Facile and Selective Synthesis of 4-Methyl- and 4-Phenylthiosemicarbazide (= *N*-Methyl- and *N*-Phenylhydrazinecarbothioamide) Derivatives of Benzil (= 1,2-Diphenylethane-1,2-dione)

by **David G. Calatayud**, **Francisco J. Escolar**, **Elena López-Torres**, and **M. Antonia Mendiola***

Departamento de Química Inorgánica, Universidad Autónoma de Madrid, E-28049 Madrid (phone: +34914944844; fax: +34914974833; e-mail: antonia.mendiola@uam.es)

A selective synthesis of 4-methylthiosemicarbazide (= *N*-methylhydrazinecarbothioamide; **4a**) derivatives by reaction with benzil (= 1,2-diphenylethane-1,2-dione; **3**) is described. The reaction conditions determined the condensation product formed. The most important factor was the acid used: in the presence of conc. HCl solution, the open-chain 2 : 1 compound **1a** was exclusively obtained, whereas in the presence of 2M HCl, the cyclic 1 : 1 condensation product **2a** was formed. The alcohol used, the presence of H_2O, and the time of heating were additional crucial factors. The new cyclic compound **2a** with a MeO group was exclusively formed when working under high-dilution conditions. The reaction with the 4-phenyl derivative **4b** gave new cyclic compounds as the major products under all conditions used (*Scheme*).

1. Introduction. – There is considerable current interest in the biological activity of *Schiff*-base macroligands derived from thiosemicarbazides (= hydrazinecarbothioamides) and their complexes. Bis(thiosemicarbazones) (= 2,2′-(alkanediylidene)bis[hydrazinecarbothioamides]) of type **1** have been known for over fifty years, and they have shown interesting biological activity as free ligands and as their metal complexes [1]. Recently, it has become apparent that they may also provide a convenient way of labeling biologically active molecules to act as imaging agents for both fluorescence (M = Zn) and positron emission tomography (PET) (M = Cu) [2]. On the other hand, in the last few years, a great deal of research has been aimed to design highly selective and sensitive compounds to heavy-metal ions, from the point of view of chemical, biological, and environmental processes [3]. Among the many different strategies proposed, the preparation of electrochemical and fluorescent sensors should be highlighted, and thiosemicarbazones (= 2-alkylidenehydrazinecarbothioamides) are good candidates in this field. Although apparently simple, the synthesis of bis(thiosemicarbazone) ligands from diketones with aryl substituents can be problematic due to the formation of cyclic products [4]. In particular, reactions with 4-methylthiosemicarbazide (= *N*-methylhydrazinecarbothioamide; **4a**) in EtOH and in the presence of H_2SO_4 gave a mixture of the open-chain and cyclic compounds [4a].

We have been interested in the preparation of carbohydrazones, thiocarbohydrazones, semicarbazones, and thiosemicarbazones derived from benzil (= 1,2-diphenylethane-1,2-dione; **3**) and their coordination compounds to get potential modifiers of

standard electrodes [5]. Some of their complexes (Cu and Hg) have been used in the preparation of potentiometric sensors for these metals, and the Cd and Hg complexes of thiosemicarbazone have shown promising antibacterial properties [6]. In our experience, the synthesis of semi- and thiosemicarbazone ligands is rarely straightforward, but we have reported selective procedures to obtain the open-chain and the cyclic compounds. The optimum conditions to get the open-chain molecules *vs.* the heterocycles depend on the diamine precursor. In particular, the open-chain product formally derived from benzil/semicarbazide 1:2 was prepared in the presence of LiOH, whereas the cyclic compound was obtained in acidic medium [5b]. However, in the case of thiosemicarbazide (*i.e.*, **4** with R = H), derivatives of both types (*i.e.*, **1** and **2** with R = H) were obtained in the presence of HCl. The cyclic compound was obtained pure and in almost quantitative yield working under high-dilution conditions, but under all the other conditions, the open-chain product was also formed [5b][7].

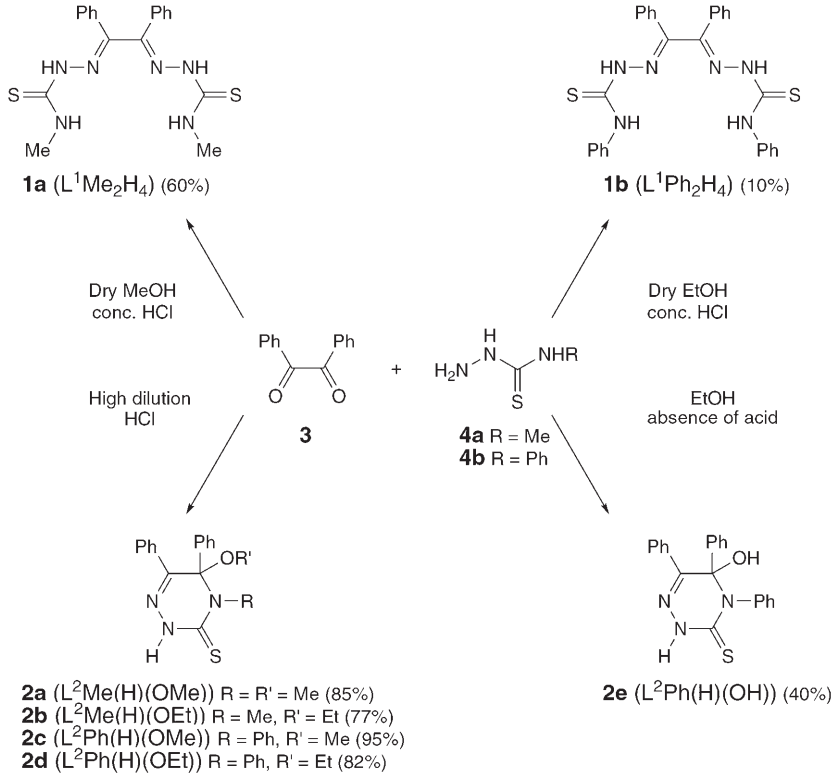
Our recent interest concerns the effect of the presence of an organic group at N(4) of the starting thiosemicarbazide (*i.e.*, 4-methyl- and 4-phenylthiosemicarbazide = *N*-methyl- and *N*-phenylhydrazinecarbothioamide; **4a** and **4b**, resp.) on the structure of the condensation products with benzil (**3**). The structural characteristics of such condensation products determine their properties, reactivity, and potential applications for preparing sensors for toxic metals, and small structural changes like substitution of an H-atom by a Me or Ph group can have strong effects on the biological properties. The aim of this work was to find the reaction conditions yielding only a specific compound (*i.e.*, of type **1** or **2**) and to elaborate the procedures permitting the selective synthesis of the desired product. Here we present the selective routes, spectroscopic characterization, and X-ray structure analysis of the compounds derived from 4-substituted thiosemicarbazides **4a**,**b**, including of those previously published by alternative synthetic routes [8].

2. Results and Discussion. – *Syntheses.* From the reactions between benzil (**3**) and 4-methyl- or 4-phenylthiosemicarbazide (**4a** or **4b**) as precursors, we isolated and characterized the two open-chain molecules **1a** and **1b** and the five 1:1 condensation products **2a**–**e** (*Scheme*). Our results pointed out that the cyclic molecules were formed easier than the open-chain products under all the conditions studied. Thus, the substitution of an H-atom of a 'primary-amino' group by a Me or a Ph group increased the ease of obtaining the cyclic 1:1 products **2** and concomitantly increased the difficulty to get pure 1:2 products **1** in high yield. This fact can be explained by the high stability of the 4-methyl- or 4-phenyl-substituted 1,2,4-triazine rings of **2a**–**e**, which show a better charge delocalization than the triazine obtained from the unsubstituted thiosemicarbazide. The Ph derivatives **2c**–**e** are even more stable than the Me analogues **2a**,**b**, probably due to the aromatic ring at N(1)[1]) of the triazine ring, which gives rise to a more extended electron delocalization.

We then confirmed that the reaction conditions can determine the structure of the condensation products obtained from 4-methylthiosemicarbazide (**4a**) and benzil (**3**) as precursors (*Scheme*). In the presence of AcOH, only a mixture of the reagents was obtained, and with H_2SO_4, the 1:2 product **1a** was isolated but contaminated with other

[1]) Arbitrary atom numbering.

