to the solution of **2a-i** in ethyl acetate, the presence of **4** is definitely required for the transformations observed. So, charge-transfer complexation may (but does not necessarily have to) play an intermediate role. Since the cyclization involves intramolecular nucleophilic attacks on cycloalkylidene-C=N, it is conceivable that **4** could accelerate the process in the form of a proton or Lewis acid through the intermediate **5** (Scheme **2**). This could lead to activating the respective C=N bond towards nucleophilic addition. This behavior may supported the polar nature of the solvent in stabilizing the zwitterionic adducts **5**. After cyclization, **4** is released and

reacts with the spiro-dihydrotriazolethiones **3** to give the dihydroquinone (Q-H_2, **6a,b**) and the corresponding spiro-triazolethione derivatives **7a-j** (Scheme 2).

In striking contrast to the results above: heating of equimolar amounts of **2a-j** with 2,3-dichloro-1,4-naphthoquinone in ethyl acetate gave 2,3-dithioxo-2,3-dihydronaphthalene-1,4-dione **12** (Scheme 3) instead of the above mentioned spiro compounds; cycloalkanones were separated as side products.



Scheme 3. Proposed route to the formation of 2,3-dithioxo-2,3-dihydronaphthalene-1,4-dione (**12**).

Here, naphthoquinone **4b** has reacted under heating as a building block synthon rather than an oxidant. A nucleophilic attack of the sulfur atom on the C/C double bond of **4b** followed by elimination of HCl could afford intermediate **8** which in turn could undergo elimination of cycloalkylideniminocarbodiimide **9** to give the intermediate **10.** The latter could react with another molecule of **2** to afford ultimately the product 2,3-dithioxo-1,4-naphthoquinone **12** *via* the dithiol **11.** Several attempts to isolate the *N*-[(cycloalkylidenehydrazono)methylene]-substituted amines **9 (**using plc-chromatography) failed; instead cycloalkanones were separated; compound **9** may be hydrolyzed upon work-up.

The ^{13}C NMR spectrum of **12** showed the characteristic absorption signal of the carbonyl carbon atoms of naphthoquinone at 176.22[37-43], also another downfield signal at 181.33 ppm for (C=S)[43].

Compound **12** was also confirmed by the single crystal X-ray structure determination. A perspective view of the molecule with the crystallographic atoms numbering is given in fig. 3. (Note that the crystallographic numbering does not conform with the systematic IUPAC numbering rules).

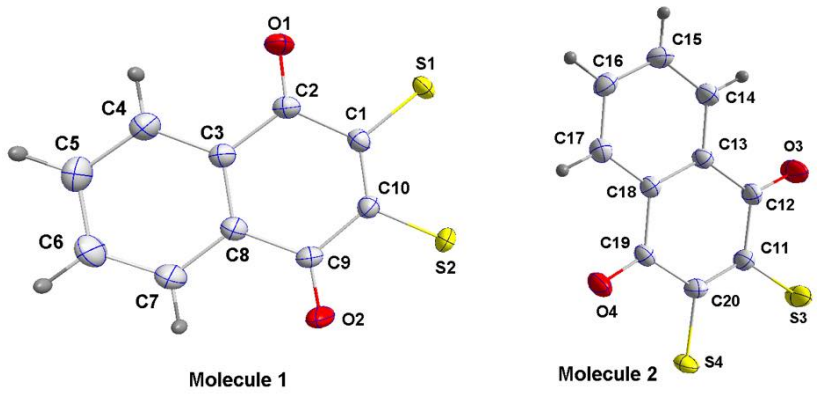


Figure 3. The asymmetric unit of **12** with numbering scheme and 50% probability ellipsoids.

In the compound **12** (Fig. 3), there are two independent molecules in the asymmetric unit. Each molecule forms π-stacking interactions with its centrosymmetrically related counterpart (Figs. 4 and 5) to generate stacks running approximately parallel to the *a* axis. The centroid-to-centroid distance in the stack is 3.454(1) Å, while the perpendicular distance between the mean planes of the molecules is 3.358(1) Å. For molecule 2, the corresponding values are 3.485(1) and 3.401(1) Å. The crystal data and experimental details are listed in Table 3, and selected bond lengths and bond angles are given in table 4 (see supplementary data).

