Dithiocarbamates, Thiocarbamic Esters, Dithiocarboimidates, Guanidines, Thioureas, Isothioureas, and Tetraazathiapentalene Derived from 2-Aminobenzothiazole

Fabiola Téllez,[a] Alejandro Cruz,[b] Horacio López-Sandoval,[a] Iris Ramos-García,[a] Martha Gayosso,[a] R. Nely Castillo-Sierra,[b] Brenda Paz-Michel,[a] Heinrich Nöth,[c] Angelina Flores-Parra,[a] and Rosalinda Contreras*[a]

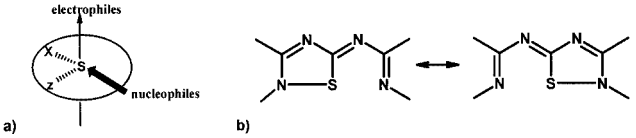
Keywords: 2-Aminobenzothiazole / Dibenzothiazolyltetraazathiapentalene / Electrophilic and nucleophilic sulfur atoms

Reactions between CS_2 and the exocyclic amino groups of 2-aminobenzothiazoles gave series of molecules bearing thiourea, isothiourea, dithiocarbamate, dithiocarboimine, dimethyldithiocarbamate, methyldithiocarbamate, *S*-CH_3 and *O*-alkyl thiocarbamic ester, and guanidine groups. Preferred tautomers and conformers were determined. Most compounds present coordinative bonds between the endocyclic sulfur atom, which behaves as a Lewis acid, and oxygen, nitrogen, and sulfur acting as bases. A new dibenzothiazolyltetraazathiapentalene containing a T-shaped hypervalent sulfur atom and displaying "single bond-no bond resonance" is discussed. X-ray structures of eleven compounds are reported.

Introduction

We are currently investigating the structures of biologically active, aromatic nitrogenated heterocycles[1−4] with free lone pairs, labile hydrogen atoms, and planar delocalized acyclic groups. Here we report the preparation and a structural study of a series of compounds, including fourteen new ones, derived from 2-aminobenzothiazole (**1**) and 5,7-di-*tert*-butyl-2-aminobenzothiazole (**1a**). The studied compounds have functional groups such as guanidine, thiourea, isothiourea, dithiocarbamate, dithiocarboimine, dimethyl dithiocarbamate, methyldithiocarbamate, and *S*-methyl and *O*-alkyl thiocarbamic esters. The new compounds have very reactive functional groups that can be used for the synthesis of more complex molecules, together with rigid frameworks with several lone pairs available for coordination, and so are potentially interesting ligands for metallic compounds. X-ray diffraction structures of eleven compounds are analyzed.

The relevance of the studied molecules lies in their "Y-type" aromatic conjugation,[5] in their biological activity,[6−9] and in their use as building units in supramolecular structures or in materials science. The investigated compounds can be described by many different conformers and tautomers, and these complex systems merit careful analysis in order to understand the structural implications of weak interactions such as hydrogen bonds and Lewis acid/base contacts giving ordered and rigid structures.[10,11] In particular, we are interested in studying weak interactions at sulfur atoms, which can have significant influence, not always recognized, in the preferred conformers and in the structures of molecular conglomerates. The sulfur atoms present coordinating contacts with lone pair-donating atoms, with atomic distances of less than 3.70 Å (for S···S; 3.25 Å for S···O, and 3.35 Å for S···N).[12−14] The divalent sulfur in these contacts may act either as a donor on an axis perpendicular to the plane of the X−S−Z sulfur bonds or as a Lewis acid following the axis of one of the two X−S or S−Z bonds (Scheme 1, a). S···S interactions in particular can be regarded as acceptor-donor pairs,[14,15] while S···O interactions have biological relevance.[12,16−18]



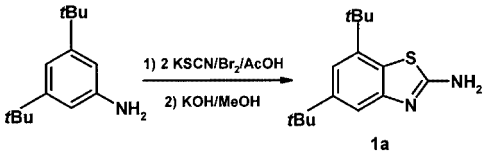
Scheme 1

[a] Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN,
A. P. 14-740, CP 07000, D. F., México
[b] Departamento de Química, Unidad Profesional Interdisciplinaria de Biotecnología del IPN,
Av. Acueducto de Guadalupe, s/n Col. Barrio la Laguna, Ticomán, D.F. México
[c] Department de Chemie, Ludwig-Maximilians Universität,
Butenandt-Straße 5−13 (Haus D), 81377 München, Germany

