Ethenetetracarbonitrile and Heterocyclization of Symmetrical Dithiobiurea as well as Thioureidoethylthiourea Derivatives

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Dedicated to Professor Dietrich Döpp on the occasion of his 65th birthday

N,N'-Disubstituted hydrazinecarbothioamides **6a – c** and substituted thioureidoethylthioureas **12a – c** react with ethenetetracarbonitrile (TCNE) in ethyl acetate or chlorobenzene to form the derivatives of pyrazole **7**, **8**; thiadiazole **10**, **11** thiadiazepine **9**, thiadiazepane **13**, imidazolidine **14** and diazepine **15**.

Key words: Ethenetetracarbonitrile, Dithiobiurea, Thioureidoethylthiourea Derivatives, Heterocyclization

Introduction

Ethenetetracarbonitrile (TCNE) is considered as a highly electron-deficient and strongly electrophilic reagent, due to the fact that the cyano group is a powerful electron-withdrawing group and a poor dipolarophile [1 – 3]. As a consequence, TCNE shows high reactivity towards many nucleophiles like alcohols, amines and thiols [3] and easily forms molecular complexes by intermolecular charge-transfer interactions [1, 3 – 5]. Its affinity for electrons is high, as demonstrated by the formation of stable radical anion as well as dianion, through two reversible processes [6, 7]. The recent literature is enriched with progressive findings about the reactions of TCNE with thiocarbonylylides [8], thiophenone *S*-methylide [9], alkylidenecyclobutenes [10], *N*-arylbenzo[*d,e*]isoquinolines [11] and *N*-aryldibenz[*c,e*]azepines [11] as well as *N*-arylisoindolines [12].

On the other hand, the interaction of thiosemicarbazide and dithiocarbazate derivatives with TCNE and benzo- as well as naphthoquinones as π-acceptors afforded various heterocyclic compounds *via* a single-electron transfer mechanism [13 – 17].

Recently, we have demonstrated that 4-substituted thiosemicarbazides **1 a – c** reacted with TCNE in ethyl acetate with admission of air to give products **2 – 5** [18].

These results prompted us to continue our investigations on the behaviour of other electron poorer analogous, namely *N,N'*-disubstituted hydrazinecarbothioamides **6 a – c** and thioureidoethylthiourea derivatives **12a – c** towards TCNE.

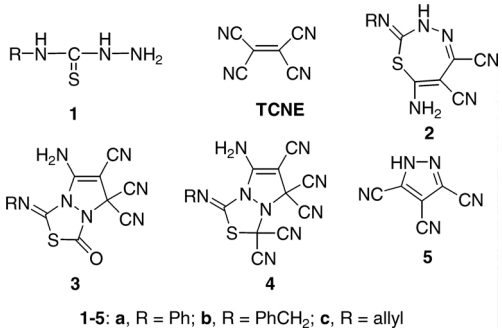

Chart 1.

Results and Discussion

Addition of two equivalents of TCNE to a solution of **6c** in ethyl acetate as a solvent at room temperature resulted in a green colouration of the solution, which later became dark brown. This behaviour may be explained as due to the initial formation of unstable charge-transfer (CT) complexes, followed by chemical reaction. Monitoring of the reaction by visible spectroscopy failed, since the reaction is fast and also, at lower concentrations no significant colour changes were observed any more.

The concentration residue was subjected to vacuum sublimation to remove any unreacted TCNE. Chro-

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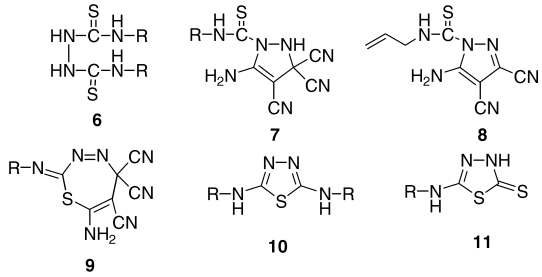


6, **7**, **9-11**: **a**, R = Ph; **b**, R = $PhCH_2$; **c**, R = allyl

Chart 2.

