Reaction of 4-Substituted Thiosemicarbazides with (2,4,7-Trinitro-9*H*-fluoren-9-ylidene)propanedinitrile

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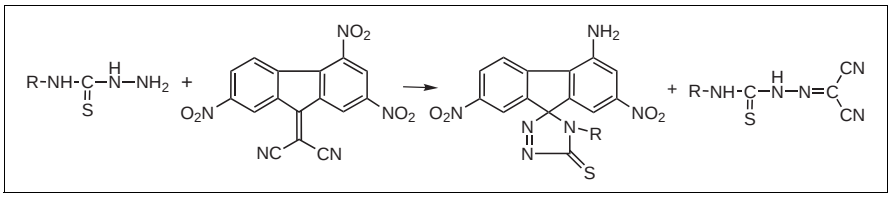

4-Substituted thiosemicarbazides **4a-c** reacted with (2,4,7-trinitro-9*H*-fluoren-9-ylidene)-propanedinitrile (**2**) in pyridine with admission of air to form spiro[fluorene-9,3'-(1,2,4-triazole)]derivatives **5a-c** and (4-substituted thiosemicarbazono)propanedinitriles **6a-c** in modest yields. 2,4,7-Trinitro-9-fluorenone (**8**) as well as one reduction product thereof and of **2**, namely compounds **9** and **10**, respectively are also found. A rationale for the conversions observed is presented.

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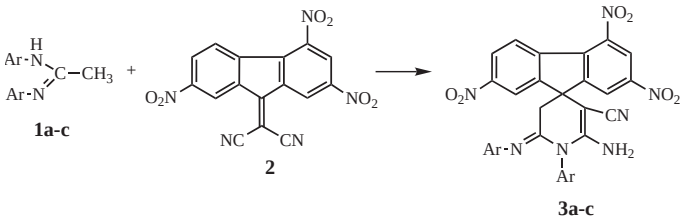
Introduction.

Thiosemicarbazides are easily cyclized by action of bases, acids or oxidants therefore they are useful and versatile building blocks for the preparation of various heterocycles. For examples, oxidation of aldehyde semicarbazone and thiosemicarbazone derivatives by metal salts has been used for the synthesis of 1,2,4-triazole, 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives [1-6]. The heterocyclizations of 1,4-disubstituted thiosemicarbazides - in basic or acidic media and under various reaction conditions - were investigated [7-10]. Four-, five-, six- and seven-membered heterocyclic compounds were prepared by reaction of thiosemicarbazide derivatives with a- and β-haloketones [11-14]. In addition, microwave (MW) heating of thiosemicarbazides has been employed for rapid synthesis of a wide variety of heterocyclic compounds such as thiadiazole, triazole-3-thiol, thioxoimidazole and thiadiazepine derivatives [15,16]. Also, the thermal cyclization of 1-aryl/alkyl-2-alkylisothiobiureas afforded 1,2,4-triazolines [17]. Irradiation of glyoxylic acid methylester thiosemicarbazones in methanol solution gave triazines [18]. On the other hand, the interaction of thiosemicarbazides with ethenetetracarbonitrile and benzo- as well as naphthoquinones as π-acceptors afforded thiazole, thiazine, thiadiazole, thiadiazine, thiadiazepine, pyrazine and indazole derivatives [19-25].

Since N^2 of the thiosemicarbazide group is a softer nucleophilic center than the harder and more powerful terminal nitrogen N^1, reagents susceptible to nucleophilic attack by N^1 may in a second step undergo cyclization to afford the aforesaid heterocycles in excellent yields, even under mild reaction conditions [8,9,15].