This report describes a new and original hexacyclic pentalene bearing a hypervalent sulfur atom, analogous bicyclic and tetracyclic structures being very scarce.[19] Sulfur atoms in such compounds are tricoordinate with T-shape geometries and are bonded to one carbon and two nitrogen atoms,[20] presenting N−S−N linear arrangements with bond orders of less than one[21] and delocalized systems with single bond-no bond resonance (Scheme 1, b). The scarcity of NMR spectroscopic data for such compounds is due to their low solubilities.[23−25] The metallic character of the sulfur in tetraazathiapentalenes is evidenced by its substitution by palladium and platinum, giving metallic compounds which acquire square planar geometry.[22]

Results and Discussion

Insertion of CS_2 at the exocyclic nitrogen atoms of 2-aminobenzothiazole (**1**) and 3,5-di-*tert*-butyl-2-aminobenzothiazole (**1a**) in the presence of a base was used for the preparation of a series of compounds. Compound **1** is commercially available, whereas **1a** was obtained from 2,5-di-*tert*-butylaniline, KSCN, and Br_2 in acetic acid (Scheme 2).



Scheme 2

Treatment of these compounds with CS_2 in the presence of a base (Scheme 3) afforded *N*-(benzothiazolyl)dithiocarboimidates **2** and *N*-(benzothiazolyl)dithiocarbamates **3**, intermediates for compounds **4** and **5**, which are starting materials for more complex molecules through substitution of their thiomethyl groups.

Compounds **2-Na** and **3-Na** have been reported without characterization.[26] The synthetic interest of compounds **2** and **3** stimulated us to analyze their structures by NMR (**2-Na**, **2-K**, **3-Na**, **3-Li**) and X-ray diffraction (**2-Na** and **3-Li**). The preparation of **2** and **3** depends on the reaction

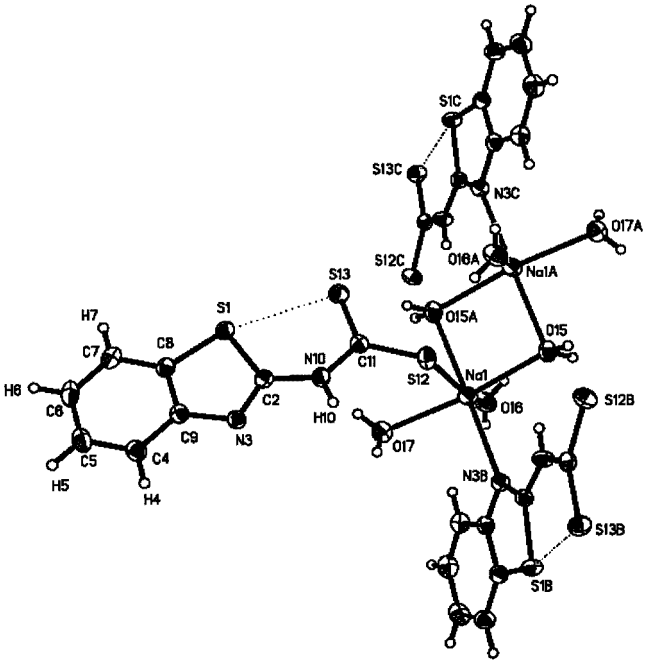
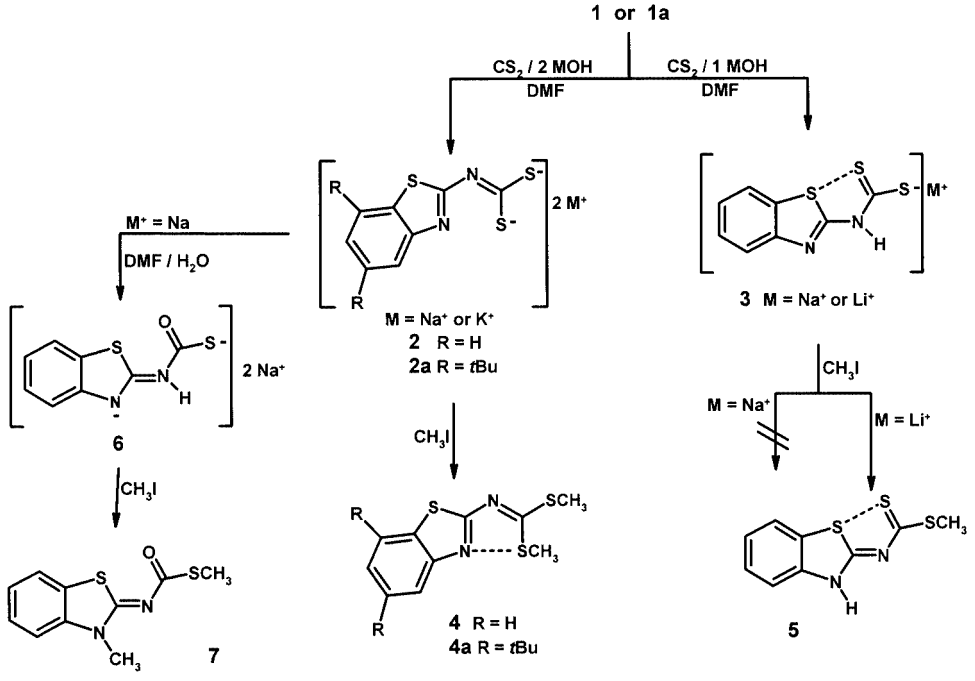