matographic separation of the residue obtained after sublimation gave numerous zones, from which products **7 – 11** could be isolated (Chart 2). Due to insufficient solubility of **6b, c** in ethyl acetate, the reaction was carried out in chlorobenzene at room temperature. In the latter solvent, nearly quantitative conversions were achieved already after four days, but yields **7**, **9 – 11** tended to be moderate. The structure of **7 – 9** were delineated from the spectroscopic properties as follows: The IR spectrum of **7a** shows absorption characteristic of NH_2 and NH groups at 3410, 3370 cm^{-1}, cyano groups at 2218 and 2210 cm^{-1}, C=S at 1360 cm^{-1}. The ^{1}H NMR spectrum of **7a** clearly shows the presence of three different broad signals centered at 7.30, 9.67 and 11.40 ppm with the ratio 2:1:1 due to exocyclic NH_2, NH attached to phenyl, as well as pyrazole-NH, respectively. In its ^{13}C NMR spectrum pyrazole-C-3, -C-4 and –C-5 resonate at $\delta =$ 46.36, 59.76 and 153.66 ppm, respectively. Further peaks at 117.92, 119.25 ppm (CN) and 175.46 ppm (C=S), besides the aromatic carbons support the assigned structure. The elemental analysis of **7a** suggested a gross formula $C_{13}H_9N_7S$. This was confirmed by the mass spectrum, which exhibited a molecular ion at 295 (100%). The analytical data of compound **7a** also matched another isomers which could be ruled out on the basis of ^{1}H-NMR, ^{13}C NMR, and the fragment ions in the mass spectrum of **7a** at *m/z* 268, 202, 135, 119, 104, 77 and 51. The structure of **7a** fits best to all the spectroscopic data (see Experimental Section).

Interestingly the molecular modeling (MM2) [19] of **7a**, as an example, supported the suggested structural feature of **7** as indicated in Chart 2. Since the bond distance between the hydrogen atom in NH and the NH_2 group is found to be 1.5 Å, we can suggest a hydrogen bond is formed between them. Consequently, this hydrogen bond can offer the formation of another six membered ring (Fig. 1). Additionally,

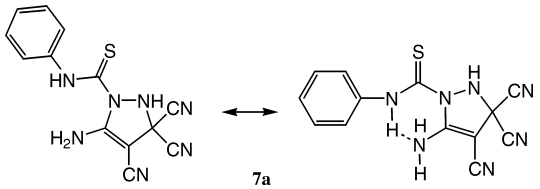


Fig. 1. Suggested hydrogen Bond formation in coumpund **7a**.

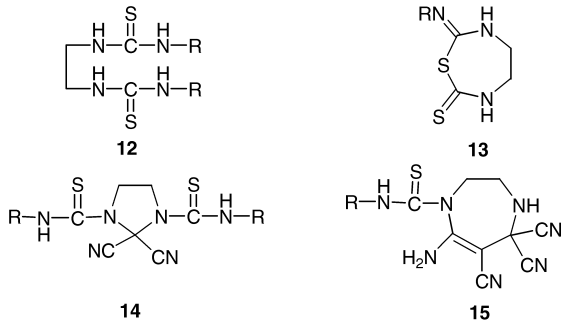
the steric energy value of compound **7a** is found to be ΔE = 25.36 Kcal/mol based on the aforementioned semi-empirical calculations using the MM2 level of theory [19], whereas this value is diminished in case of hydrogen bonding to become ΔE = 15.50 Kcal/mol. The stability of compounds **7** in this form supports the exclusion of any other expected isomeric forms. Furthermore, compound **7a** was also assigned on the basis of intramolecular H bridge detected by IR (in dilute CCl_4) and ^{1}H NMR (see the Experimental Section).

On the other hand, the formation of compound **8** supports our suggested structure (Chart 2). The ^{1}H NMR spectrum of **8** clearly shows the absence of pyrazole-NH and the presence of exocyclic NH_2 at 7.25 ppm as well as allyl-NH at 7.57 ppm. The ^{13}C NMR shows signals at 141.12, 88.64 and 152.26 ppm due to pyrazole-C-3, C-4 and C-5, respectively. Also, the ^{13}C NMR of **8** clearly indicates the presence of allyl group at 43.12, 114.63 and 134.32 ppm as well as C=S at 176.32 ppm. The mass spectrum of compound **8** exhibited a molecular ion peak at *m/z* 232 (43%).