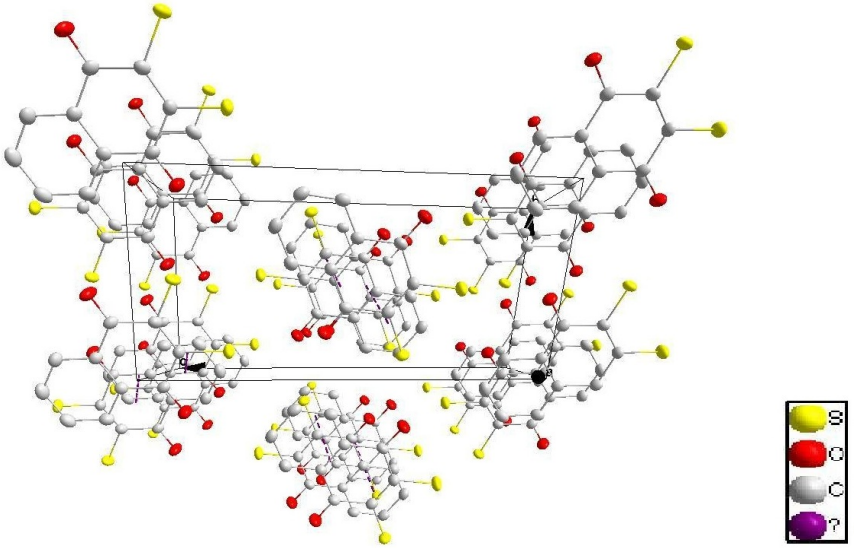


Figure 4. Packing viewed down the *a* axis for **12**.

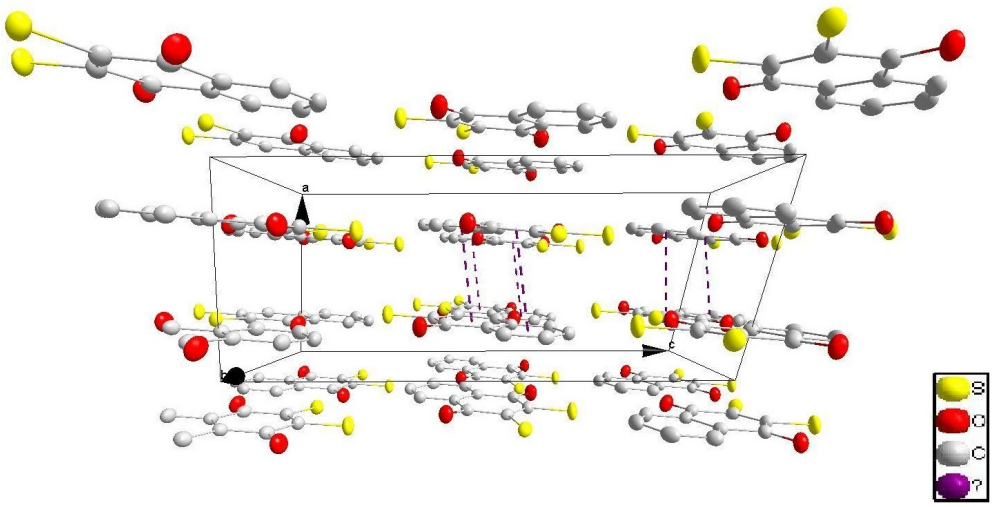


Figure 5. Packing viewed down the *b* axis. Selected examples of the *a*-stacking interactions are shown by dotted lines for **12**.

H-atoms in **12** were placed in calculated positions (C—H = 0.95 Å) and included as riding contributions with isotropic displacement parameters 1.2 times those of the attached carbon atoms.

Conclusions

A series of spiro-cycloalkylidene[1,2,4]triazole-3-thione derivatives was synthesized *via* oxidative cyclization of cyclic-ylidene-*N*-substituted hydrazinecarbothioamides by using benzo- and naphthoquinone derivatives. The simple reactivity of cycloalkylidene-*N*-substituted hydrazinecarbothioamides required the availability of cyclic-C=N and the nucleophilic sites thioamide-NH's.

It was found that solvent, temperature and the molar ratio of reactants may all play a critical role in the reaction efficiency. The influence of different solvents have been studied and found that ethyl acetate was a superior solvent compared to benzene, THF, DMF and ethylene chloride, which gave only traces of **7a-j**.