Figure 1. Molecular structure of compound **3-Na**



Scheme 3

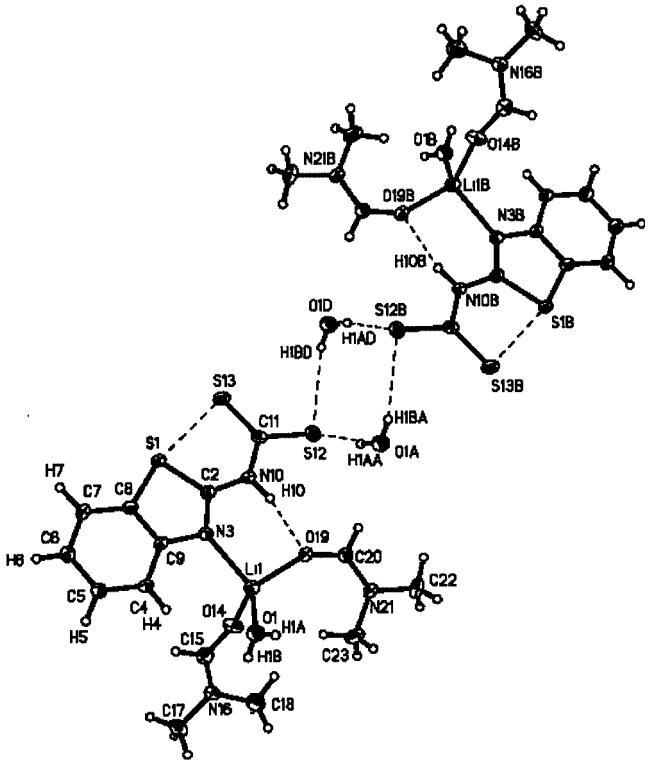


Figure 2. Molecular structure of compound **3-Li**

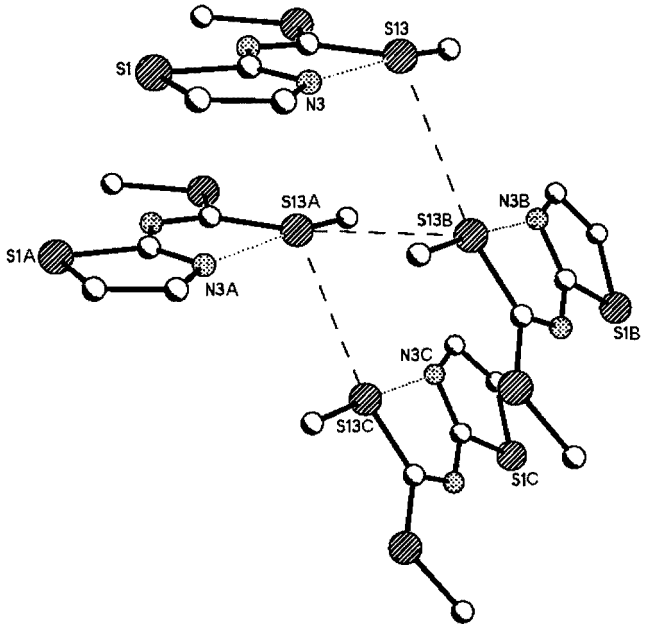


Figure 3. Molecular structure of compound **4**; intra- and intermolecular interactions are shown

stoichiometry and on the nature of the base. Treatment of **1** with two equivalents of NaOH and CS_2 and subsequent addition of $CHCl_3$ gave a yellow precipitate, its ^1H and ^{13}C NMR spectra indicating a mixture (60:40) of the two sodium compounds **2-Na** and **3-Na**. The two products can be distinguished by their ^{13}C data [C11 appears at δ = 193 ppm in **2-Na**, but at δ = 213.7 ppm in **3-Na**]. The **2-Na/3-Na** mixture was crystallized from ethanol/water (50:50), and the obtained crystals (**3-Na**) were analyzed by X-ray diffraction (Figure 1).