For the formation of thiadiazepines **9**, the IR spectrum of **9a** shows characteristic bands at 3380 cm^{-1} (NH_2), 2225 and 2215 cm^{-1} for cyano groups, in addition to C=N as well as Ar-C=C groups at 1630 and 1590 cm^{-1}. The ^{1}H NMR of **9a** shows one broad singlet at 7.41 ppm due to NH_2 as well as the aromatic protons. The ^{13}C NMR of **9a** shows signals at 33.12, 87.94, 150.33 and 161.74 ppm due to thiadiazepine-C-5, -C-6, -C-7 and -C-2, respectively.

The presence of TCNE is very important and essential to allow the formation of thiadiazoles **10** and **11**, because on addition of **6a – c** to ethyl acetate or chlorobenzene without TCNE for 96 hours, gave again compounds **6a – c** and did not follow the previous sequence of chemical reactions. The structures of thiadiazoles **10** and of thiadiazole-2-thiones **11** were confirmed by comparison with authentic samples.

The weaker donor **12** was expected to react similarly to TCNE with **6a – c**. Treatment of **12a – c** with two equivalents of TCNE in tetrahydrofuran as sol-



12-15: **a**, R = Ph; **b**, R = $PhCH_2$; **c**, R = allyl

Chart 3.

vent at room temperature resulted in a green colouration of the solution, which later became dark brown. The residue remaining after concentration was subjected to preparative layer chromatography to give 7-substituted imino-[1,3,6]thiadiazepines **13a – c** in (63 – 69%) yield. Refluxing the reaction mixture for 3 h and concentration the preparative runs followed by chromatographic separation, products **14** and **15** could be isolated.

The molecular formula of compounds **14a – c** is supported by the mass spectra, which gave the predicted molecular ion peaks, and were further confirmed by elemental analysis. The IR spectrum of (for example) **14a** shows a sharp absorption characteristic of cyano groups at 2220 cm^{-1} and several peaks at 1620 and 1590 cm^{-1} for skeletal vibration of aryl groups, as well as another absorption at 1350 cm^{-1} due to C=S. The ^{1}H NMR spectrum of **14a** clearly shows the presence of two equivalent methylene groups at $\delta = 3.70$ ppm and one broad singlet at 9.59 ppm due to phenyl-NH, in addition to the aromatic protons. The presence of methylene groups is also evident from the ^{13}C DEPT NMR spectrum exhibiting negative signals at $\delta = 50.66$ ppm. The decoupled carbon spectrum of **14a** showed another signal at $\delta = 181.33$ ppm assigned to C=S, pointing out that the addition did not occur at the sulphur atom.

The elemental analysis of **15c** suggested a gross formula $C_{12}H_{13}N_7S$. This was confirmed by the mass spectrum, which exhibited a molecular ion at *m/z* 287 (16%). The IR spectrum showed strong bands at 2218 and 2210 cm^{-1} due to cyano groups, 3410, 3380, 3200 cm^{-1} (NH_2 and NH) as well as 1350 cm^{-1} (C=S). The ^{1}H NMR spectrum clearly indicates the presence of two multiplets at $\delta = 3.37 - 3.44$ and $3.56 - 3.62$ ppm are assigned to diazepine-C-3 and C-2 methylene groups. The ^{13}C DEPT NMR spectrum showed negative signals at $\delta = 43.77$ and 47.76 ppm, confirming the presence of two different methylene groups in diazepine ring. The ^{1}H NMR showed also, the presence of allyl group which appeared as three multiplets centered at $\delta = 3.91 - 3.96$, $5.04 - 5.15$ and $5.88 - 5.96$ ppm due to allyl-CH_2N, allyl-CH_2= and allyl-CH=, respectively. In addition the ^{1}H NMR spectrum exhibited three broad singlets centered at 7.20, 7.54 and 7.83 ppm due to exocyclic NH_2, allyl-NH and diazepine-NH, respectively. The decoupled carbon spectrum of **15c** showed signals at $\delta = 178.81$ ppm assigned to C=S; 33.11, 61.22 and 166.83 ppm due to diazepine C-5, C-6 and C-7 respectively, in addition to the allyl carbons. The structure of thiadiazepane **13** as confirmed on the basis of spectroscopic data and comparison with authentic samples.