Scheme. *Best Synthetic Routes for the Synthesis of 4-Substituted Thiosemicarbazide Derivatives* **1** *and 1,2,4-Triazine-3(2*H*)-thiones* **2**



compounds, including the 1:1 product **2a**. However, in the presence of HCl, both condensation products could easily and selectively be synthesized, improving the previous reaction conditions which led to a mixture **1a**/**2b** (in EtOH) [4a]. The solvent used also affected the results. In EtOH, only the 1:1 compound **2b** was formed, but in MeOH both types of compounds, **1a** and **2a**, were present. The crystal structure of the EtO derivative **2b**, obtained from the reaction of 4-ethylthiosemicarbazide with 1,2,8,9-tetraphenyl-3,7-diazanona-1,9-dione in the presence of $Cu(OAc)_2$, has been previously published [8]. The pure 1:2 condensation product **1a** was obtained as the major compound if the reaction was carried out in dry MeOH with some drops of conc. HCl solution. However, the reaction in 2M HCl and commercial MeOH yielded **1a** and **2a**; the open-chain product **1a** precipitated first, and the 1:1 product **2a** was isolated from the filtrate. The 1:1 molecule **2a** was exclusively formed working under high-dilution conditions in the presence of HCl. An additional factor was the time of heating: Best results were achieved under anhydrous conditions by heating 45 min under reflux.

From 4-phenylthiosemicarbazide (**4b**) and following the same procedures as those described for the Me derivatives **4a**, also 1:1 and 1:2 products could be synthesized

(*Scheme*). The cyclic compounds **2c** and **2d** were formed in the presence AcOH but in a very low yield and isolated together with the unreacted precursor **4b**. In dry MeOH or EtOH, even controlling the temperature and the heating time, **2c** and **2d** were always obtained contaminated with the 1:2 product **1b**. Again, **2c** and **2d** were isolated pure and in almost quantitative yield under the high-dilution conditions. Unlike **1a**, the 1:2 product **1b** was only obtained when working in EtOH, but in a very poor yield (10%) and together with the cyclic derivative **2d** as the major product. In addition, the reaction of benzil (**3**) and 4-phenylthiosemicarbazide (**4b**) gave, in the absence of any acid, a new cyclic compound **2e** containing an OH instead of the MeO or EtO group. It was not possible to obtain such a compound from the 4-methylthiosemicarbazide (**4a**) under the same conditions. However, the corresponding 5-hydroxy-4-methyl-1,2,4-triazine derivative has been isolated as an unexpected product from the reaction between 4-methylthiosemicarbazide (**4a**) and bis(benzil)-1,3-diiminopropane (='1,2,8,9-tetraphenyl-3,7-diazanona-2,7-diene-1,9-dione' [9] =2,2′-(propane-1,3-diyldinitrilobis[1,2-diphenylethanone]) in the presence of copper(II) acetate [9].

Spectroscopy. The IR spectra of the compounds **1** and **2** show bands between 3450–3220 cm^{-1} corresponding to the N–H stretching, as well as the bands related to the thioamide groups (see *Exper. Part*).

The FAB-MS (positive mode) of **1a** shows a peak at *m*/*z* 385.2 corresponding to the molecular ion and a peak at *m*/*z* 769.6 corresponding to a dimer, suggesting the presence of strong intermolecular interactions. Additional peaks assigned to different fragments can also be observed. The FAB-MS of **1b** shows a peak at *m*/*z* 509.3, which corresponds to the proposed molecular mass.

The FAB-MS (positive mode) of **2a** and **2b** are very similar. Peaks at *m*/*z* 312.2 and 326.2 corresponding to the molecular ions are observed, as well as the interaction of two molecules by H-bonds. Additional peaks at lower *m*/*z* are observed, the first, corresponds to the loss of the MeO or EtO group. From this peak on, both spectra show the same fragments. The FAB-MS (positive mode) of **2c** and **2d** are similar to those of the Me derivatives, and the peaks at *m*/*z* 374.0 and 388.0 confirm the 1:1 condensation products with one MeO or EtO group attached at C(2)[1]). The formation of **2e**, with a hydroxy group at C(2), is confirmed by a peak at *m*/*z* 360.0.

The ^{1}H-NMR spectra of **1a** (*Fig. 1*) show the presence of two kinds of NH groups at low field with different multiplicities, a *m* for the H-atoms of the Ph groups, and a *s* attributable to the Me groups. The ^{1}H-NMR spectrum of **1b** shows two *s* arising from the NH groups and *m*s for the Ph groups. In both spectra, the integrals confirm the 1:2 condensation and suggest a symmetric structure in solution. The NH signals appear at lower field in the case of the Ph derivative **1b** than in the Me derivative **1a**. The ^{13}C-NMR spectra confirm the proposed structures.

The ^{1}H-NMR spectra of the cyclic compounds **2a**–**e** show one *s* for the NH group and one *m* for the Ph groups. In **2a**–**d**, peaks due to the MeO or EtO groups are observed, while in **2e**, these signals have disappeared. In addition, compounds **2a** and **2b** also show one *s* corresponding to the Me group attached to N(4). The ^{13}C-NMR spectra in solution confirm the formation of the triazine rings, as well as the presence of an MeO (**2a** and **2c**) or EtO group (**2b** and **2d**), and of the imino and thioamide moieties. In **2e**, the signal corresponding to the quaternary C-atom is shifted with respect to the alkoxy derivatives.

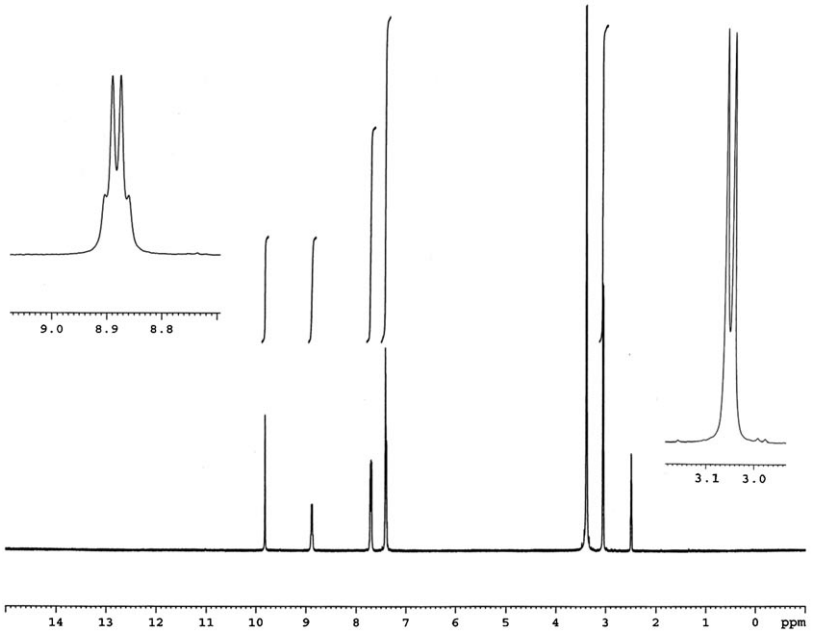


Fig. 1. *^{1}H-NMR Spectrum* ((D_6)-DMSO) *of* **1a**

X-Ray Structure Determination. *Compound* **1a**. The structure of **1a** contains a disordered molecule of DMSO of crystallization, which could not be satisfactorily modelled. The contribution from this solvent molecule was removed from the observed data by using SQUEEZE in the software program PLATON [10]. Compound **1a** crystallizes in the monoclinic system. This system, the space group, the cell parameters of the crystal, and other data included in the *Exper. Part* are different from those previously published for this compound [4a]. This fact is probably due to the different solvent used for crystallization. The crystal structure (*Fig. 2*) shows that the molecule exists in the thione form, supported by the presence of hydrazinic N–H and C–S bond distances, the latter being much shorter than a single C–S bond. These data correspond to a structure where the two 4-methylthiosemicarbazone moieties are on the same side (*cisoid*) of the single bond C(2)–C(3)[1]), which explains the deviation from the previously published structure, in which the thiosemicarbazone moieties were in *transoid* position [4a][5d]. This difference can be explained by the absence of H-bonds in the bis(4-methylthiosemicarbazone) **1a** recristallized from DMSO.