Condensation reactions performed with LiOH and with KOH selectively afforded dithiocarboimidate **3-Li** and dithiocarbamate **2-K**, respectively (Scheme 3 and Figure 2).

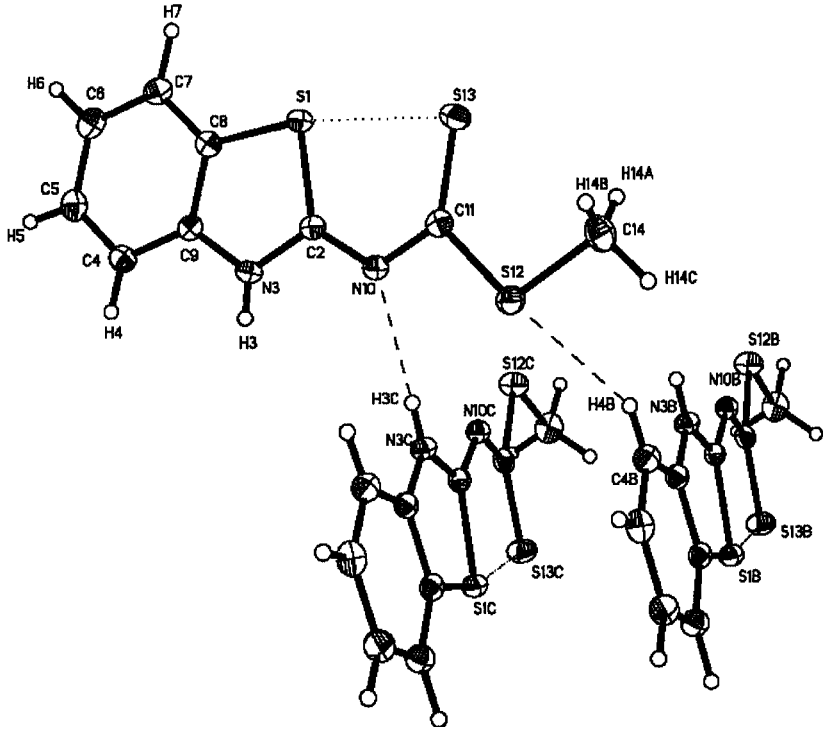
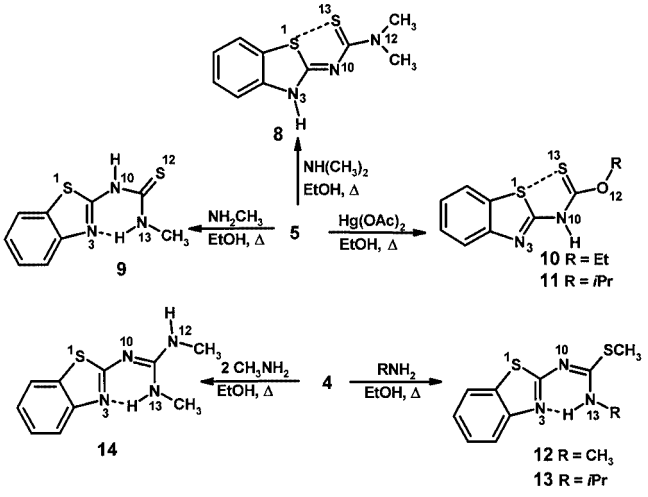


Figure 4. Molecular structure of compound **5**; intra- and intermolecular interactions are shown

Anions **2** and **3** reacted differently in methylation reactions to give compounds **4** and **5**, respectively,[26] and these are useful precursors for functionalized heterocycles.[27−36] Compound **2-K** selectively afforded dimethyl compounds **4** and **4a**, whereas the S-methyl ester **5** could be prepared in high yield by methylation of compound **3-Li** (Scheme 3). Use of the **2-Na/3-Na** mixture gave a mixture of **4** and **5**, from which **4** could be separated by recrystallization from methanol. In the literature the characterization of **4** and **5** was only supported by ^{1}H NMR and mass spectra.[26] Compounds **4** and **5** were crystallized from methanol and ethanol, respectively; both are planar with U-shaped arms (Figures 3 and 4). It is interesting that the thione group in **3** or **5** prefers to be *cis* to the endocyclic C−S bond, whereas in compounds **2** and **4** the endocyclic imine bond is *cis* to the exocyclic C−S bond. On treatment of **2-Na** with CH_3I a second compound **7** was isolated from the mother liquors, and was crystallized from CH_3OH. It is assumed that **7** arises from methylation of the hydrolyzed disodium salt **6** (Scheme 3). The solid-state structure is shown in Figure 5.