It had been reported earlier that (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**2**) and other 9-(dicyanomethylene)nitrofluorene derivatives react with secondary amines with subsequent substitution of cyano by amino groups to afford trinitro-substituted-9-(aminomethylene)-fluorenes [26], while we have reported the complex

Scheme 1



1a-c **2** **3a-c**

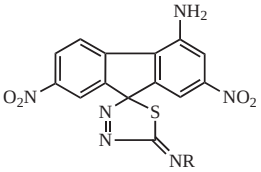
1 , **3**: **a**: Ar = *p*-CH_3-C_6H_4 ; **b**: Ar = *p*-CH_3O-C_6H_4 ; **c**: Ar = *p*-Cl-C_6H_4

reaction of N-arylisoindolines (being tertiary amines) with **2** [27]. Recently, it has been found that addition of N^2 of amidines **1a-c** to one of the cyano groups of **2**, followed by intramolecular conjugate addition of the methylene-active α-carbon atom of the acetamidine moiety to C-9 of the fluorene gives spiro[fluorene-9,4'-(1',2',3',4'-tetrahydropyridine]-5'-carbonitriles **3a-c** (Scheme 1) [28]. This fascinating versatility in the chemistry of **2** is intriguing and justifies further investigations of reactions of this acceptor with suitable donors. In this paper we describe the reaction of 4-substituted thiosemicarbazides **4a-c** with (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**2**,

previously referred to as 9-dicyanomethylene-2,4,7-trinitro-fluorene).

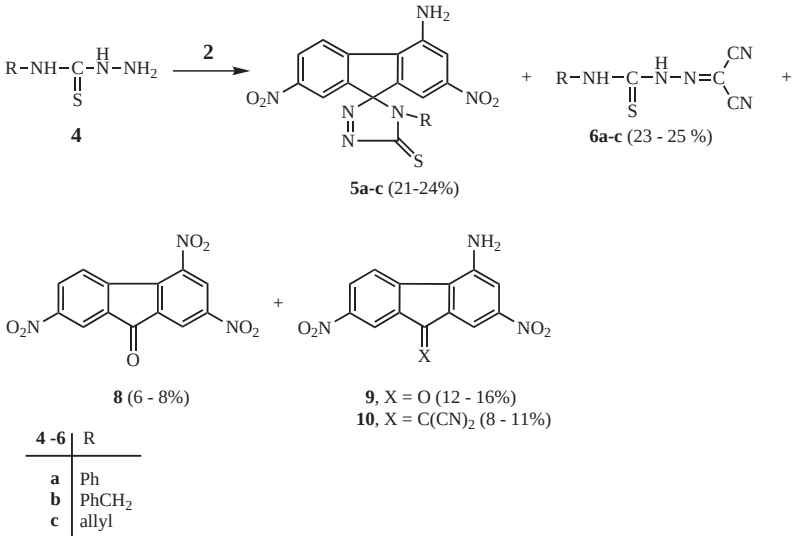
Results and Discussion.

Pyridine solutions of **2** and 4-substituted thiosemi–car–bazides **4a-c** in a molar ratio of 2:1 were kept at 100 °C for **3** hours with admission of air. Chromatographic separ–ation of the residue after concentration gave numerous colored zones, from which products **5a-c** and **6a-c** could be isolated. In addition, the known compounds **8 [**29] and **9**,**10 [**27] were found in small quantities in all cases (Scheme 2). Structural assignments of products **5** and **6** are based on spectral data and on combustion analyses.



7a, R = Ph
7b, R = $PhCH_2$
7c, R = allyl

Scheme 2



4 -6	R
a	Ph
b	$PhCH_2$
c	allyl

Compounds **5a-c**.

The molecular ions in their EI- mass spectra confirm the molecular masses and the gross compositions. Further, the following common features of the fragmentation patterns lend support to the assigned structures: Loss of N_2 giving intense (M^+-28) ions, and loss of R-NCS giving rise to the ion *m/z* = 297 common in the spectra of all three compounds. The odd-electron fragments represent the three isocyanates indicating that the charge during fragmentation may remain both with the nitroarene body or the isothiocyanate fragments. The ir spectra show characteristic absorptions for the NH_2 groups in the ranges of 3417 to 3437 (NH_2); and 1343-1354 as well as 996-1020 cm^{-1} to strong vibrational coupling of C=S and C-N entities. Two bands around 1530 and 1340 cm^{-1} have to be assigned to the nitro groups.