An excess of the benzo- or naphthoquinone derivatives (**4a,b**) was not necessary to obtain the products in pure and high yields. Therefore, carrying out the reactions in ethyl acetate at room temperature and using equimolar ratios of **2a-j** and **4** are chosen as the optimized reaction conditions.

Experimental Section

General. Melting points were determined in open glass capillaries on a Gallenkamp melting apparatus. The IR spectra were recorded from potassium bromide disks with a Shimadzu 408. ^{1}H-and ^{13}C-NMR spectra (300 MHz for ^{1}H, 75 MHz for ^{13}C) were observed on Varian mercury plus 300 spectrometer with tetramethylsilane as the internal standard. The ^{13}C-NMR signals were assigned with the aid of DEPT experiments. Mass spectra were obtained in Varian MAT311 double focusing instrument using electron impact ionization (70 eV). The X-ray intensity data were measured on a Bruker D8 Venture Photon 100 CMOS system equipped with a mirror monochromator and a Cu-Kα Incoatec IμS micro-focus source (λ = 1.54178 Å). Elemental analyses were carried out at Microanalytical Center, Cairo University, Egypt. Thin layer chromatography (TLC) was performed on analytical Merck 9385 Silica aluminum sheets (Kieselgel 60) with Pf_{254} indicator, TLCs were viewed at λ_{max} = 254 nm. Preparative layer chromatography (plc) used air dried 1.0 mm thick layers of slurry applied silica gel (Merck Pf_{254}) on 48 cm wide and 20 cm high glass plates using the solvents listed.

Starting materials

N-Cycloalkylidene-hydrazinecarbonthioamides **2a-j** were prepared according to the published procedures.[26-30]

(*E*)-2-(3,4-Dihydronaphthalene-1(2*H*)-ylidene)-*N*-phenyl(hydrazincarbothioamide) (**2d**).. Colourless crystals (ethanol) (2.71 g, 92%), mp 186-188 °C. IR (KBr): ν_{max} 3381-3296 (NH's), 3089 (Ar-CH), 2967 (Ali-CH), 1624 (C=N), 1568 (NH-def. and C-N), 1354, 957 (C=S and C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.96-2.01 (m, 2H, CH_2), 2.64-1.67 (m, 2H, CH_2), 2.75-2.82 (m, 2H, CH_2), 7.19-7.24 (m, 2H, Ar-H), 7.26-7.32 (m, 3H, Ar-H), 7.38-7.42 (m, 2H, Ar-H), 8.02-8.04 (m, 2H, Ar-H), 8.87 (br, s, 1H, NH), 9.45 (br, s, 1H, NHPh); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 21.5, 25.7, 29.4 (CH_2), 124.6, 125.2, 126.8, 128.9, 129.4, 130.0 (Ar-CH), 131.5,138.0, 140.6 (Ar-C), 147.2 (C=N), 176.2 (C=S). MS (EI): *m/z* 295 (M^+, 65), 277 (43), 160 (71), 135 (81), 77(100). *Anal*. Calcd. for $C_{17}H_{17}N_3S$ (295.40): C, 69.12; H, 5.80; N, 14.22; S, 10.85. Found C, 68.97; H, 5.88; N, 14.09; S, 11.02.

***N*-Benzyl-2-cyclohexylidene(hydrazinecarbothioamide)** (**2e**). Colourless crystals (ethanol) (2.37 g, 91%), mp 102-103 °C IR (KBr): ν_{max} 3376-3255 (NH's), 3077 (Ar-CH), 2984 (Ali-CH), 1567 (NH-def. and C-N), 1349, 962 (C=S and C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 1.50-1.57 (m, 2H, CH_2), 2.17-2.19 (m, 4H, CH_2), 2.37-2.40 (m, 4H, CH_2), 4.74 (s, 2H, CH_2Ph), 7.18-7.24 (m, 2H, Ar-H), 7.26-7.27 (m, 3H, Ar-H), 8.32 (br, s, 1H, $NHCH_2Ph$), 8.62 (br, s, 1H, NH),; ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 26.20, 27.79, 35.40 (CH_2), 46.98 (CH_2Ph), 127.25, 127.93, 128.65 (Ar-CH), 140.02 (Ar-C), 157.55 (C=N), 178.78 (C=S). MS (EI), m/z= 261 (M^+, 32), 233(61), 149 (67), 91 (76), 77(100). *Anal*. Calcd. For $C_{14}H_{19}N_3S$ (261.39), C, 64.33; H, 7.33; N, 16.08; S, 12.27. Found C, 64.47; H, 7.28; N, 15.95; S, 12.42.