Both thiosemicarbazone moieties of **1a** adopt an (*E*) configuration with respect to the C=N bond. Bond distances and angles of both thiosemicarbazone moieties are very similar, and the molecular conformation of the S-atoms and the azomethine N-atoms N(2) and N(3) are *anti*-periplanar with respect to the C(1)–N(1) and C(4)–N(4) bonds[1]). The N–N distances are shorter than 1.44 Å (typical value for an N–N single bond) and agree well with those of similar thiosemicarbazones [11]. The C–S bond distances of 1.681(4) and 1.675(4) Å are intermediate between those of a single and double bond (1.82 and 1.56, resp.) [12], showing the partial double-bond character

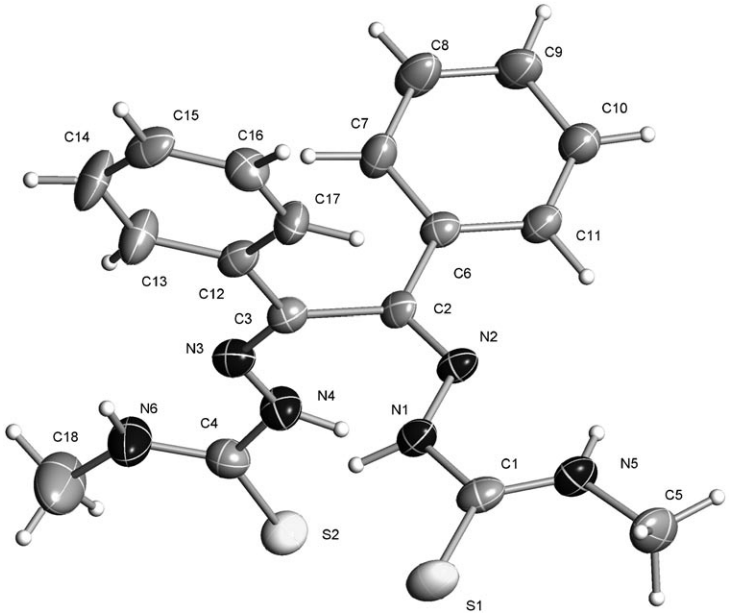


Fig. 2. *Molecular structure of* **1a**[1]). Thermal ellipsoids at 50% probability. Selected bond distances [Å]: C(1)–N(5) 1.320(5), C(1)–N(1) 1.378(4), C(1)–S(1) 1.681(4), C(2)–N(2) 1.302(4), C(2)–C(3) 1.505(5), C(4)–N(6) 1.348(5), C(4)–S(2) 1.675(4), C(3)–N(3) 1.287(5), N(1)–N(2) 1.370, and N(4)–N(3) 1.354.

implied by the canonical structures usually considered for thiosemicarbazones. The azomethine C=N bond lengths are likewise short enough to imply a partial double bond.

Compounds **2a**–**e**. The crystal structures of **2a** and **2b** (*Figs. 3* and *4*) confirm the formation of the 1,2,4-triazines. The data of **2b** are similar to those previously published for **2b** obtained from other precursor molecules [8], and we have included them here only for comparison purposes. The C–S distances of **2a** and **2b** (1.684(14) and 1.687(19) Å, resp.) are much shorter than a C–S single bond, which indicates that the ligands are in the thione form. The same electron delocalization is present in the triazine ring of all compounds **2**; whereas the C(3)–N(2) bond distances agree with the predicted C=N bond of 1.28 Å, both C(1)–N(1) and C(1)–N(3) are considerably shorter than the single bond expected and thus have considerable double bond character[1]). The C(2)–N(1) distances are consistent with a C–N single bond, but the C(2)–C(3) distances are slightly shorter than the predicted 1.54 Å for a single bond, and the N(2)–N(3) distances are significantly shorter than the expected N–N single-bond distances. This delocalization is in accordance with an almost planar triazine moiety of all compounds **2**, some π-electron density is probably derived from the thione bond, but it is in the range expected for a C=S bond. The C–O bonds are slightly shorter than predicted for a single bond. The C(2)–C(3) bonds are longer than the 1.50 Å for a C(sp^3)–C(sp^2) single bond. Thus, there is no strong evidence that the two Ph substituents or the O-atom contribute to the π character of the triazine. Therefore,

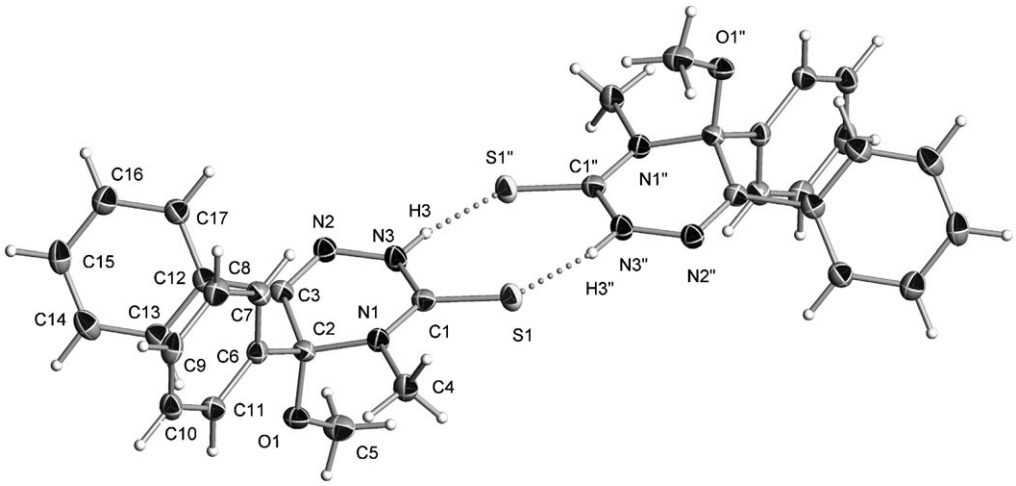


Fig. 3. *Molecular structure of* **2a** *including the H-bonds*[1]). Thermal ellipsoids at 50% probability. Selected bond distances [Å]: C(1)–S(1) 1.684(14), C(1)–N(1) 1.347(17), C(1)–N(3) 1.351(18), C(2)–O(1) 1.418(15), C(2)–N(1) 1.470(17), C(2)–C(3) 1.527(18), C(3)–N(2) 1.287(17), and N(2)–N(3) 1.373(17).

the three N-atoms of the triazine ring of **2** must delocalize their non-bonding electrons to give the ring its planarity even though there is formally only one double bond. Each NH group forms a H-bond with the S-atom of a neighboring molecule (*Fig. 3*), and in **2a** the molecules are linked together by $\pi-\pi$ interactions with a distance of 3.569 Å.

The crystal structures fo **2c**–**e** (*Figs. 5–7*) confirm their cyclic structures. The bond distances and angles of these compounds are similar to those observed for the Me derivatives **2a**,**b**. In the alkoxy derivatives **2c** and **2d**, the molecules are linked by H-bonds NH–S (*Figs. 5* and *6*). In addition, the molecules are linked together by $\pi-\pi$ interactions, at a distance of 3.422 and 3.443 Å, respectively. The presence of a molecule of DMSO in the hydroxy derivative **2e** causes H-bonds involving the O-atoms of the solvent with the H–N(3) and with the H-atom of the OH group.

The lengths of the C–O bonds exhibit the most important differences among the cyclic compounds **2**. The shortest C–O length, close to that of the Me derivative LMe(H)(OH) published by other authors [9], is observed for the hydroxy derivative **2e** and the largest for **2a**. The C–O length in **2b** is exactly the same as in the thiosemicarbazide derivative (LH_2(OMe)) previously published [5b]. The complete sequence is **2e** < LMe(H)(OH) [9] < **2d** < **2b** < **2c** < **2a**. This order can be explained taking into account the small size of the H-atom, the planar structure of the benzene ring, and the lesser steric requirements of the CH_2 than of the Me groups.