The ^1H nmr spectra show the presence of NH_2 groups by broad signals for 2H between δ = 6.45 and 6.50 ppm and for additionally **5c**, the expected signals for the allyl group. The *a priori* possible isomeric structures **7a-c** were ruled out on the basis of the lowest field signals in the ^{13}C nmr spectra (**5a**: 181.8, **5b**: 181.4 and **5c**: 181.3 ppm) which clearly support a C=S group and not an isothiourea carbon as in **7**.

Compounds **6a-c**.

The ir spectra (in KBr) showed conjugated CN groups at 2220-2225 cm^{-1}, NH absorptions at 3315-3344 and 3268-3280 cm^{-1}, and bands characteristic of vibrational coupling of C=S and C-N groups at 1355 and 998-1015 cm^{-1} The ^1H nmr spectra clearly show two broad signals (N^2H and N^4H) at 9.71 and 9.88 for **6a**, 8.65 and 9.45 for **6b** as well as 7.89 and 8.69 ppm for **6c**. Signals around 118.3 (CN) , 157 (C=N) and 183.7 ppm (C=S) in the ^{13}C nmr spectra lend further support to the structures assigned to **6a-c**. The mass spectra of thiosemicarbazones **6** are, on the other hand, better explained assuming a degradation *via* a cyclic tautomer **A** (Scheme 3).

Such ring-chain tautomeric equilibria for aldehyde thiosemicarbazones and their role in mass spectral fragmentation have been discussed before [29-33]. Both 1,2,4-thiazolidine-3-thiones [29,30] (under neutral conditions) and 1,3,4-thiazolidineimines [29,31] (in acidic medium) may exist in equilibrium with the thiosemi-

Scheme 3

6a-c **A**

carbazone. The photochemical cyclization of some aldehyde-semicarbazones to triazolinethiones has also been reported [18], and the differences in the mass spectral fragmentation between thiosemicarbazones and thiosemicarbazones of aldehydes and ketones has been noted early by Djerassi [32] and coworkers who interpreted the fragmentations of thiosemicarbazones to occur from cyclic ions of 1,3,4-thiadiazolium connectivity.

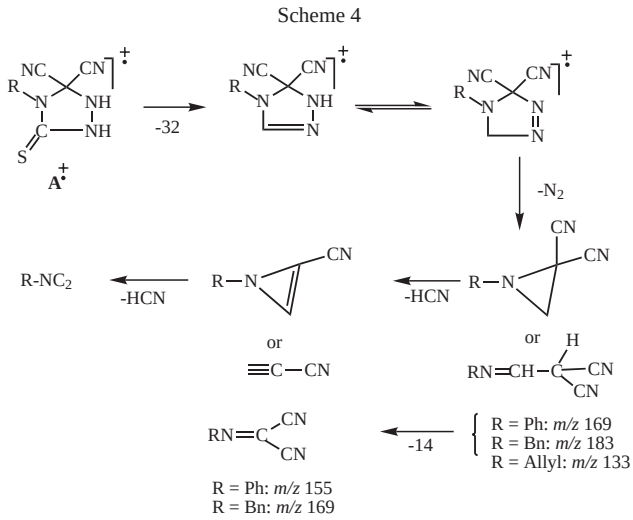
The EI mass spectra of **6a-c** are characterized by molecular ions of low intensity and the loss of 32 a. m. u. (representing sulphur). The resulting fragment ions undergo loss of 28 a. m. u. (most likely dinitrogen), followed by loss of either mass 14 or (successively) two units of 27 a. m. u. (probably 2 x HCN) suggesting tautomerization of **6a-c** to 4-organyl-5-thioxo-3,3-dicarbonitrile radical cation $A^{\bullet+}$ on electron impact prior to fragmentation (see Scheme 4).

The identity of reduction products **9** and **10** as well as 2,4,7-trinitro-9-fluorenone (**8**) derived from **2** was demonstrated by comparison with authentic samples [27]. Formation of the spiro compounds **5a-c** and the thiosemicarbazonopropanedinitriles **6a-c** as well as products **8**-**10** derived from **2** may be rationalized as outlined in Scheme 5.