***E*-2-(3,4-Dihydronaphthalene-1(2*H*)-ylidene)-*N*-benzyl(hydrazinecarbothioamide)** (**2f**). Colourless crystals (ethanol) (2.78 g, 90%), mp 140-141 ºC. IR (KBr): ν_{max} 3376-3289 (NH's), 3096-3065 (Ar-CH), 2982 (Ali-CH), 1574 (NH-def. and C-N), 1361, 955 (C=S and C-N str.) cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$) δ_H = 1.75-1.78 (m, 4H, CH_2), 2.68-2.70 (m, 2H, CH_2), 4.84 (s, 2H, CH_2-Ph), 7.28-7.34 (m, 2H, Ar-H), 7.38-7.40 (m, 3H, Ar-H), 7.48-7.52 (m, 4H, Ar-H), 8.29 (br, s, 1H, NH), 8.58 (br, s, 1H, $NHCH_2Ph$); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 21.85, 26.40, 29.41 (CH_2), 47.24 (CH_2Ph), 125.81, 126.62, 127.18, 127.67, 128.66, 129.66 (Ar-CH), 132.43, 140.03, 140.64 (Ar-C), 148.47 (C=N), 178.94 (C=S). MS (EI m/z= 309 (M^+, 54), 160 (66), 149 (82), 132 (32), 91 (100), 77 (57). Anal. Calcd. for $C_{18}H_{19}N_3S$ (309.43): C, 69.87; H, 6.19; N, 13.58; S, 10.36. Found C, 70.03; H, 6.24; N, 13.47; S, 10.22.

***N*-Allyl-2-cyclopentylidene(hydrazinecarbothioamide)** (**2g**). Colourless crystals (ethanol) (1.75 g, 89%), mp 102-103 ºC. IR (KBr): ν_{max} 3392-3277 (NH's), 2987-2965 (Ali-CH), 1618 (C=N), 1571 (NH-def. and C-N), 1361, 953 (C=S and C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.60-1.71 (m, 2H, CH_2), 2.26-2.28 (m, 2H, CH_2), 2.32-2.34 (m, 4H, CH_2), 4.09-4.11 (m, 2H, allyl CH_2N), 5.02-5.07 (m, 2H, allyl CH_2=), 5.78-5.85 (m, 1H, allyl CH=), 7.64 (br, s, 1H, NH-allyl), 8.76 (br, s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 25.1, 29.0, 33.6 (CH_2), 46.1 (allyl CH_2N), 116.05 (allyl CH_2=), 135.6 (allyl CH=), 164.0 (C=N), 178.1 (C=S). MS (EI): *m/z* 197 (M^+, 100), 169 (26), 98 (54), 54 (26), 41 (81). *Anal*. Calcd. for $C_9H_{15}N_3S$ (197.30): C, 54.79; H, 7.66; N, 21.30; S, 16.25. Found C, 54.61; H, 7.74; N, 21.43; S, 16.12.

(*E*)-2-(3,4-Dihydronaphthalene-1(2*H*)-ylidene)-*N*-allyl(hydrazinecarbothioamide) (**2i**): colourless crystals (2.38 g, 92%), mp 120-121 ºC (ethanol). IR (KBr): ν_{max} 3335-3276 (NH's), 3091 (Ar-CH), 2937 (Ali-CH), 1624 (C=N), 1602 (Ar-C=C), 1556 (NH-def and C-N str.), 1360, 962 (C=S and C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H = 1.74-1.77 (m, 2H, CH_2), 2.64-2.65 (m, 2H, CH_2), 2.67-2.70 (m, 2H, CH_2), 4.19-4.22 (m, 2H, allyl CH_2N), 5.03-5.12 (m, 2H, allyl CH_2=), 5.84-5.88 (m, 1H, allyl CH), 7.12-7.25 (m, 2H, Ar-H), 8.24-8.26 (m, 2H, Ar-H), 7.66 (br, s, 1H, NH-allyl), 8.81 (br, s, 1H, NH).^{13}C NMR (75 MHz, $CDCl_3$) δ_C = 21.85, 26.36, 29.40 (CH_2), 46.4 (allyl CH_2N), 115.95 (allyl CH_2=), 125.7, 126.6, 129.65 (Ar-CH), 132.4. 140.6 (Ar-C) 135.65 (allyl CH), 148.3 (C=N), 178.5 (C=S). MS (EI): *m/z* 259 (M^+, 100), 160 (76), 132 (34), 104 (22). *Anal*. Calcd. for $C_{14}H_{17}N_3S$ (259.37): C, 64.83; H, 6.61; N, 16.20; S, 12.36. Found: C, 64.71; H, 6.70; N, 16.06; S, 12.47.