Experimental Section

Mp's were determined in open glass capillaries on Gallen-Kamp melting point apparatus and are uncorrected. The IR spectra were recorded with a Shimadzu 408 or Bruker Vactor 22 FT IR instruments, using potassium bromide pellets or CCl_4. The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM 300 instrument, chemical shifts are expressed as δ (ppm) with tetramethylsilane as internal references, s = singlet, t = triplet, m = multiplet, br = broad; ^{13}C-assignment have been made with the aid of DEPT 135/90 spectra. The mass spectra (70 eV, electron impact mode) were obtained with a Varian MAT 311 doubly focusing instrument. Elemental analyses were determined at the Microanalytical Center, Cairo University, Egypt. For preparation layer chromatography 48 cm wide and 20 cm tall glass plates, covered with a 1 mm thick layer of slurry applied and air-dried silica gel Merck PF_{254}, were used. Zones were detected by their colour or by quenching of indicator fluorescence upon exposure to 254 nm light.

Starting materials

N,N'-Disubstituted hydrazinecarbothioamides **6a – c** and substituted thioureidoethylthioureas **12a – c** were prepared according to published procedures [20 – 27], as were *N,N'*-diphenylhydrazinecarbothioamide (**6a**) [20, 21], *N,N'*-dibenzylhydrazinecarbothioamide (**6b**) [22], *N,N'*-diallylhydrazinecarbothioamide (**6c**) [23, 24], 1-phenyl-3-[2-(3-phenylthioureido)ethyl]thiourea (**12a**) [25], 1-benzyl-3-[2-(3-benzylthioureido)ethyl]thiourea (**12b**) [26] and 1-allyl-3-[2-(3-allylthioureido)ethyl]thiourea (**12c**) [27]. Ethenetetracarbonitrile (TCNE, Merck) was purified by crystallization from chlorobenzene and sublimed, m. p. 198 – 199 °C.

Reaction of N,N'-disubstituted hydrazinecarbothioamides **6a** – **c** *with TCNE*

A solution of **6a, b** (2 mmol) in dry cholorobenzene 25 ml, or in 15 ml of ethyl acetate in case of **6c** was added dropwise with stirring at room temperature to TCNE (4.0 mmol) in chlorobenzene (20 ml) or ethyl acetate (10 ml). The reaction mixture colour changed gradually from green to brown. The stirring was containued for 48 h (in presence of ethyl acetate, and 96 h in case of chlorobenzene) with admission of air to complete the reaction. After concentration to dryness the residue was sublimed at 80 °C under vacuum to remove all unreacted TCNE. The residue was then separated by preparative layer chromatography (100 mg per plate) using a suitable solvent mixture as eluent (cyclohexane/ethyl acetate 3:1) to give numerous coloured zones, the five intense of which were removed and extracted. The first and second zones, which quenched all indicator fluorescence upon exposure to 254 nm UV-light, contained the thiadiazole derivatives **10a** – **c** (9 – 12%) and **11a** – **c** (8 – 10%). The third zone characterized by its brown colour contained the thiadiazepine **9a** – **c** (28 – 31%) and finally the slowest migrating zones (which always characterized by reddish brown and orange colour) contained the pyrazole derivsatives **8** (7%) and **7a** – **c** (28 – 31%). Extraction of the zones with acetone gave a residue, which was rechromatographed and recrystallized to separate the pure compounds.

*5-Amino-3,3,4-tricyano-2,3-dihydropyrazole-1-carbothioic acid phenylamide (***7a***)*

M. p. 225 °C. – IR (KBr): ν = 3410, 3370 (NH_2, NH), 2218, 2210 (CN), 1620, 1586 (Ar-C=C), 1360 (C=S) cm^{-1}, ν (CCl_4, 10^{-3} M, d = 3 cm) 3396, 3352 cm^{-1} (broad NH_2 and NH assoc.). – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 7.34 - 7.65$ (m, 5H, Ar-H), 7.30 (br, s, 2H,NH_2), 9.67 (br, s, 1H, NH), 11.40 (br, s, 1H, pyrazole-NH) the latter three signals fade upon treatment of the DMSO-d_6-solution with D_2O. – ^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 46.36 (pyrazole-C-3), 59.76 (pyrazole-C-4), 117.92, 119.25 (CN), 127.43, 128.86, 129.85, 139.42 (Ar-C), 153.66 (pyrazole-C-5), 175.46 (C=S). – MS (EI, 70 eV): *m/z* (%) = 295 (100) [M^+], 268 (33), 202 (46), 135 (48), 119 (37), 104 (94), 77 (72), 51 (48). – $C_{13}H_9N_7S$ (295.32): calcd. C 52.87, H 3.07, N 33.20, S 10.86; found C 52.94, H 2.89, N 33.04, S 10.98.