Starting material **2** is partially reduced to **10**. Both the starting thiosemicarbazide **4** and the intermediate dihydro compound **13** could serve as reducing agents. Nucleophilic attack of the terminal NH_2 of **4a-c** on C-9 of **10**, similar to the attack of **4a,b** on the C=C bond of ethanetetracarbonitrile [24] with elimination of malononitrile from adduct **11** gives rise to **12**. Intramolecular attack of the terminal R-NH group on C-9 of the fluorene skeleton of **12** leads to the intermediates **13a-c** which have to be dehydrogenated (pobably by another molecule of **2** or air-oxygen) to give the spiro products **5a-c**. The alternative option, namely nucleophilic attack by the thione sulphur atom on C-9 of **12**, is not observed since a product of structure **7** instead of **5a-c** is not found. Alternatively to attacking C-9, however, N^1 of **4a-c** can add to the dicyanomethylene carbon of **2** (again in analogy with the reaction of **4a,b** with ethenetetracarbonitrile [24]).

Adduct **14** in turn may release **6a-c** and 2,4,7-trinitrofluorene (**15**) (Scheme 3). It is conceivable that compound **10** instead of **2** undergoes such a sequence as well. The fluorenes may then undergo multistep oxidations with air-oxygen to yield the fluorenones **8** and **9**.

Scheme 4



The latter compound could also be formed by hydrolysis of **12** or **13** by moisture contained in the solvent pyridine. The modest yields of products **5** and **6** have to be accepted, since they are in fact overall yields obtained in multistep sequences.

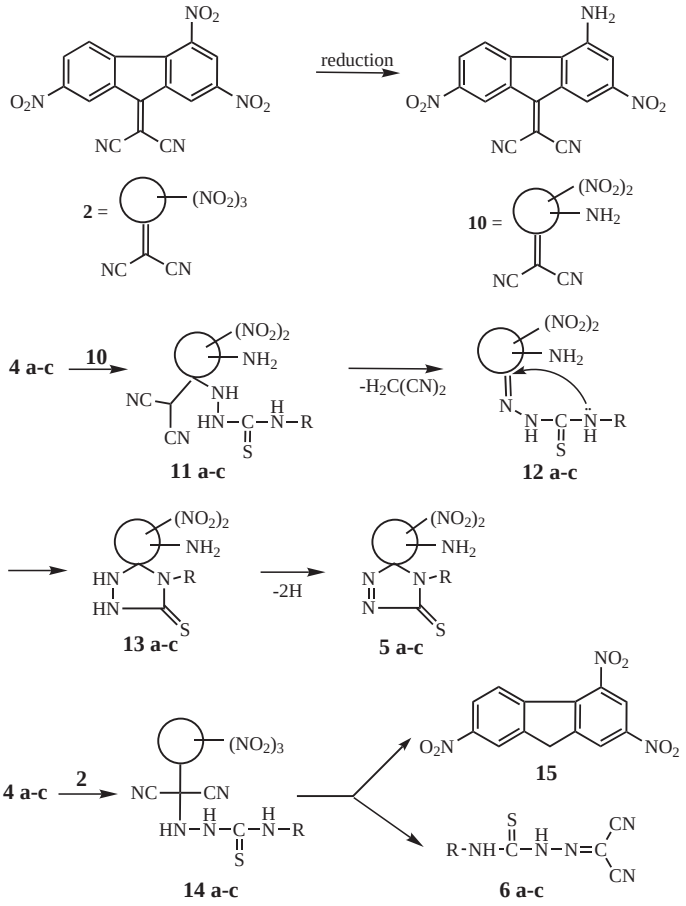
Conclusion.

The reactions and products presented here provide insight into the spontaneous reactions between the electron donating 4-substituted thiosemicarbazides **1a-c** and a suitable electron acceptor, here **2**. In a fairly complex and multistep process two types of a 3-spiro-annelated triazolethione **5** and a 1-dicyanomethylene thiosemicarbazone **6** products, are formed from **1a-c** and **2**. The latter has a dual functioning role as a dehydrogenating agent and a source of the dicyano-methylene units. The results reported here supplement the rich chemistry of (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**2**).