2-Cycloheptylidene-*N*-cyclohexyl(hydrazinecarbothioamide) (**2j**): colourless crystals (2.32 g, 87%), mp 104-105 ºC (ethanol). IR (KBr): ν_{max} 3332-3261 (NH's), 2994-2980 (Ali-CH), 1618 (C=N), 1571 (NH-def and C-N str.), 1352, 954 (C=S and C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.40-1.48 (m, 4H, CH_2), 1.69-1.78 (m, 6H, CH_2), 2.28-2.36 (m, 6H, CH_2), 2.42-2.67 (m, 7H, CH_2 and cyclohexyl-CH), 7.68 (br, s, 1H, NH-cyclohexyl), 8.59 (br, s, 1H, NH),.^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 25.55, 26.20, 27.68, 27.79, 32.40, 36.90 (CH_2), 159.89 (C=N), 178.71 (C=S). MS (EI): m/z = 267 (100), 211 (42), 141 (38), 126 (44), 98 (81). *Anal*. Calcd. for $C_{14}H_{25}N_3S$ (267.43), C, 62.88; H, 9.42; N, 15.71; S, 11.99. Found: C, 63.06; H, 9.46; N, 15.65; S, 12.13.

Preparation of spiro-triazolinethiones 7a-j

Into a solution of benzo- or naphthoquinone **4a,b** (1.0 mmol) in dry ethyl acetate (10 mL), 1.0 mmol of cycloalkylidene-*N*-substituted hydrazinecarbothioamides **2a-f** in dry ethyl acetate (15 mL) was added with stirring over 2h. The pink coloration of the solution turned quickly into reddish brown, and the mixture was left standing for 72 hours at room temperature. The resulting precipitate of the hydroquinone was separated. The filtrate was concentrated under vacuum and the residue was chromatographed on thin layer chromatography (plc) using a mixture of toluene/ethyl acetate (10/2 *vv*) as an eluent to give numerous colored zones, the most intense zone contained compounds **7a-j**. Recrystallization from ethanol afforded the pure products.

4-Phenyl-1,2,4-triazaspiro[4.4]non-1-ene-3-thione (**7a**):[44] Orange crystals (ethanol) (0.187 g, 81%). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C = 24.5, 33.1 (cyclopentyl-CH_2), 113.8 (spiro-C), 128.1, 129.6, 130.15 (Ar-CH), 134.9 (Ar-C), 187.4 (C=S). MS (70 eV): *m/z* (%) 231 (M^+, 12), 203(26), 168 (56), 135 (86), 77 (100), 54 (26).

4-Phenyl-1,2,4-triazaspiro[4.5]dec-1-ene-3-thione (**7b**):[44] Reddish brown crystals (0.203 g, 83%). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C = 23.6, 24.5 and 33.9 (cyclohexyl-CH_2), 112.2 (spiro-C), 127.8, 129.9, 130.2 (Ar-CH), 135.1 (Ar-C), 187.6 (C=S).