*5-Amino-3,3,4-tricyano-2,3-dihydropyrazole-1-carbothioic acid benzylamide (***7b***)*

M. p. 244 °C. – IR (KBr): ν = 3422, 3360 (NH_2, NH), 2220, 2210 (CN), 1630, 1600 (Ar-C=C), 1354 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 4.65 (br, s, 2H, CH_2Ph), 7.24 (br, s, 2H, NH_2), 7.28 – 7.68 (m, 5H, Ar-H), 9.61 (s, br, 1H, NH), 11.28 (br, 1H, pyrazole-NH). – ^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 46.20 (pyrazole-C-3), 52.90 (CH_2Ph), 59.88 (pyrazole-C-4), 117.89, 119.12 (CN), 126.86, 127.12, 128.96, 139.12 (Ar-C), 152.18 (pyrazole-C-5), 176.10 (C=S). – MS (EI, 70 eV): *m/z* (%) = 309 (100) [M^+], 282 (38), 214 (41), 149 (38), 133 (42), 118 (83), 77 (62). – $C_{14}H_{11}N_7S$ (309.35): calcd. C 54.36, H 3.58, N 31.69, S 10.37; found C 54.28, H 3.46, N 31.77, S 10.29.

*5-Amino-3,3,4-tricyano-2,3-dihydropyrazole-1-carbothioic acid allylamide (***7c***)*

M. p. 194 °C. – IR (KBr): ν = 3415, 3360 (NH_2, NH), 2965, 2860 (Ali-CH), 2225, 2210 (CN), 1565 (C=C), 1355 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 4.11 (m, 2H, allyl-CH_2N), 5.17 – 5.21 (m, 2H, allyl-CH_2=), 5.88 – 5.95 (m, 1H, allyl-CH=), 7.22 (br, s, 2H,NH_2), 7.57 (br, s, allyl-NH), 11.33 (br, s, 1H, pyrazole-NH). – ^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 43.56 (allyl-CH_2N), 46.31 (pyrazole-C-3), 59.72 (pyrazole-C-4), 115.08 (allyl-CH_2=), 118.12, 119.20 (CN), 134.83 (allyl-CH=), 152.93 (pyrazole-C-5), 176.12 (C=S). – MS (EI, 70 eV): *m/z* (%) = 259 (86) [M^+], 232 (36), 166 (51), 104 (88), 99 (34), 41 (100). – $C_{10}H_9N_7S$ (259.29): calcd. C 46.32, H 3.50, N 37.81, S 12.37; found C 46.48, H 3.41, N 37.94, S 12.52.

*5-Amino-3,4-dicyanopyrazole-1-carbothioic acid allylamide (***8***)*

M. p. 167 °C. – IR (KBr): ν = 3430, 3386 (NH_2, NH), 2968, 2946 (Ali-CH), 2222 (CN), 1625 (C=N), 1565 (C=C), 1360 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 4.08 (m, 2H, allyl-CH_2N), 5.16 – 5.22 (m, 2H, allyl-CH_2=), 5.88 – 5.91 (m, 1H, allyl-CH=), 7.25 (br, s, 2H,NH_2), 7.57 (br, s, 1H,allyl-NH). – ^{13}C NMR (DMSO-d_6): δ = 43.12 (allyl-CH_2N), 88.64 (pyrazole-C-4), 114.63 (allyl-CH_2=), 117.32, 118.93 (CN), 134.32 (allyl-CH=), 141.12 (pyrazole-C-3), 152.26 (pyrazole-C-5), 176.32 (C=S). – MS (EI, 70 eV): *m/z* (%) = 232 (43) [M^+], 166 (23), 138 (18), 104 (61), 99 (76), 41 (100). – $C_9H_8N_6S$ (232.27): calcd. C 46.54, H 3.47, N 36.18, S 13.81; found C 46.68, H 3.53, N 36.10, S 13.64.