3. Conclusions. – Our results show that substitution of an 'amino' H-atom by a Me or a Ph group increased the ease and speed of formation of the cyclic molecules **2** from benzil (**3**) and a thiosemicarbazide as compared to the formation of the open-chain compounds which were thus more difficult to get pure and with high yield. We established the optimum working conditions for the facile and selective synthesis of the

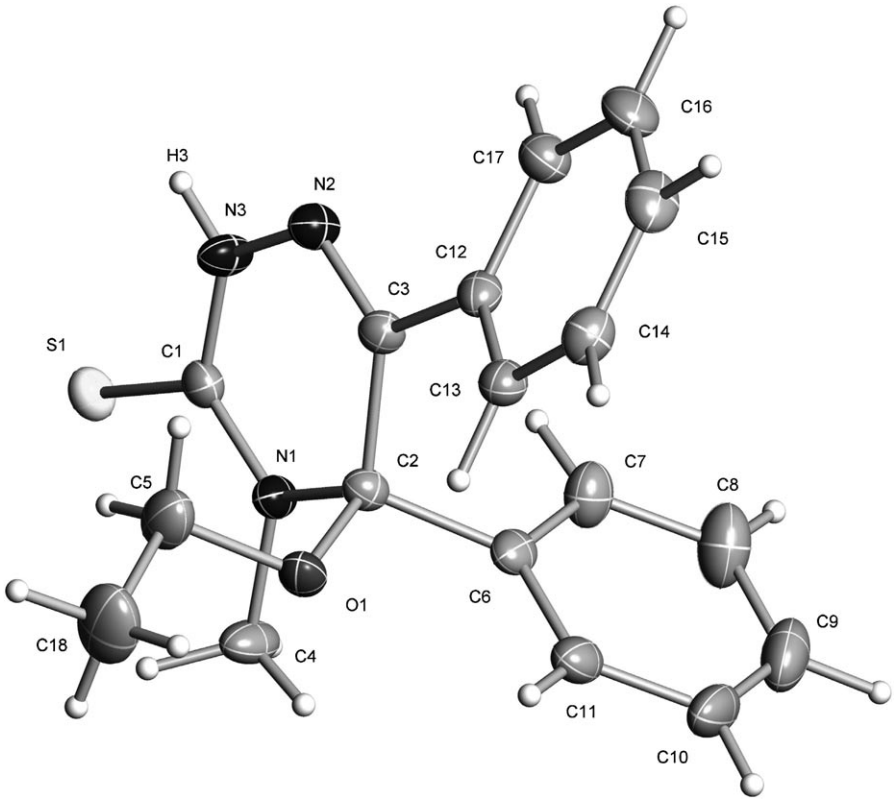


Fig. 4. *Molecular structure of* **2b**[1]). Thermal ellipsoids at 50% probability. Selected bond distances [Å]: C(1)–S(1) 1.687(19), C(1)–N(1) 1.345(2), C(1)–N(3) 1.342(3), C(2)–O(1) 1.410(2), C(2)–N(1) 1.483(2), C(2)–C(3) 1.526(3), C(3)–N(2) 1.286(2), and N(2)–N(3) 1.365(2).

open-chain benzil bis(4-methylthiosemicarbazone) (**1a**) and of the cyclic 4,5-dihydro-5-methoxy-4-methyl-5,6-diphenyl-1,2,4-triazine-3(2*H*)-thione (**2a**) and 5-ethoxy-4,5-dihydro-4-methyl-5,6-diphenyl-1,2,4-triazine-3(2*H*)-thione (**2b**), *i.e.*, both types of compounds were selectively synthesized in the presence of HCl in MeOH or EtOH, the cyclic molecules **2a** and **2b** in the presence of H_2O, and the open-chain molecule **1a** under anhydrous conditions and with a controlled heating time. The results obtained from the reactions with 4-phenylthiosemicarbazide (**4b**) were similar leading to the corresponding compounds **1b**, **2c**, and **2d**. A new cyclic compound, **2e**, with an OH instead of a MeO or EtO group was obtained working in EtOH and in the absence of acid. Another difference was the low yield of the open-chain compound **1b**, which is probably due to the presence of four Ph groups in the molecule and the easier formation of the cyclic molecule **2d**.

These results respresent an important synthetic improvement and open new ways to selectively prepare compounds of type **1** or **2** with different structures and specific reactivity from particular precursor molecules.

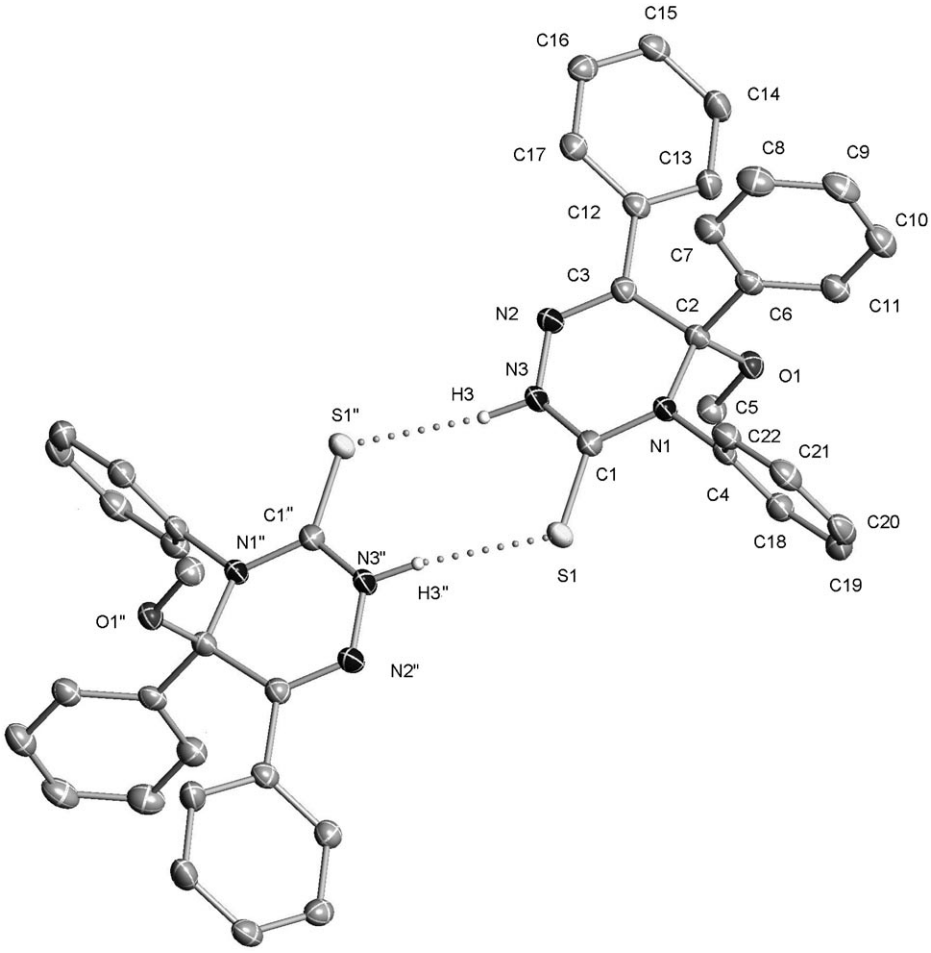


Fig. 5. *Molecular structure of* **2c** *including the H-bonds*[1]). Thermal ellipsoids at 50% probability. Selected bond distances [Å]: C(1)–S(1) 1.6851(15), C(1)–N(1) 1.353(2), C(1)–N(3) 1.350(2), C(2)–O(1) 1.4124(19), C(2)–N(1) 1.4915(19), C(2)–C(3) 1.526(2), C(3)–N(2) 1.287(2), and N(2)–N(3) 1.3726(18).

We thank *César J. Pastor* and *Manuela E. Medina* from the Servicio Interdepartamental de Investigación de la Universidad Autónoma de Madrid (SIDI) for the X-ray diffraction measurements. We also thank *DGICYT* for financial support (project CT2005-07788/BQU) and the Universidad Autónoma de Madrid for a grant to *D. G. C.*

Experimental Part

1. *General.* Commercially available reagents were used without further purification. Solvents were dried, when necessary, by standard methods. IR Spectra: *Jasco FT/IR-410* spectrophotometer; 4000–400 cm^{-1} range; KBr pellets. ^{1}H-and ^{13}C-NMR Spectra: *Bruker AMX-300* spectrometer; at r.t., in $CDCl_3$ or (D_6)DMSO. MS: *VG Auto-Spec* instrument, with Cs as the fast atom and 3-nitrobenzyl alcohol