4-Phenyl-1,2,4-triazaspiro[4.6]undec-1-ene-3-thione (**7c**): Yellow crystals (0.202 g, 78%), mp 176-177 ºC. IR (KBr): ν_{max} 3049 (Ar-CH), 2938 (Ali-CH), 1595 (Ar-C=C), 1352, 954 (C=S, C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ_H = 1.42-1.44 (m, 2H, CH_2), 1.60-1.68 (m, 2H, CH_2), 1.81-1.90 (m, 2H, CH_2), 1.92-1.98 (m, 2H, CH_2), 2.08-2.15 (m, 4H, CH_2), 7.31-7.32 (m, 2H, Ar-H), 7.53-7.59 (m, 3H, Ar-H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C = 22.65, 29.5, 29.3, 34.3, 34.5 (CH_2), 115.5 (spiro-C), 128.0, 129.6, 130.0 (Ar-CH), 135.3 (Ar-C), 186.5 (C=S). MS (70 eV) *m/z* (%) 259 (M^+, 61), 231 (73), 196 (46), 135 (71), 82 (26), 77 (100). *Anal*. Calcd. for $C_{14}H_{17}N_3S$ (259.37): C, 64.83; H, 6.61; N, 16.20; S, 12.36. Found: C, 65.02; H, 6.52; N, 16.05; S, 12.44.

4-Phenyl-3,4-dihydro-2*H*-spiro[naphthalene-1,3′-[1,2,4]-triazol]-5′-(4′*H*)-thione (**7d**): Orange crystals, (0.249 g, 85%), mp 212-214 ºC. IR (KBr): ν_{max} 3049 (Ar-CH), 2938 (Ali-CH), 1595 (Ar-C=C), 11356, 958 (C=S, C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ_H = 1.99-2.01 (m, 2H, CH_2), 2.60-2.67 (m, 2H, CH_2), 2.73-2.79 (m, 2H, CH_2), 7.20-7.24 (m, 2H, Ar-H), 7.32-7.35 (m, 2H, Ar-H), 7.69-7.71 (m, 3H, Ar-H), 8.02-8.04 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C = 22.6, 25.8, 29.6 (CH_2), 114.3 (spiro-C), 125.3, 125.9, 126.85, 128.9, 129.6, 130.2 (Ar-CH), 131.7, 138.3,140.5 (Ar-C), 187.5 (C=S). MS (70 eV): *m/z* (%) 293 (M^+, 39), 265 (27), 130 (62), 77 (100), 65 (51). *Anal*. Calcd. for $C_{17}H_{15}N_3S$ (293.39): C, 69.59; H, 5.15; N, 14.32; S, 10.93. Found: C, 69.44; H, 5.22; N, 14.46; S, 11.06.

4-Benzyl-1,2,4-triazaspiro[4.5]dec-1-ene-3-thione (**7e**): Orange crystals (0.207 g, 80%), mp 162-163 ºC. IR (KBr): ν_{max} 3088 (Ar-CH), 2982-2966 (Ali-CH), 1348, 956 (C=S, C-N str.) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ_H = 1.68-1.71 (m, 2H, CH_2), 1.79-1.83 (m, 2H, CH_2), 1.92-1.96 (m, 4H, CH_2), 2.26-2.33 (m, 2H, CH_2), 4.52 (s, 2H, CH_2Ph), 7.11-7.18 (m, 1H, Ar-H), 7.32-7.36 (m, 2H, Ar-H), 7.55-7.62 (m, 2H, Ar-H). ^{13}C-NMR (75 MHz, DMSO-d$_6$): δ_C= 23.62, 24.54, 33.96 (CH_2), 47.54 (Ph-CH_2), 113.55 (spiro-C), 127.84, 129.81, 129.96 (Ar-CH), 135.12 (Ar-C),

186.86 (C=S). MS (EI): *m/z* 259 (M^+, 44), 231 (53), 149 (66), 91 (100), 82 (14), 68 (22). *Anal*. Calcd for $C_{14}H_{17}N_3S$ (259.37): C, 64.83; H, 6.61; N, 16.20; S, 12.36. Found: C, 65.01; H, 6.72; N, 16.09; S, 12.21.