A demonstration of the synthetic use of compound **5** can be seen in the preparation of thioureas **8** and **9**, in its reactions with the corresponding amines, and in the synthesis of thiocarbamic esters **10** and **11** in the presence of the corresponding alcohols and mercuric acetate as a catalyst. On the other hand, isothioureas **12** and **13** and guanidine **14** can be prepared by treatment of compound **4** with the corresponding amines in ethanol at reflux (Scheme 4).



Scheme 4

Compounds **9** and **12**−**14** have U conformations with N3 and N13 in *cis* arrangements stabilized by N13−H13···N3 hydrogen bonds, as deduced from their high-frequency ^{1}H NMR signals [**12**, δ = 10.64; **13**, 10.70; **14**, 9.6 ppm]. Compound **9** has two N−H resonances at δ = 9.83 and 12.04 ppm, the first (H13) a quadruplet because of coupling to the NCH_3 group. In their ^{13}C NMR spectra, compounds **8**−**11** ([D_6]DMSO) and **12**−**14** ($CDCl_3$) present broad signals for C2, C8, C9, and C11, due to the dynamic behavior of the arms. The ^{1}H NMR spectra of compounds **8**, **10**, and **11** show broad signals above δ = 10 ppm for N−H [**8**, δ = 10.86; **10**, 13.43; **11**, 13.34 ppm] indicating strong intermolecular bonds. The solid-state structures for com-

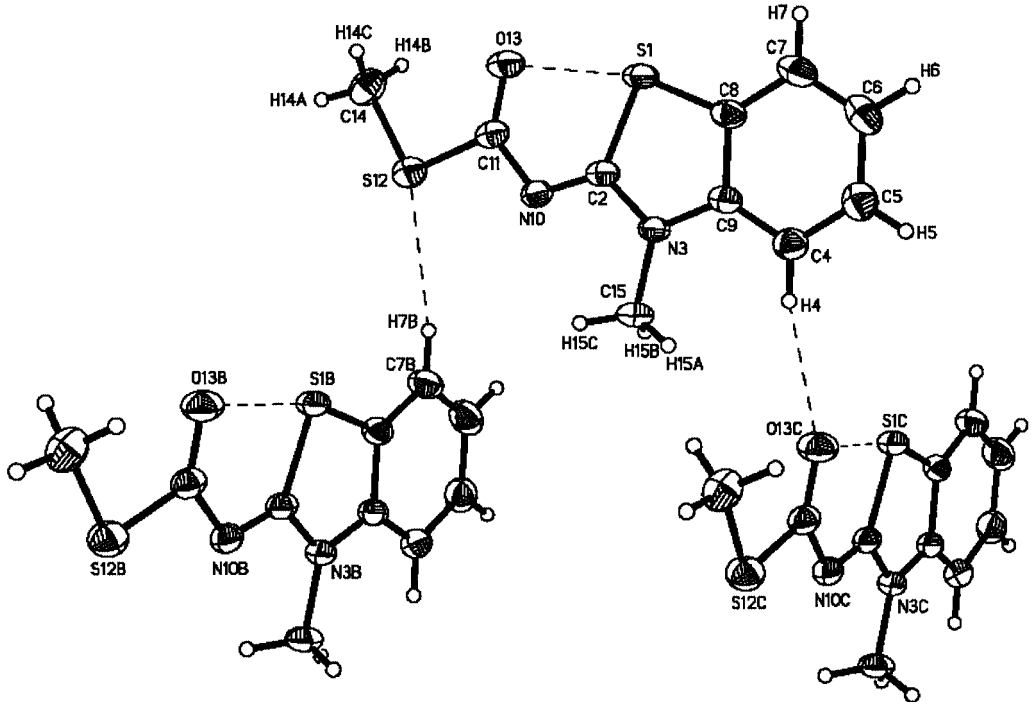


Figure 5. Molecular structure of compound **7** showing intra- and intermolecular interactions

pounds **7**−**11** and **13** were determined (Figures 6, 7, 8. and Figure 9).