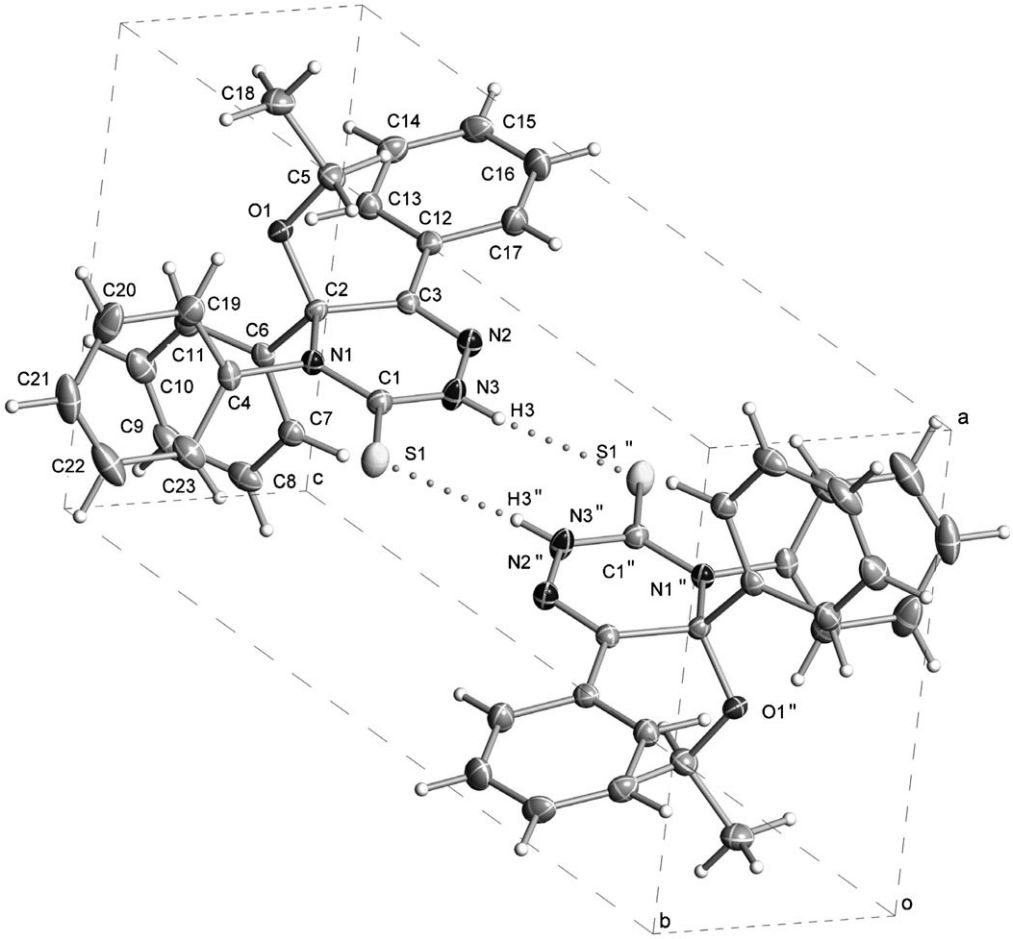


Fig. 6. *Molecular structure of* **2d** *including the H-bonds*[1]). Thermal ellipsoids at 50% probability. Selected bond distances [Å]: C(1)–S(1) 1.6845(15), C(1)–N(1) 1.3490(19), C(1)–N(3) 1.3472(19), C(2)–O(1) 1.4086(16), C(2)–N(1) 1.4999(17), C(2)–C(3) 1.5286(18), C(3)–N(2) 1.2830(19), and N(2)–N(3) 1.3677(17).

(3NBA) as the matrix for FAB; *Bruker Reflex-III* mass spectrometer equipped with a N_2 laser emitting at 337 nm and dithranol as matrix for MALDI-TOF; in *m*/*z* (rel. %). Microanalyses: *Perkin-Elmer 2400-II-CHNS/O* elemental analyzer.

2. *Benzil Bis(4-methylthiosemicarbazone)* (=*2,2′-(1,2-Diphenylethane-1,2-diylidene)bis[*N*-methylhydrazinecarbothioamide*]; **1a**). A soln. of benzil (**3**; 1.503 g, 7.15 mmol) and conc. HCl soln. (10 drops) in dry MeOH (75 ml) was added to a soln. of 4-methylthiosemicarbazide (**4a**; 1.504 g, 14.30 mmol) in dry MeOH (125 ml) and 1 ml of conc. HCl soln. (1 ml). The mixture was stirred under reflux for 45 min. After cooling to r.t., the pale yellow precipitate was filtered off, washed (cold dry MeOH), and dried: **1a** (60%). Recrystallization from DMSO gave pale yellow crystals suitable for X-ray crystallography. M.p. 224°. IR (KBr): 3435*s* and 3335*s* (NH), 1601*w* (CN), 1546*s* (thioamide II), 845*w* (thioamide IV). ^{1}H-NMR ((D_6)DMSO): 9.85 (*s*, 2 NH); 8.89 (*q*, *J* = 4.6, 2 NHMe); 7.72 (*m*, 4 arom. H); 7.38 (*m*, 6 arom. H); 3.01 (*d*, *J* = 4.6, 2 Me). ^{1}H-NMR ($CDCl_3$): 8.52 (*s*, 2 NH); 7.81 (*q*, *J* = 4.6, 2 N*H*Me); 7.74 (*m*, 4 arom.

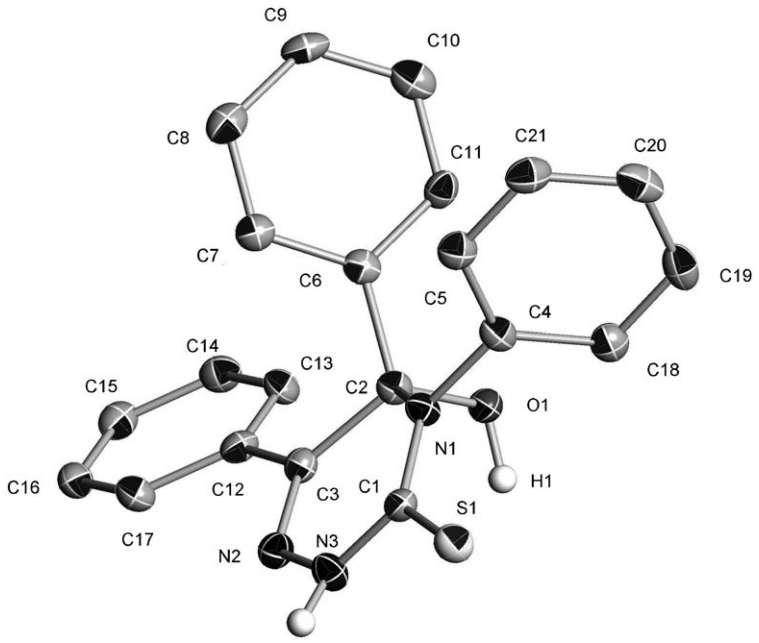


Fig. 7. *Molecular structure of* **2e**[1]). Thermal ellipsoids at 50% probability. Selected bond distances [Å]: C(1)–S(1) 1.680(3), C(1)–N(1) 1.351(4), C(1)–N(3) 1.350(4), C(2)–O(1) 1.404(4), C(2)–N(1) 1.503(4), C(2)–C(3) 1.533(4), C(3)–N(2) 1.298(4), and N(2)–N(3) 1.365(4).

H); 7.32 (*m*, 6 arom. H); 3.31 (*d*, $J = 4.6$, 2 Me). ^{13}C-NMR ((D$_6$)DMSO): 178.6 (C=S); 140.4 (C=N); 133.2–126.8 (Ph); 31.5 (Me). FAB-MS (pos.): 769.6 (10, $[2M+1]^+$), 385.2 (80, $[M+1]^+$). Anal. calc. for $C_{18}H_{20}N_6S_2$ (384.52): C 56.22, H 5.17, N 21.86, S 16.68; found: C 55.90, H 5.24, N 21.71, S 16.49.

A soln. of **3** (0.105 g, 0.50 mmol) in MeOH (5 ml) was added to a soln. of **4a** (0.150 g, 1 mmol) in MeOH (10 ml) and AcOH (5 drops) or H_2SO_4 (3 drops). The mixture was stirred under reflux for 8 h and then concentrated until a solid was formed: **3**/**4a** (AcOH) or **1a**/**2a**/unknown compounds (H_2SO_4).

A soln. of **3** (0.210 g, 1.00 mmol) in EtOH (20 ml) was added to a soln. of **4a** (0.210 g, 2.00 mmol) in EtOH (20 ml). The mixture was stirred under reflux for 3 h. Then, the solvent was partially evaporated, and the mixture kept cold during two days. The precipitate formed was filtered off and dried. The solid contains at least two compounds: a crystalline yellow compound, *i.e.*, **3**, and a white one, *i.e.*, **4a**.