4′-Benzyl-3,4-dihydro-2*H*-spiro[naphthalene-1,3′-[1,2,4]triazole]-5′(4′H)-thione (**7f**): Orange crystals (0.251 g, 82 %), mp 176-177 °C. IR (KBr): ν_{max} 3092-3071 (Ar-CH), 2988-2953 (Ali-CH), 1362, 955 (C=S, C-N str.) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ_H = 1.78-1.82 (m, 2H, CH_2), 1.91-1.94 (m, 2H, CH_2), 2.69-2.73 (m, 2H, CH_2), 4.88 (s, 2H, CH_2Ph), 7.18-7.28 (m, 2H, Ar-H), 7.32-7.33 (m, 3H, Ar-H), 7.64-7.68 (m, 2H, Ar-H), 8.29-8.32 (m, 2H, Ar-H). ^{13}C-NMR (75 MHz, DMSO-d_6): δ_C = 22.1, 26.6, 29.8 (CH_2), 47.4 (Ph-CH_2), 114.4 (spiro-C), 125.9, 126.8, 127.3, 127.9, 128.2, 128.85, 129.4 (Ar-CH), 132.6, 139.9, 140.3 (Ar-C), 186.8 (C=S). MS (EI): *m/z* 307 (M^+, 100), 279 (55), 149 (63), 130 (52), 92 (31), 77 (65). *Anal*. Calcd. for $C_{18}H_{17}N_3S$ (307.41): C, 70.33; H, 5.57; N, 13.67; S, 10.43. Found: C, 70.46; H, 5.52; N, 13.55; S, 10.54.

4-Allyl-1,2,4-triazaspiro[4.4]non-1-ene-3-thione (**7g**): Orange crystals (0.158 g, 81%), mp 146-147 °C. IR (KBr): ν_{max} 2982-2964 (Ali-CH), 1358, 959 (C=S, C-N str.) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ_H = 1.64-1.73 (m, 4H, CH_2), 2.35-2.37 (m, 4H, CH_2), 4.06-4.08 (m, 2H, allyl CH_2N), 5.06-5.09 (m, 2H, allyl CH_2=), 5.85-5.89 (m, 1H, allyl CH=). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C = 24.91, 25.14, 29.16, 33.60 (CH_2), 46.27 (allyl CH_2N), 112.76 (spiro-C), 116.14 (allyl CH_2=), 135.86 (allyl CH=), 186.55 (C=S). MS (EI): m/z = 195 (M^+, 42), 167 (63), 68 (31), 41 (100). *Anal*. Calcd. for $C_9H_{13}N_3S$ (195.28): C, 55.35; H, 6.71; N, 21.20; S, 16.42. Found: C, 55.51; H, 6.62; N, 21.39; S, 16.51.

4-Allyl-1,2,4-triazaspiro[4.5]dec-1-ene-3-thione (**7h**): Yellow crystals (0.173 g, 83%), mp 141-142 °C. IR (KBr): ν_{max} 2996-2976 (Ali-CH), 1360, 959 (C=S, C-N str.) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ_H = 1.56-1.63 (m, 2H, CH_2), 2.24-2.28 (m, 4H, CH_2), 2.39-2.41 (m, 4H, CH_2), 4.13-4.18 (m, 2H, allyl CH_2N), 5.07-5.12 (m, 2H, allyl CH_2=), 5.88-5.94 (m, 1H, allyl CH=). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C = 26.3, 27.85, 33.5 (CH_2), 46.3 (allyl CH_2N), 112.5 (spiro-C),116.2 (allyl CH_2=), 135.8 (allyl CH=), 186.7 (C=S). MS (EI): *m/z* 209 (M^+, 100), 181 (46), 99 (63), 82 (54), 68 (14) *Anal*. Calcd. for $C_{10}H_{15}N_3S$ (209.31): C, 57.38; H, 7.22; N, 20.08; S, 15.32. Found: C, 57.46; H, 7.14; N, 19.93; S, 15.26.

4-Allyl-3,4-dihydro-2*H*-spiro[naphthalene-1,3′-[1,2,4]triazole]-5′(4′*H*)-thione (**7i**): Reddish orange crystals (0.213 g, 83%), mp 157-158 °C. IR (KBr): ν_{max} 3066 (Ar-CH), 2986-2957 (Ali-CH), 1354, 948 (C=S, C-N str.) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ_H = 1.94-2.03 (m, 2H, CH_2), 2.58-2.64 (m, 2H, CH_2), 2.75-2.78 (m, 2H, CH_2), 4.14-4.17 (m, 2H, allyl CH_2N), 5.11-5.14 (m, 2H, allyl CH=), 5.91-5.94 (m, 1H, allyl CH=), 7.28-7.31 (m, 2H, Ar-H), 7.33-7.37(m, 1H, Ar-H), 7.62-7.66 (m, 1H, Ar-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C = 21.9, 26.5, 29.7 (CH_2), 46.45 (allyl CH_2N), 114.15 (spiro-C), 116.1 (allyl CH_2=), 125.8, 126.7, 129.7 (Ar-H), 132.61, 140.52 (Ar-C), 135.69 (allyl CH=), 186.76 (C=S). MS (EI): m/z = 257 (M^+, 51), 229 (43), 130 (52), 102 (19), 99 (62), 41 (100). *Anal*. Calcd for $C_{14}H_{15}N_3S$ (257.35): C, 65.34; H, 5.87; N, 16.33; S, 12.46. Found: C, 65.46; H, 5.96; N, 16.19; S, 12.32 %.