*7-Amino-2-phenylimino-2H-[1,3,4]thiadiazepine-5,5,6-tricarbonitr ile (***9a***)*

M. p. 212 °C. – IR (KBr): ν = 3380 (NH_2), 2225, 2215 (CN), 3068 (Ar-H), 1630 (C=N), 1590 (Ar-C=C) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 7.41 (br, s, 2H,NH_2), 7.53 – 7.70 (m, 5H, Ar-H). – ^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 33.12 (thiadiazepine-C-5), 87.94 (thiadiazepine-C-6), 116.22, 117.41 (CN), 123.14, 127.23, 128.88 (Ar-CH), 143.92 (Ar-C=N), 150.33 (thiadiazepine-C-7), 161.74 (thiadiazepine-C-2). – MS (EI, 70 eV): *m/z* (%) = 293 (100) [M^+], 267 (11), 227 (11),

201 (18), 196 (22), 135 (27), 119 (25), 104 (81), 77 (47), 51 (28). – $C_{13}H_7N_7S$ (293.31): calcd. C 53.23, H 2.41, N 33.43, S 10.93; found C 53.37, H 2.53, N 33.29, S 11.12.

*7-Amino-2-benzylimino-2H-[1,3,4]thiadiazepine-5,5,6-tricarbonitrile (***9b***)*

M. p. 226 °C. – IR (KBr): $\nu = 3395$ (NH_2), 2960 (Ali-CH), 2222, 2215 (CN), 3080 (Ar-CH), 1625 (C=N), 1580 (Ar-C=C) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 4.64$ (br, s, 2H, CH_2Ph), 7.38 (br, s, 2H,NH_2), 7.48 – 7.68 (m, 5H, Ar-H). – ^{13}C NMR (75.47 MHz, DMSO-d_6): $\delta = 32.96$ (thiadiazepine-C-5), 48.68 (CH_2Ph), 88.14 (thiadiazepine-C-6), 115.92, 117.22 (CN), 125.21, 128.56, 129.20, 137.74 (Ar-C), 150.76 (thiadiazepine-C-7), 162.10 (thiadiazepine-C-2). – MS (EI, 70 eV): *m/z* (%) = 307 (100) [M^+], 180 (13), 241 (8), 210 (19), 149 (34), 118 (83), 77 (35), 51 (22). – $C_{14}H_9N_7S$ (307.33): calcd. C 54.71, H 2.95, N 31.90, S 10.43; found C 54.58, H 3.11, N 32.11, S 10.31.

*7-Amino-2-allylimino-2H-[1,3,4]thiadiazepine-5,5,6-tricarbonitrile (***9c***)*

M. p. 181 °C. – IR (KBr): $\nu = 3375$ (NH_2), 2960, 2870 (Ali-CH), 2225, 2210 (CN), 1628 (C=N), 1565 (C=C) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 4.12$ (m, 2H, allyl-CH_2N), 5.15 – 5.17 (m, 2H, allyl-CH_2=), 5.92 – 6.00 (m, 1H, allyl-CH=), 7.36 (br, s, 2H, NH_2). – MS (EI, 70 eV): *m/z* (%) = 257 (100) [M^+], 191 (34), 163 (22), 99 (73), 64 (21), 41 (89). – $C_{10}H_7N_7S$ (257.28): calcd. C 46.68, H 2.74, N 38.11, S 12.46; found C 46.55, H 2.83, N 38.24, S 12.31.

N,N'-Diphenyl-[1,3,4]thiadiazole-2,5-diamine (**10a**) (Lit. [28, 29]).

N,N'-Dibenzyl-[1,3,4]thiadiazole-2,5-diamine (**10b**) (Lit. [22]).

N,N'-Diallyl-[1,3,4]thiadiazole-2,5-diamine (**10c**) (Lit. [26, 30]).

5-Phenylamino-3H-[1,3,4]thiadiazole-2-thione (**11a**) (Lit. [27, 31]).

5-Benzylamino-3H-[1,3,4]thiadiazole-2-thione (**11b**) (Lit. [32]).

5-Allylamino-3H-[1,3,4]thiadiazole-2-thione (**11c**) (Lit. [23, 26]).

Reaction of substituted thioureidoethylthioureas **12a** – **c** *with TCNE*

Solutions (2 mmol) of **12a** – **c** in 30 ml of tetrahydrofuran (THF) were treated with 512 mg (4 mmol) of TCNE and stirred at room temperature for 48 h, during which time the original colour changed from yellow to green and finally to brown. After concentration, the solid residue was treated with a few ml of acetone and subjected to plc using cyclohexane/ethyl acetate (3:1) as eluent to afford one zone contained the thiadiazepane derivatives **13a** – **c**.