3. *4,5-Dihydro-5-methoxy-4-methyl-5,6-diphenyl-1,2,4-triazine-3(2*H*)-thione* (**2a**). A soln. of **3** (0.210 g, 1.00 mmol) and conc. HCl soln. (2 drops) in MeOH (13 ml) was added to a soln. of **4a** (0.210 g, 2.00 mmol) in MeOH (12 ml), conc. HCl soln. (1 ml), and 2M HCl (10 ml). The mixture was stirred under reflux for 3 h. After cooling to r.t., the pale yellow precipitated **1a** was filtered off, washed with MeOH, dried, and characterized (see above). From the filtrate, a white solid was collected: **2a** (40%). White crystals suitable for X-ray crystallography were formed by slow evaporation of the mother liquor. White-solid data: M.p. 136°. IR (KBr): 3229*s* (NH), 1612*w* (CN), 1511*s* (thioamide II), 846*w* (CS). ^{1}H-NMR ((D$_6$)DMSO): 12.26 (*s*, NH); 7.52–7.21 (*m*, 2 Ph); 3.18 (*s*, MeO); 2.93 (*s*, MeN). ^{1}H-NMR ($CDCl_3$): 9.50 (*s*, NH); 7.61–7.13 (*m*, 2 Ph); 3.43 (*s*, MeO); 3.10 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO): 171.7 (C=S); 141.4 (C=N); 139.9–126.4 (Ph); 87.1 (MeO*C*); 51.10 (MeO); 33.3 (Me). FAB-MS (pos.): 622.5 (10, $2M^+$), 312.2 (100, $[M+1]^+$), 280.2 (13, $C_{16}H_{14}N_3S^+$), 118.1 (8, $C_7H_6N_2^+$), 105.1 (20, $[C_7H_6N+1]^+$), 77.0 (9, Ph^+). Anal. calc. for $C_{17}H_{17}N_3OS$ (311.40): C 65.56, H 5.50, N 13.50, S 10.30; found: C 65.62, H 5.51, N 13.51, S 10.17.

A soln. of **4a** (1.05 g, 10.00 mml) in MeOH/2M HCl 1:1 (48 ml) and conc. HCl soln. (1 ml), and a soln. of **3** (2.10 g, 10.00 mmol) in MeOH (200 ml) were each added dropwise and slowly with strong stirring to MeOH (150 ml). After completion of the addition of all the reagents, the mixture was stirred for 24 h. The soln. was concentrated, and a crystalline white solid formed. The precipitate was filtered off and dried: **2a** (85%). Spectroscopic data: see above.

4. *5-Ethoxy-4,5-dihydro-4-methyl-5,6-diphenyl-1,2,4-triazine-3(2*H*)-thione* (**2b**). A soln. of **3** (0.105 g, 0.50 mmol) and conc. HCl soln. (1 drop) in EtOH (6 ml) was added to a soln. of **4a** (0.105 g, 1.00 mmol) in EtOH (6 ml), conc. HCl soln. (2 drops), and 2M HCl (5 ml). The mixture was stirred under reflux for 3 h. After cooling at 5° for 24 h, a white solid was obtained, which was filtered and dried: **2b** (77%). White crystals suitable for X-ray crystallography were formed by slow evaporation of the mother liquor. M.p. 185°. IR (KBr): 3278*s* (NH), 1618*w* (CN), 1511*s* (thioamide II), 885*w* (CS). ^{1}H-NMR ((D$_6$)DMSO): 12.22 (*s*, NH); 7.58–7.21 (*m*, 2 Ph); 2.94 (*s*, MeN); 1.35 (*t*, *J* = 7.0, *Me*CH$_2$O). ^{1}H-NMR (CDCl$_3$): 9.596 (*s*, NH); 7.60–7.08 (*m*, 2 Ph); 3.52 (*q*, *J* = 7.0, MeC*H*$_2$O); 3.07 (*s*, MeN, 3 H); 1.34 (*t*, *J* = 7.0, *Me*CH$_2$O). ^{13}C-NMR ((D$_6$)DMSO): 171.5 (C=S); 141.8 (C=N); 140.0–126.3 (Ph); 86.3 (EtO*C*); 59.4 (Me*C*H$_2$O); 33.3 (MeN); 14.6 (*Me*CH$_2$O). FAB-MS (pos.): 650.5 (10, 2*M*$^+$), 326.2 (100, [*M* + 1]$^+$), 280.2 (8, $C_{16}H_{14}N_3S^+$), 118.1 (4, $C_7H_6N_2^+$), 105.1 (33, [C_7H_6N + 1]$^+$), 77.0 (11, Ph$^+$). Anal. calc. for $C_{18}H_{19}N_3OS$ (325.43): C 66.43, H 5.89, N 12.92, S 9.85; found: C 66.02, H 5.93, N 12.96, S 9.75.

5. *4,5-Dihydro-5-methoxy-4,5,6-triphenyl-1,2,4-triazine-3(2*H*)-thione* (**2c**). The reaction was carried out following the second procedure described for **2a**, but with **4b** (1.05 g, 10.00 mmol): **2c** (95%). M.p. 247°. IR (KBr): 3229*s* (NH), 1612*w* (CN), 1511*s* (thioamide II), 845*w* (CS). ^{1}H-NMR ((D$_6$)DMSO): 12.55 (*s*, NH); 7.57–6.90 (*m*, 13 arom. H); 6.31 (*d*, 2 arom. H); 3.57 (*s*, MeO). ^{1}H-NMR (CDCl$_3$): 9.80 (*s*, NH); 7.65–6.92 (*m*, 13 arom. H); 6.32 (*d*, *J* = 7.9, 2 arom. H); 3.54 (*s*, MeO). ^{13}C-NMR ((D$_6$)DMSO): 172.3 (C=S); 142.6 (C=N); 139.3–126.9 (Ph); 87.5 (MeO*C*); 51.2 (MeO). FAB-MS (pos.): 746.9 (2, 2*M*$^+$), 374.0 (100, [*M* + 1]$^+$), 105.1 (25, [C_7H_6N + 1]$^+$), 77.0 (35, Ph$^+$). Anal. calc. for $C_{22}H_{19}N_3OS$ (373.47): C 70.80, H 5.09, N 11.26, S 8.58, found: C 70.69, H 5.10, N 11.36, S 8.61.

A soln. of **3** (0.105 g, 0.50 mmol) and conc. HCl (2 drops) in MeOH (13 ml) was added to a soln. of **4b** (0.167 g, 1.00 mmol) in MeOH (12 ml), conc. HCl soln. (1 ml), and 2M HCl (10 ml). The mixture was stirred under reflux for 3 h. After cooling to r.t., the precipitate formed was filtered off, washed with MeOH, and dried: **2c**/unknown compound. ^{1}H-NMR ((D$_6$)DMSO): 12.55 (*s*, 1 H, NH); 10.51 (*s*, 0.37 H, NH); 10.38 (*s*, 0.37 H, NH); 9.80 (*s*, 0.8 H, NH); 7.72–6.69 (*m*, 18 H, Ph); 6.32 (*d*, *J* = 7.9, 2 H, Ph); 3.64 (*s*, 3 H, MeO). FAB-MS (pos.): 509.0 (40, [$C_{28}H_{24}N_6S_2$ + 1]$^+$), 374 (100, [$C_{22}H_{19}N_3OS$ + 1]$^+$), 105.1 (25, [C_7H_6N + 1]$^+$), 77.0 (35, Ph$^+$).

A soln. of **3** (2.10 g, 10.00 mmol) and conc. HCl soln. (10 drops) in dry MeOH (75 ml) was added to a soln. of **4b** (1.05 g, 10.00 mmol) in dry MeOH (125 ml) conc. HCl soln. (1 ml). The mixture was stirred at r.t. for 8 h. The white solid formed was filtered off and dried in vacuum: **2c**. White crystals suitable for X-ray crystallography were formed by slow evaporation of the mother liquor. Spectroscopic data: see above.

A soln. of **3** (2.10 g, 10.00 mmol) and conc. HCl soln. (10 drops) in dry MeOH (75 ml) was added to a hot soln. of **4b** (1.05 g, 10 mmol) in dry MeOH (125 ml) and conc. HCl soln. (10 ml). Immediately, a solid was formed. The mixture was heated under reflux for 45 min. The yellow solid (impure **2c**) was filtered off and dried.