EXPERIMENTAL

Melting points (uncorrected) were determined in open glass capillaries on a Gallenkamp melting point apparatus. The ir spectra were recorded from potassium bromide disks with a Shimadzu 408 or Bruker Vector 22 FT-IR instrument. The 300 MHz ^{1}H and 75 MHz ^{13}C nmr spectra were observed on a Bruker WM 300 instrument with tetramethylsilane as the internal standard using dimethylsulfoxide-d_6 as solvent, br = broad. The ^{13}C nmr signals were assigned on the basis of DEPT 135/90 spectra for **5c** and **6c**. The mass spectra (70 eV, electron impact mode) were recorded on an AMD 604 instrument. Elemental analyses were carried out at the Microanalytical Center, Cairo University, Egypt. Preparative layer chromatography was performed on 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. Zones were detected by their color or by

Scheme 5



quenching of indicator fluorescence upon exposure to 254 nm light.

Starting Materials.

4-Phenylthiosemicarbazide (**4a**) [35,36], 4-benzylthiosemicarbazide (**4b**) [36,37] and 4-(2-propenyl)thiosemicarbazide (**4c**) [37,38] were prepared according to literature procedures. (2,4,7-Trinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**2**) was prepared from 2,4,7-trinitro-9-fluorenone and malononitrile according to Mukherjee [39].

Reaction of 4-Substituted Thiosemicarbazides **4a-c** with **2**.

A solution of substituted thiosemicarbazides 4a-c (1 mmol) in 10 mL of dry pyridine was added dropwise to a solution of 2 (2 mmol) in 15 mL of dry pyridine with stirring. The mixture was heated gently without increasing the temperature above 100 ºC for 3 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 cyclohexane/ ethylacetate (5:1) as eluent into numerous zones, three of which were extracted.

The fastest migrating zone contained 2,4,7-trinitro-9-fluorenone (**8**), the second and third zones which quenched all indicator fluorescence upon exposure to 254 nm uv-light contained compounds **5a-c** and **6a-c**. The material confined to the start was rechromatographed using cyclohexane/ ethylacetate (2:1) to give another two zones, the faster migrating one of which contained orange coloured 4-amino-2,7-dinitro-9-fluorenone (**9**) whereas the second zone (deep blue) contained (4-amino-2,7-dinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**10**). Extraction of the zones with acetone gave a residue, which was rechromatographed with the same eluent to enhance separation. Recrystallization from suitable solvents afforded compounds **5, 6, 8-10**.

4-Amino-2,7-dinitro-4'-phenyl-4',5'-dihydrospiro[fluoren-9,3'-(1,2,4-triazole)]-5'-thione (**5a**).

This compound had mp 286-288º, pale reddish orange crystals from acetonitrile, yield 91 mg (21 %); ir: 3437, 3356 (NH_2), 1600 (aryl), 1352, 1020 (C=S, C-N), 1528, 1340 (NO_2) cm^{-1}; ^1H nmr: δ 6.48 (br, 2H, NH_2), 7.29-7.46, 8.11-8.71 and 9.06-9.24 (all m, 10H, aryl H); ^{13}C nmr : δ 71.66 (C-9 = C-3´), 114.00, 121.6, 124.0, 124.5, 125.3, 128.8 and 129.2 (all aryl CH), 139.40 (phenyl C-1), 141.6 (C-8a), 142.36 (C-9a), 143.8 (C-4b), 145.6 (C-4), 147.8, 148.6 (C-7, C-2) and 181.8 (C=S); EI-MS m/z*:* % 432 (M^+, 11), 404 ([M - N_2]$^+$, 74), 297 ([M - PhNCS]$^+$, 28), 205 ([297 - 2 NO_2]$^+$, 36), 189 (18), 135 ([PhNCS]$^+$, 62), 77 (Ph^+, 100), 65 (42).