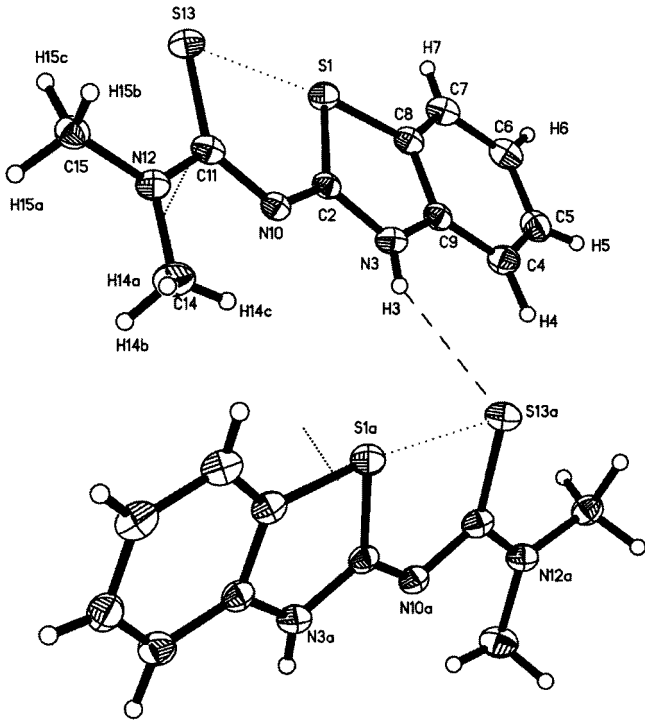


Figure 6. Molecular structure of compound **8** and intra- and intermolecular hydrogen bonds

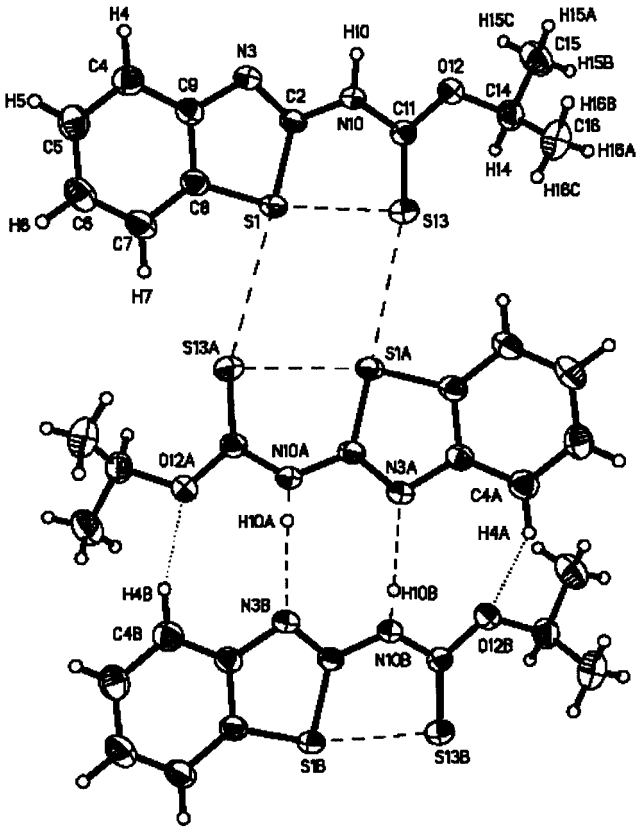


Figure 8. Molecular structure of compound **11** showing intra- and intermolecular interactions