A soln. of **3** (0.105 g, 0.50 mmol) in MeOH (5 ml) was added to a soln. of **4b** (0.167 g, 1 mmol) in MeOH (10 ml) and AcOH (5 drops). The mixture was stirred under reflux for 8 h and then concentrated until a solid formed: **2c** (1%). The reagent **4b** was recovered from the filtrate.

6. *Benzil Bis(4-phenylthiosemicarbazone)* (*=2,2′-(1,2-Diphenylethane-1,2-diylidene)bis[*N*-phenylhydrazinecarbothioamide]*; **1b**) *and 5-Ethoxy-4,5-dihydro-5,6-triphenyl-1,2,4-triazine-3(2*H*)-thione* (**2d**). A soln. of **3** (0.105 g, 0.5 mmol) and conc. HCl soln. (1 drop) in EtOH (20 ml) was added to a soln. of **4b** (0.161 g, 1 mmol) in EtOH (30 ml), conc. HCl soln. (2 drops), and 2M HCl (5 ml). The mixture was stirred under reflux for 3 h. After cooling to r.t., yellowish white solid **1b** was obtained (5%), which was filtered off and dried. From the filtrate white solid **2d** was isolated.

Data of **1b**: M.p. 223°. IR (KBr): 3340*s*, 3266*s* (NH), 1616*w* (CN), 1593*s* (thioamide II), 871*w* (thioamide IV). ^{1}H-NMR ((D$_6$)DMSO): 10.52 (*s*, 2 NH); 10.40 (*s*, 2 NH); 7.87 (*m*, 4 arom. H); 7.72–7.20 (*m*, 16 arom. H). ^{13}C-NMR ((D$_6$)DMSO): 171.3 (C=S); 141.6 (C=N); 139.0–125.7 (Ph). FAB-MS

(pos.): 509.3 (5, $[M+1]^+$), 388.2 (45, $C_{18}H_{21}N_3S^+$). MALDI-TOF-MS: 509.1 (2100 a.i., $[M+1]^+$), 388.1 (1700 a.i., $C_{18}H_{21}N_3S^+$). Anal. calc. for $C_{28}H_{24}N_6S_2$ (509.04): C 66.14, H 4.72, N 16.53, S 12.59; found: C 66.11, H 4.90, N 16.35, S 12.38.

Data of **2d**: M.p. 205°. IR (KBr): 3162*s* (NH), 1594*w* (CN), 1505*s* (thioamide II), 812*w* (CS). ^{1}H-NMR ((D$_6$)DMSO): 12.53 (*s*, NH); 7.58–6.30 (*m*, 3 Ph); 3.48 (*q*, $J=7.0$, MeCH_2O); 1.39 (*t*, $J=7.0$, *Me*CH_2O). ^{13}C-NMR ((D$_6$)DMSO): 172.5 (C=S); 143.3 (C=N); 139.6–126.6 (Ph); 86.9 (EtO*C*); 59.34 (MeCH_2O); 14.6 (*Me*CH_2O). FAB-MS (pos.): 775.1 (5, $[2M+1]^+$), 388.0 (100, $[M+1]^+$), 105.0 (40, $[C_7H_6N+1]^+$) 77.0 (21, Ph^+). Anal. calc. for $C_{23}H_{21}N_3OS$ (387.50): C 71.03, H 5.40, N 10.80, S 8.30; found: C 70.72, H 5.30, N 10.90, S 8.31.

A soln. of **3** (0.105 g, 0.5 mmol) and conc. HCl soln. (1 drop), in abs. EtOH (30 ml) was added to a soln. of **4b** (0.161 g, 1.0 mmol) in abs. EtOH (20 ml) and conc. HCl soln. (2 drops). The mixture was stirred at r.t. for 3 h, then the yellowish solid formed was filtered and dried: **1b** (10%). From the filtrate, a white solid was isolated: **2d**. Spectroscopic data: see above.

A soln. of **4b** (1.67 g, 10.00 mml) in EtOH/2M HCl 1:1 (80 ml) and conc. HCl soln. (1 ml), and a soln. of **3** (2.10 g, 10.00 mmol) in EtOH (200 ml) were added alternatively dropwise and slowly with strong stirring to EtOH (150 ml). After completion of the addition of all the reagents, the mixture was stirred for 4 days. The soln. was concentrated, and the crystalline white solid was filtered off and dried: **2d** (82%). Crystals suitable for X-ray studies were grown by keeping the concentrated mother liquor int the fridge.

7. *4,5-Dihydro-5-hydroxy-4,5,6-triphenyl-1,2,4-triazine-3(2*H*)-thione* (**2e**). A soln. of **3** (0.210 g, 1.00 mmol) in EtOH (20 ml) was added to a soln. of **4b** (0.322 g, 2.00 mmol) in EtOH (20 ml). The mixture was stirred under reflux for 3 h. Then the white solid formed was filtered and dried: **2e** (40%). Crystals suitable for X-ray diffraction studies were formed by slow evaporation of a DMSO soln. M.p. 193°. IR (KBr): 3230*s* (NH), 1615*w* (CN), 1498*s* (thioamide II), 872*w* (CS). ^{1}H-NMR ((D$_6$)DMSO): 8.43 (*s*, NH); 7.61–6.89 (*m*, 3 Ph); 6.09 (*d*, $J=8.0$, OH). ^{13}C-NMR ((D$_6$)DMSO): 170.9 (C=S); 146.4 (C=N); 141.1–126.6 (Ph); 82.3 (OH–*C*). FAB-MS (pos.): 719.0 (5, $[2M+1]^+$), 360.0 (35, $[M+1]^+$). Anal. calc. for $C_{21}H_{17}N_3OS$ (359.44): C 70.19, H 4.73, N 11.69, S 8.91; found: C 69.96, H 4.79, N 11.69, S 8.88.

8. *Crystal-Structure Determinations.* Crystallographic data of compounds are summarized in the *Table*. Crystals of compounds were mounted on a glass fiber and transferred to a *Bruker SMART-6K-CCD* area-detector three-circle diffractometer with a rotating anode (CuK_α radiation, λ 1.54178 Å) generator from *MAC Science Co., Ltd.*, equipped with *Goebel* mirrors at settings of 45 kV and 110 mA. X-Ray data were collected at 100 K, with a combination of six runs at different φ and 2θ angles, 3600 frames. The data were collected by using 0.3° wide ω scans with a crystal-to-detector distance of 4.0 cm. The substantial redundancy in data allowed empirical absorption corrections (SADABS) [13] to be applied by using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.560366 for **1a**, 0.769374 for **2a**, 0.607923 for **2b**, 0.824277 for **2c**, 0.616163 for **2d**, and 0.490640 for **2e**. The unit cell parameters were obtained by full-matrix least-squares refinements of 4228 reflections for **1a**, 7400 for **2a**, 5854 for **2b**, 3955 for **2c**, 5195 for **2d**, and 5701 for **2e**. The raw intensity data frames were integrated with the SAINT [14] program, which also applied corrections for *Lorentz* and polarization effects. The software package SHELXTL [15] version 6.10 was used for space-group determination, structure solution, and refinement. The space-group determination was based on a check of the *Laue* symmetry and systematic absences and was confirmed by using the structure solution. The structure was solved by direct methods (SHELXS-90) [16], completed with difference *Fourier* syntheses, and refined with full-matrix least squares by using SHELXL-97 [17] minimizing $\omega(F_o^2-F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2; conventional R factors (R) are based on F. All non-H-atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library. The high quality of the data set allowed that all H-atoms were located by difference maps and refined isotropically in all compounds, except for some H-atoms of **1a** and **2e**.