Anal. Calcd. for $C_{20}H_{12}N_6O_4S$ (432.41): C, 55.55; H, 2.80; N, 19.44; S, 7.42. Found: C, 55.69; H, 2.71; N, 19.29; S, 7.58.

4-Amino-4'-benzyl-2,7-dinitro-4',5'-dihydrospiro[fluoren-9,3'-(1,2,4-triazole)]-5'-thione (**5b**).

This compound had mp 272-273º, pale reddish orange crystals from acetonitrile, yield 103 mg (23 %); ir: 3420, 3342 (NH_2), 1595 (aryl), 1354, 996 (C=S, C-N), 1525 and 1344 (NO_2) cm^{-1}; ^1H nmr: δ 4.35 (br, 2H, CH_2Ph), 6.45 (br, 2H, NH_2), 7.22-7.32, 8.16-8.68 and 9.10-9.22 (all m, 10H, aryl H); ^{13}C nmr: δ 71.12 (C-9 = C-3′), 114.8, 122.1, 123.8, 126.4, 128.1, 128.3, 128.6, 129.1 (all aryl *C*H), 142.9 (C-4b), 141.1 (C-8a), 141.8 (C-9a), 146.4 (C-4), 147.5 (C-7), 148.8 (C-2) and 181.4 (C=S); EI-MS m/z*:* % 446 (M^+, 7), 418 ([M - N_2]$^+$, 69), 297 ([M - $PhCH_2NCS$]$^+$, 21), 205([297 - 2 NO_2]$^+$, 28), 189 (11), 149 ([$PhCH_2NCS$]$^+$, 83), 91 ($PhCH_2^+$, 100), 77 (Ph^+, 43).

Anal. Calcd. for $C_{21}H_{14}N_6O_4S$ (446.44): C, 56.50; H, 3.16; N, 18.82; S, 7.18. Found: C, 56.39; H, 3.33; N, 18.67; S, 7.05.

4-Amino-2,7-dinitro-4'-(2-propenyl)-4',5'-dihydrospiro[fluoren-9,3'-(1,2,4-triazole)]-5'-thione (**5c**).

This compound had mp 212-214°, pale reddish orange crystals from ethanol, yield 95 mg (24 %); ir: 3417, 3338 (NH_2), 1588 (aryl), 1348, 1010 (C=S, C-N), 1530 and 1338 (NO_2) cm^{-1}; ^1H nmr: δ 4.23 (br, 2H, allyl CH_2N), 5.24-5.36 (m, 2H, allyl CH_2=), 6.05-6.15 (m, 1H, allyl CH=), 6.50 (br, s, 2H, NH_2), 8.05-8.64, 9.02-9.20 (two m, 5H, aryl H); ^{13}C nmr: δ 43.12 (allyl *C*H_2-N), 71.08 (C9 = C3′), 115.42 (allyl *C*H_2=), 121.6, 124.0, 128.8 and 129.2 (all aryl *C*H), 135.13 (allyl *C*H=), 141.3 (C-8a), 142.1 (C-9a), 143.6 (C-4b), 146.0 (C-4), 147.4, 148.3 (C-7, C-2) and 181.3 (C=S); EI-MS m/z*:* % 396 (M^+, 11), 368 ([M - N_2]$^+$, 100), 297 ([M - Allyl-NCS]$^+$, 12), 205 (14), 99 (81), 41 (98).

Anal. Calcd. for $C_{17}H_{12}N_6O_4S$ (396.38): C, 51.51; H, 3.05; N, 21.20; S, 8.09. Found: C, 51.34; H, 2.92; N, 21.36; S, 7.92.

(4-Phenylthiosemicarbazono)propanedinitrile (**6a**).