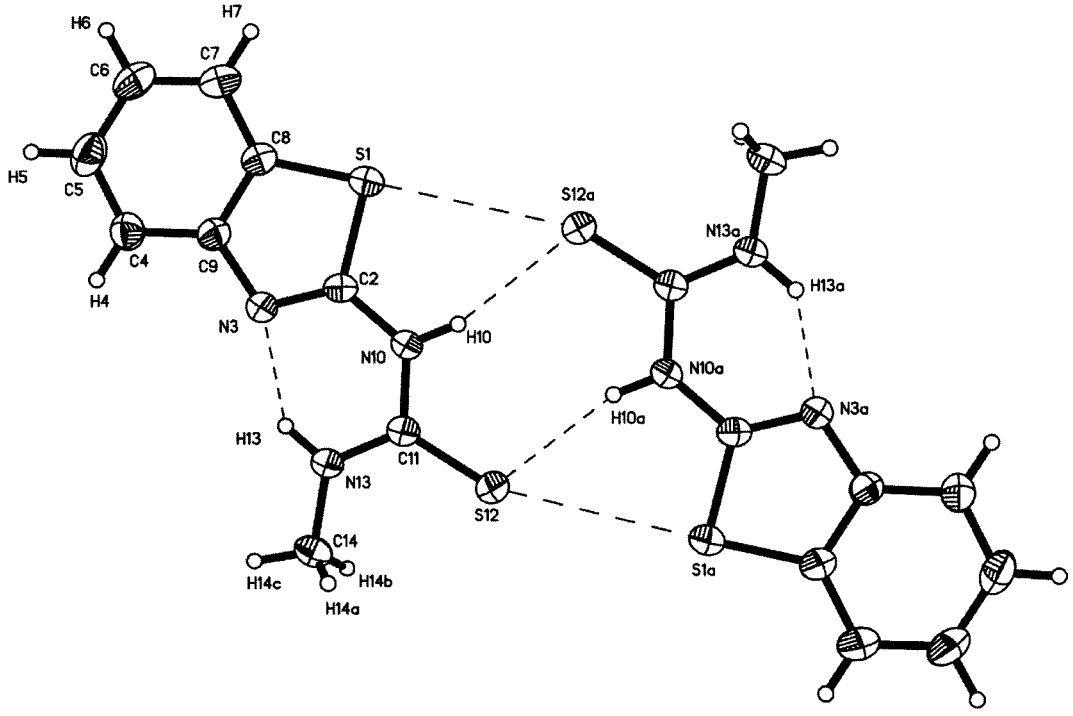


Figure 7. Molecular structure of compound **9** and intra- and intermolecular interactions

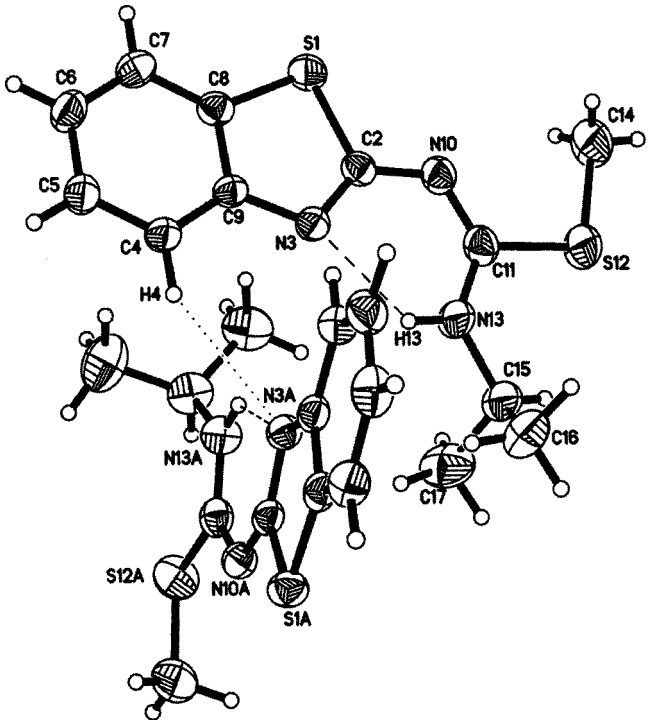


Figure 9. Molecular structure of compound **13**

Treatment of compound **1** with **5** gave *N*,*N*′-bis(benzothiazol-2-yl)thiourea (**15**; Scheme 5). Compound **15** can be represented by five tautomers each having one or two intramolecular hydrogen bonds in a planar rearrangement. At the same time, each tautomer of **15** may have several conformers; six conformers can be written for the tautomer represented in Scheme 5, for example. In spite of this, compound **15** seems to exist in a preferred conformation.

Compound **15** is not very soluble in [D_6]DMSO, so its ^{13}C spectrum was recorded at 120°; the two benzothiazole rings appear equivalent in the NMR spectra, and C11 and C2 have resonances at higher frequencies (δ = 182.2 and 163.8 ppm, respectively). It can be deduced that the hydrogen atom is at N10, since the chemical shift of C9 at δ = 143.8 ppm indicates that N3 is unprotonated.[35] On the other hand, the high-frequency N−H signal (δ = 12.57 ppm) shows that it is involved in a strong intermolecular hydrogen bond. In the solid state, the IR does not show S−H bands, while a strong band for C=S was found at 1250 cm^{-1}. The band for N−H is characteristic of a hydrogen bond ($\tilde{\nu}$ = 3265, sharp). A conjecture for the structure can be deduced from the solid-state structures of compounds **5**, **8**, **10**, and **11**, which each have a C=S double bond *cis* to the endocyclic C−S bond. The proposed conformation is also supported by the fact that the more stable isomer for thiathiophthenes has the three sulfur atoms interacting in a linear rearrangement.[36]