Supplementary crystallographic data have been deposited as CCDC-624595 for **2b**, -624596 for **1a**, -624597 for **2a**, -624598 for **2d**, -624599 for **2e**·DMSO, and -624600 for **2c** with the *Cambridge*

Table. *Crystal Data and Structure Refinement for Compounds* **1a** *and* **2a**–**e**

		1a	**2a**	**2b**	**2c**	**2d**	**2e** · DMSO
Formula		$C_{18}H_{20}N_6S_2$	$C_{17}H_{17}N_3OS$	$C_{18}H_{19}N_3OS$	$C_{22}H_{19}N_3OS$	$C_{23}H_{21}N_3OS$	$C_{23}H_{23}N_3S_2O_2$
M_r		384.52	311.40	325.42	373.46	387.49	437.58
Crystal system		monoclinic	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
Space group		*C*2/*c*	$P2_1/c$	$P2_12_12_1$	*P*-1	*P*-1	*Pc*
Cell dimensions:	*a* [Å]	27.8876(11)	8.7829(3)	8.61800(10)	6.7781(2)	8.54120(10)	5.9258(2)
	b [Å]	10.9794(4)	14.4974(6)	12.82350(10)	11.3880(3)	10.71760(10)	11.6604(4)
	c [Å]	19.8996(7)	12.6161(4)	15.46510(10)	13.1330(3)	11.88610(10)	31.3453(10)
	α [°]	90	90	90	86.842(2)	88.3350(10)	90
	β [°]	129.648(2)	102.9000(10)	90	75.471(2)	71.2360(10)	98.010(2)
	γ [°]	90	90	90	74.549(2)	70.5870(10)	90
	V [Å^3]	4691(3)	1565.85(10)	8871.7(2)	945.76(4)	967.967(17)	2144.74(12)
Z		8	4	4	2	2	4
D_c [Mg m^{-3}]		1.089	1.321	1.265	1.311	1.329	1.355
Absorption coefficient [mm^{-1}]		2.150	1.873	1.737	1.646	1.627	2.452
Goodness of fit on F^2		1.084	1.032	1.035	1.044	1.062	1.005
Reflections collected		16309	14601	9472	5890	9980	12397
Independent reflections		4449 (R(int) = 0.0661)	2915 (R(int) = 0.0281)	3125 (R(int) = 0.0267)	3047 (R(int) = 0.0181)	3491 (R(int) = 0.0219)	6757 (R(int) = 0.0391)
Final $R^1$and wR^2($I > 2\sigma(I)$)		0.0691, 0.1711	0.0327, 0.0860	0.0332, 0.0874	0.0343, 0.0911	0.0351, 0.0920	0.0384, 0.0916
R indices (all data)		0.0860, 0.1796	0.0353, 0.0885	0.0340, 0.0881	0.0382, 0.0945	0.0382, 0.0948	0.0435, 0.0946
Largest diff. peak and hole [e · A^{-3}]		0.619 and −0.345	0.325 and −0.175	0.181 and −0.157	0.249 and −0.187	0.293 and −0.254	0.361 and −0.226

Crystallographic Data Centre. These data can be obtained free of charge *via* www.ccdc.cam.ad.uk/data_request/cif.

REFERENCES

[1] D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, R. G. Yeranda, *Coord. Chem. Rev.* **1993**, *123*, 49 and refs. cit. therein; A. E. Liberta, D. X. West, *Biometals* **1992**, *5*, 121; D. X. West, S. B. Padhye, P. B. Sonawane, *Struct. Bonding* **1991**, *76*, 1; 'International Encyclopedia of Pharmacology and Therapeutics', Eds. J. G. Cory and A. H. Cory, Pergamon Press, New York, 1989; R. Pedrido, M. R. Bermejo, M. J. Romero, M. Vázquez, A. M. González-Noya, M. Maneiro, M. J. Rodríguez, M. I. Fernández, *Dalton Trans.* **2005**, 572; I. H. Hall, K. G. Rajendran, D. X. West, A. E. Liberta, *Anticancer Drugs* **1993**, *4*, 231; M. Belicchi-Ferrari, F. Bisceglie, C. Casoli, S. Durot, I. Morgenstern-Baradau, G. Pelosi, E. Piloti, S. Pinelli, P. Tarasconi, *Med. Chem*. **2005**, *48*, 1671; H. Beraldo, D. Cambino, *Mini-Rev. Med. Chem.* **2004**, *4*, 31; A. G. Quiroga, C. N. Ranninger, *Coord. Chem. Rev.* **2004**, *248*, 119; N. C. Kasuga, K. Onodera, S. Nakano, K. Hayashi, K. Nomiya, *J. Inorg. Biochem*. **2006**, *100*, 1176.

[2] A. R. Cowley, J. Davis, J. R. Dilworth, P. S. Donnelly, R. Dobson, A. Mightingale, J. M. Peach, B. Shore, D. Ker, L. Seymour, *Chem Commun*. **2005**, *7*, 845; J. P. Holland, J. C. Green, J. R. Dilworth, *Dalton Trans.* **2006**, 783; A. R. Cowley, J. R. Dilworth, P. S. Donnelly, J. M. White, *Inorg. Chem*. **2006**, *45*, 496.

[3] M. M. Reinoso García, W. Verboom, D. N. Reinhoudt, E. Malinowska, M. Pietrzak, D. Wojciechowska, *Tetrahedron* **2004**, *60*, 11299; G. E. Tumambac, M. Rosencrance, C. Wolf, *Tetrahedron* **2004**, *60*, 11293; S.-M. Cheung, W.-H. Chan, *Tetrahedron* **2006**, *62*, 8379.

[4] a) L. Alsop, A. R. Cowley, J. R. Dilworth, P. S. Donnelly, J. M. Peach, J. T. Rider, *Inorg. Chim. Acta* **2005**, *358*, 2770; b) M. Christlieb, J. R. Dilworth, *Chem.–Eur. J.* **2006**, *12*, 6194; c) M. Christlieb, H. J. Claughton, A. R. Cowley, J. M. Heslop, J. R. Dilworth, *Transition Met. Chem.* **2006**, *31*, 88.

[5] a) P. Souza, M. A. Mendiola, A. Arquero, V. Fernández, E. Gutiérrez-Puebla, C. Ruíz-Valero, *Z. Naturforsch, B* **1994**, *49*, 263; b) A. Arquero, M. Cañadas, M. Martinez-Ripoll, M. A. Mendiola, A. Rodriguez, *Tetrahedron* **1998**, *54*, 11271; c) M. A. Blanco, E. López-Torres, M. A. Mendiola, E. Brunet, M. T. Sevilla, *Tetrahedron* **2002**, *58*, 1525; d) E. López-Torres, M. A. Mendiola, C. J. Pastor, B. Souto Pérez, *Inorg. Chem*. **2004**, *43*, 5222 and refs. cit. therein; e) E. López-Torres, M. A. Mendiola, C. J. Pastor, *Inorg. Chem.* **2006**, *45*, 3103 and refs. cit. therein; f) E. López-Torres, M. A. Mendiola, C. J. Pastor, *Polyhedron* **2006**, *25*, 1464.

[6] M. J. Gismera, M. A. Mendiola, J. Rodríguez-Procopio, M. T. Sevilla, *Anal. Chim. Acta* **1999**, *385*, 143; J. Ruipérez, M. A. Mendiola, M. T. Sevilla, J. Rodríguez-Procopio, L. Hernández, *Electroanalysis* **2002**, *14*, 532; M. Colilla, M. A. Mendiola, J. R. Procopio, M. T. Sevilla, *Electroanalysis* **2005**, *17*, 933; F. Zani, D. G. Calatayud, E. López-Torres, M. A. Mendiola, J. R. Procopio, 'EUROBIC 8 Conference book', ISBN 989-20-0305-5, Aveiro, Portugal, 2006, p. 153.

[7] E. Franco, E. López-Torres, M. A. Mendiola, M. T. Sevilla, *Polyhedron* **2000**, *19*, 441.

[8] E. Bermejo, A. Castiñeiras, D. X. West, *J. Mol. Struct*. **2003**, *650*, 93.

[9] A. Castiñeiras, E. Bermejo, D. X. West, *J. Mol. Struct*. **1999**, *478*, 73.

[10] A. L. Spek, PLATON, The University of Utrecht, Utrecht, 2004.

[11] E. Bermejo, A. Castiñeiras, R. Dominguez, R. Carballo, C. Maiche-Mössmer, J. Strähle, D. X. West, *Z. Anorg. Allg. Chem*. **1999**, *625*, 961.

[12] E. Sutton, 'Tables of Interatomic Distances and Configuration in Molecules and Ions (Suplement)', The Chemical Society, London, 1965.

[13] G. M. Sheldrick, SADABS version 2.03, Program for Empirical Absorption Corrections, Universität Göttingen, Göttingen, 1997–2001.

[14] G. M. Sheldrick, SAINT+NT (version 6.04) SAX, Area-Detector Integration Program, *Bruker AXS*, Madison, WI, 1997–2001.

[15] *Bruker AXS* SHELXTL (version 6.10), Structure Determination Package, *Bruker AXS*, Madison, WI, 2000.

[16] G. M. Sheldrick, SHELXS-90, Program for Structure Solution: Direct Methods, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
[17] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Göttingen, 1997.

Received May 30, 2007