This compound had mp 218-220º, brown crystals from ethanol), yield 57 mg (25 %); ir: 3315 and 3280 (NH), 2225 (CN), 1635 (C=N), 1570 (NH def. and C-N str.), 1358, 998 (C=S, C-N) cm^{-1}; ^1H nmr: δ 7.14-7.17, 7.24-7.36, 7.49-7.58 (all m, 5H, phenyl H), 9.71 (br, 1H, NH), 9.88 (br, 1H, NH-Ph); ^{13}C nmr: δ 118.3 (CN), 122.9, 125.6, 128.8 (phenyl *C*H), 141.2 (phenyl C-1), 157.8 (C=N), 183.7 (C=S); EI-MS m/z: % 229 (M^+, 6), 197 ([M - S]$^+$, 9), 169 ([197 - N_2]$^+$, 37), 155 ([169 - 14]$^+$, 100), 128 (67), 101 (22), 92 (76), 77 (81), 64 (18), 51 (44).

Anal. Calcd. for $C_{10}H_7N_5S$ (229.26): C, 52.39; H, 3.08; N, 30.55; S, 13.99. Found: C, 52.47; H, 2.96; N, 30.39; S, 14.14.

(4-Benzylthiosemicarbazono)propanedinitrile (**6b**).

This compound had mp 201-203º, brown crystals from acetonitrile, yield 56 mg (23 %); ir: 3330 and 3268 (NH), 2222 (CN), 1628 (C=N), 1565 (NH def. and C-N str.), 1355, 1005 (C=S, C-N); ^1H nmr: δ 4.33 (br, 2H, CH_2Ph), 7.08-7.15, 7.46-7.53 (all m, 5H, phenyl H), 8.65 (br, 1H, N*H*-CH_2Ph), 9.45 (br, 1H, N*H*-C=S); ^{13}C nmr: δ 52.6 (CH_2), 118.3 (CN), 123, 126.5, 128.3, (phenyl *C*H); 139.6 (phenyl C-1), 156.8 (C=N), 183.8 (C=S); EI-MS m/z: % 243 (M^+, 3), 211 ([M - S]$^+$, 6), 183 ([211 - N_2]$^+$, 12), 169 ([183 - 14]$^+$, 100), 142 ([169 - HCN]$^+$, 77), 115 ([142 - HCN]$^+$, 22), 104 (61), 77 (••), 64 (16), 51 (56).

Anal. Calcd. for $C_{11}H_9N_5S$ (243.29): C, 54.30; H, 3.73; N, 28.79; S, 13.18. Found: C, 54.19; H, 3.88; N, 28.93; S, 13.29.

[4-(2-Propenyl)-thiosemicarbazono]propanedinitrile (**6c**).

This compound had mp 163-165º, pale brown crystals from ethanol, yield 48 mg (25 %); ir: 3344, 3270 (NH), 2220 (CN), 1625 (C=N), 1560 (NH def. and C-N str.), 1358, 1015 (C=S, C-N); ^1H nmr: δ 4.10 - 4.12 (br, 2H, allyl C*H*$_2$N), 5.03-5.14 (m, 2H, allyl C*H*$_2$=), 5.81-5.90 (m, 1H, allyl C*H*=), 7.89 (br, 1H, NH), 8.69 (br, 1H, NH); ^{13}C nmr: δ 43.6 (allyl *C*H_2N), 115.6 (allyl *C*H_2=), 118.2 (CN), 135.1 (allyl *C*H=), 156.9 (C=N), 183.4 (C=S); EI-MS m/z: % 193 (M^+, 6), 161 ([M - S]$^+$, 4), 133 ([161 - N_2]$^+$, 100), 106 ([133 - HCN]$^+$, 78), 79 (41), 42 (63).

Anal. Calcd. for $C_7H_7N_5S$ (193.23): C, 43.51; H, 3.65, N, 36.24; S, 16.59. Found: C, 43.68; H, 3.73; N, 36.12; S, 16.77.

2,4,7-Trinitro-9-fluorenone (**8**).

This compound had mp 173-175°C (Lit. [34], 175°C), (6 - 8 %).

4-Amino-2,7-dinitro-9-fluorenone (**9**).

This compound had mp 310-312°C (Lit. [27] 310-312°C), (12 - 16 %).

(4-Amino-2,7-dinitro-9*H*-fluoren-9-ylidene)propanedinitrile (**10**).

This compound had mp 340-342°C (Lit. [27] 340-342°C), (8 –11 %).

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[*] To whom correspondence should be addressed.

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