On the other hand, when the reaction mixture was refluxed in THF for 3 h, followed by concentration and separation the residue by tlc using cyclohexane/ethyl acetate (1:1), gave two zones. The fastest migrating one (brown colour) contained the diazepine derivatives **15** (35 – 42%), and the second zone (orange colour) contained the imidazolidine derivatives **14** (41 – 47%).

7-Phenylimino-[1,3,6]thiadiazepane-2-thione (**13a**) (Lit. [26]).

7-Benzylimino-[1,3,6]thiadiazepane-2-thione (**13b**) (Lit. [26]).

7-Allylimino-[1,3,6]thiadiazepane-2-thione (**13c**) (Lit. [26]).

*2,2-Dicyanoimidazolidine-1,3-dicarbothioic acid bis-phenylamide (***14a***)*

M. p. 291 °C. – IR (KBr): ν 3360 (NH), 2976 (Ali-CH), 2220 (CN), 1620, 1590 (Ar-C=C), 1350 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 3.70$ (t, 4H, $2CH_2$), 7.12 – 7.41 (m, 10H, Ar-H), 9.59 (br, s, 2H, 2NH). – ^{13}C NMR (75.47 MHz, DMSO-d_6): $\delta =$ 50.66 (imidazolidine-C-4, 5), 76.44 (imidazolidine-C-2), 117.20 (CN), 123.65, 125.76, 128.84, 139.40 (Ar-C), 181.33 (C=S). – MS (EI, 70 eV): *m/z* (%) = 392 (6)[M^+], 337 (8), 312 (14), 268 (24), 135 (100), 93 (34), 77 (88). – $C_{19}H_{16}N_6S_2$ (392.50): calcd. C 58.14, H 4.11, N 21.41, S 16.34; found C 57.92, H 4.22, N 21.56, S 16.51.

*2,2-Dicyanoimidazolidine-1,3-dicarbothioic acid bis-benzylamide (***14b***)*

M. p. 318 °C. – IR (KBr): $\nu = 3380$ (NH), 2960, 2880 (Ali-CH), 2218 (CN), 1585 (Ar-C=C), 1360 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 3.66$ (t, 4H, $2CH_2$), 4.64 (br, 4H, $2CH_2$Ph), 7.10 – 7.34 (m, 10H, Ar-H), 9.52 (br, s, 2H, 2NH). – ^{13}C NMR (75.47 MHz, DMSO-d_6): $\delta = 50.53$ (imidazolidine-C-4, 5), 54.66 (CH_2Ph), 76.12 (imidazolidine-C-2), 117.00 (CN), 123.44, 124.89, 128.63, 140.18 (Ar-C), 181.42 (C=S). – MS (EI, 70 eV): *m/z* (%) = 420 (11) [M^+], 365 (6), 296 (22), 149 (100), 77 (74). – $C_{21}H_{20}N_6S_2$ (420.56): calcd. C 59.97, H 4.79, N 19.98, S 15.25; found C 60.12, H 4.62, N 20.08, S 15.36.

*2,2-Dicyanoimidazolidine-1,3-dicarbothioic acid bis-allylamide (***14c***)*

M. p. 233 °C. – IR (KBr): ν 3380 (NH), 2966, 2880 (Ali-CH), 2220 (CN), 1610 (C=C), 1356 (C=S) cm^{-1}. – ^{1}H NMR

(300.13 MHz, DMSO-d_6): $\delta = 3.68$ (t, 4H, $2CH_2$), 4.10 (m, 4H, allyl-CH_2N), 5.13 – 5.17 (m, 4H, allyl-CH_2=), 5.93 – 6.03 (m, 2H, allyl-CH=), 7.49 (br, s, 2H, allyl-NH). – MS (EI, 70 eV): *m/z* (%) = 320 (12) [M^+], 221 (34), 122 (66), 99 (100), 68 (100), 68 (11), 41 (54). – $C_{13}H_{16}N_6S_2$ (320.44): calcd. C 48.73, H 5.03, N 26.23, S 20.01; found C 48.60, H 4.91, N 26.38, S 19.88.