4-Cyclohexyl-1,2,4-triazaspiro[4,6]undec-1-ene-3-thione (**7j**): Orange crystals (0.212 g, 80%), mp 166-167 °C. IR (KBr): ν_{max} 2986-2960 (Ali-CH), 1351, 948 (C=S, C-N str.) cm^{-1}. ^1H NMR

(300 MHz, DMSO-d_6) δ_H = 1.46-1.54 (m, 6H, CH_2), 1.73-1.79 (m, 6H, CH_2), 2.33-2.39 (m, 6H, CH_2), 2.46-2.74 (m, 5H, cyclohexyl-CH_2 and CH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C = 22.64, 25.81, 26. 22, 29.54, 31.14, 34.64 (CH_2), 53.12 (cyclohexyl-C), 113.66 (spiro-C), 186.55 (C=S). MS (EI): m/z = 265 (M^+, 100), 237 (77), 141 (52), 96 (27), 82 (29). *Anal*. Calcd. for $C_{14}H_{23}N_3S$ (265.42): C, 63.35; H, 8.73; N, 15.83; S, 12.08. Found: C, 63.46; H, 8.67; N, 15.92; S, 11.98 %.

Also isolated were the hydroquinones **6a**-H_2 (4-5%),[45] **6b**-H_2 (5-6%).[46]

Preparation of 2,3-dithioxo-2,3-dihydronaphthalene-1,4-dione (12)

A solution of cycloalkylidene-*N*-substituted hydrazinecarbothioamides **2a-f** (1.0 mmol) in dry ethyl acetate (15 ml) was added with stirring at room temperature to **4b** (0.227 gm, 1.0 mmol) in dry ethyl acetate (10 ml). the reaction mixture was gently refluxed with stirring for 3h. the resulting reddish brown solution was subjected to chromatographic plates (plc) and using a mixture of toluene/ethyl acetate (10/4 *vv*) as an eluent to give numerous zones, from which two zones were isolated; the first migrating zone containing cycloalkanone derivatives, whereas the slowest zone, which was characterized by a reddish-brown color, contained compound **12**. Recrystallization of compound **12** from ethanol afforded reddish-brown crystals (0.180 g, 82%) mp 164-166 ºC. IR (KBr): ν_{max} 3076 (Ar-CH), 1689 (CO), 1362 (CS) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H = 7.34-7.45 (m, 2H, Ar-H), 7.93-8.06 (m, 2H, Ar-H), ^{13}C NMR (75 MHz, DMSO-d_6) δ_C = 127.66, 129.87 (Ar-CH), 132.54 (Ar-C), 176.22 (CO), 181.33 (CS). *Anal*. Calcd. for $C_{10}H_4O_2S_2$ (220.27), C, 54.53; H, 1.83; S, 29.11. Found C, 54.68; H, 1.93; S, 28.96 %.

Crystal structure determination and the Computer programs

The crystal structure of **7h** was solved by direct methods using SHELXS-97[47] implement in WINGX[48] program suite and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-2014)[49]. The molecular graphics were drawn using the ORTEP-3 for Windows[48] and PLATON programs[48]. For compound **12**: Data collection: APEX2.[50] Cell refinement: SAINT.[50] Data reduction: SAINT.[50] Program(s) used to solve structure: SHELXT.[50] Program(s) used to refine structure: SHELXL-2014/7.[49] Molecular graphics: DIAMOND.[50] Software used to prepare material for publication: SHELXTL.[51]

Supplementary Material

CCDC 1407099 for **7h** and CCDC 1410615 for **12** contain the supplementary crystallographic data for both compounds. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk).

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