*7-Amino-5,5,6-tricyano-2,3,4,5-tetrahydro[1,4]diazepine-1-carbothioic acid phenylamide (***15a***)*

M. p. 246 °C. – IR (KBr): ν = 3410, 3356, 3290 (NH_2, NH), 2980 (Ali-CH), 2218, 2210 (CN), 1620 (Ar-C=C), 1360 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 3.56$ (m, 2H, diazepine-C-3), 3.68 (m, 2H, diazepine-C-2), 7.18 (br, s, 2H, NH_2), 7.23 – 7.64 (m, 5H, Ar-H), 7.91 (br, s, 1H, diazepine-NH), 9.68 (br, s, 1H, NHPh). – ^{13}C NMR (75.47 MHz, DMSO-d_6): $\delta = 32.86$ (diazepine-C-5), 43.82 (diazepine-C-3), 46.45 (diazepine-C-2), 60.66 (diazepine-C-6), 115.92, 117.26 (CN), 123.88, 125.36, 128.84, 139.46 (Ar-C), 166.17 (diazepine-C-7), 178.55 (C=S). – MS (EI, 70 eV): *m/z* (%) = 323 (10) [M^+], 282 (14), 241 (7), 135 (76), 77 (93), 65 (100). – $C_{15}H_{13}N_7S$ (323.38): calcd. C 55.71, H 4.05, N 30.32, S 10.11; found C 55.54, H 3.94, N 30.41, S 10.11.

*7-Amino-5,5,6-tricyano-2,3,4,5-tetrahydro[1,4]diazepine-1-carbothioic acid benzylamide (***15b***)*

M. p. 261 °C. – IR (KBr): ν 3422, 3374, 3310 (NH_2, NH), 2978, 2888 (Ali-CH), 2225, 2220 (CN), 1590 (Ar-C=C), 1355 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 3.51$ (m, 2H, diazepine-C-3), 3.66 (m, 2H, diazepine-C-2), 4.63 (br, s, 2H, CH_2Ph), 7.22 (br, s, 2H, NH_2), 7.25 – 7.61 (m, 5H, Ar-H), 7.88 (br, s, 1H, diazepine-NH), 9.53 (br, s, 1H, $NHCH_2$Ph). – ^{13}C NMR (75.47 MHz, DMSO-d_6): $\delta = 32.66$ (diazepine-C-5), 43.74 (diazepine-C-3), 47.11 (diazepine-C-2), 54.31 (CH_2Ph), 61.00 (diazepine-C-6), 116.88, 118.30 (CN), 123.77, 125.62, 128.93, 140.11 (Ar-C), 166.35 (diazepine-C-7), 178.71 (C=S). – MS (EI, 70 eV): *m/z* (%) = 337 (14) [M^+], 296 (11), 255 (8), 229 (28), 149 (82), 91 (32), 77 (100). – $C_{16}H_{15}N_7S$ (337.40): calcd. C 56.96, H 4.48, N 29.06, S 9.50; found C 57.14, H 4.39, N 28.92, S 9.66.

*7-Amino-5,5,6-tricyano-2,3,4,5-tetrahydro[1,4]diazepine-1-carbothioic acid allylamide (***15c***)*

M. p. 202 °C. – IR (KBr): ν 3410, 3380, 3200 (NH_2, NH), 2988 (Ali-CH), 2218, 2210 (CN), 1610 (C=C), 1350 (C=S) cm^{-1}. – ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 3.37 - 3.44$ (m, 2H, diazepine-C-3), 3.56 – 3.62 (m, 2H, diazepine-C-2), 3.91 – 3.96 (m, 2H, allyl-CH_2N), 5.04 – 5.15 (m, 2H, allyl-CH_2=), 5.88 – 5.96 (m, 1H, allyl-CH=), 7.20 (br, s, 2H, NH_2), 7.54 (br, s, 1H, allyl-NH), 7.83 (br, s, 1H, diazepine-NH). – ^{13}C NMR (75.47 MHz, DMSO-d_6): $\delta = 33.11$ (diazepine-C-5), 43.77 (diazepine-C-3), 47.76 (diazepine-C-2), 52.86 (allyl-CH_2N), 61.22 (diazepine-C-6), 114.92 (allyl-CH_2=), 117.32, 118.53, (CN), 135.12 (allyl-CH=), 166.83 (diazepine-C-7), 178.81 (C=S). – MS (EI, 70 eV): *m/z* (%) = 287 (16) [M^+], 247 (12), 205 (10), 179 (23), 99 (56), 56 (44), 41 (100). – $C_{12}H_{13}N_7S$ (287.34): calcd. C 50.16, H 4.56, N 34.12, S 11.16; found C 50.31, H 4.71, N 33.96, S 11.27.

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