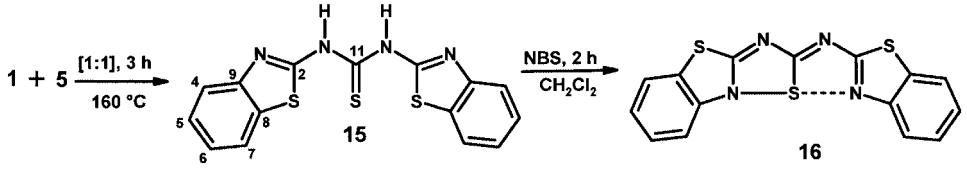
Deprotonation of **15** was performed with NaH in THF (**15**-Na) and its NMR spectra were determined at 80 °C, due to its better solubility at this temperature. The ^{13}C signals were shifted to lower frequencies (C9 at δ = 151.0, C2 at 171.8, and C11 at 188.4 ppm) as would be expected for the increase in ring electronic density due to the dianion's two extra free lone pairs.[35] The IR band for N−H disappeared.

Oxidation of **15** with *N*-bromosuccinimide afforded the crystalline tetraazathiapentalene **16** (Scheme 5). The ^{1}H spectrum of **16** (in DMSO) does not show the N-H signal. In the ^{13}C spectrum at room temperature only seven signals are observed; C11 is not detected, but at 120 °C the signal emerges at δ = 187.4 ppm. The equivalence of the ^{1}H signals of the two 2-aminobenzothiazole fragments shows that a delocalized system with "single bond-no bond resonance" is present in solution (Scheme 1).

The fact that the molecular peak (340) for **16** is the parent peak in its mass spectrum indicates that it is very stable. According to its crystalline structure (Figure 10) it can be viewed as a tetraazathiapentalene. It has a T-shaped π-hypervalent tricoordinate sulfur atom (10-S-3), connected in a linear arrangement with two nitrogen atoms.[5]

Treatment of compounds **4** (or **4a**) with two equivalents of **1** (or **1a**) gave the *N*,*N*′,*N*′′-tris(benzothiazol-2-yl)guanidines **17** (or **17a**). Treatment of **4** with two equivalents of **1a** gave the mixed compound **17b** (Scheme 6). Compound **17** is only partially soluble in DMSO at room temp., so NMR spectra were obtained at 120 °C, at which only one type of benzothiazole fragment was detected. The N-H gives a broad band at δ = 12.9 ppm. The ^{13}C spectrum also presents broad signals, indicating a dynamic equilibrium between three planar and delocalized tautomers through the of the two N-H moieties between the three endocyclic nitrogen atoms and between their conformers a or b. Conformer a could be more stable due to a stabilizing N···S interaction instead of N···N repulsions.

The more soluble compound **17a** was analyzed by NMR in $CDCl_3$ by some vt experiments. At −60 °C the ^{13}C spectrum showed 22 signals in the aromatic region for three different benzothiazole moieties. The resonances for the benzothiazol-2-ylidene fragment were assigned by comparison with **4a**, while the two other fragments showed fairly



Scheme 5

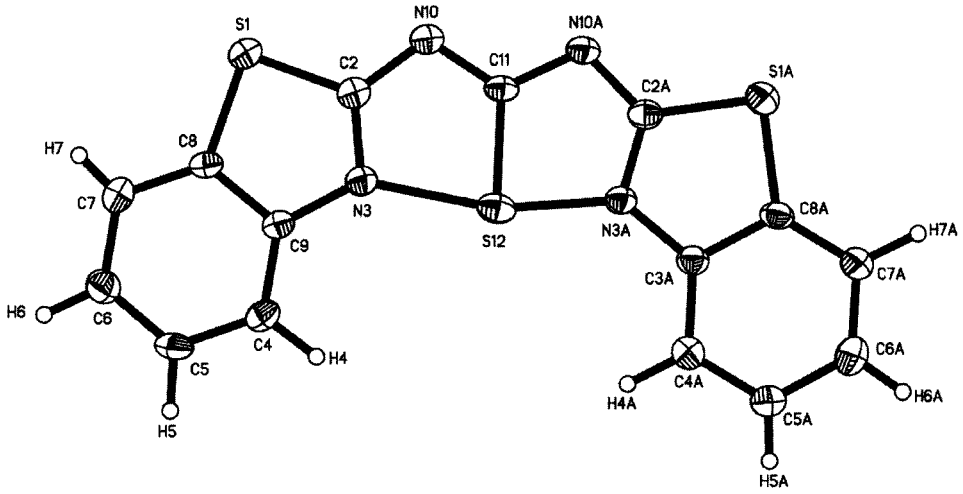
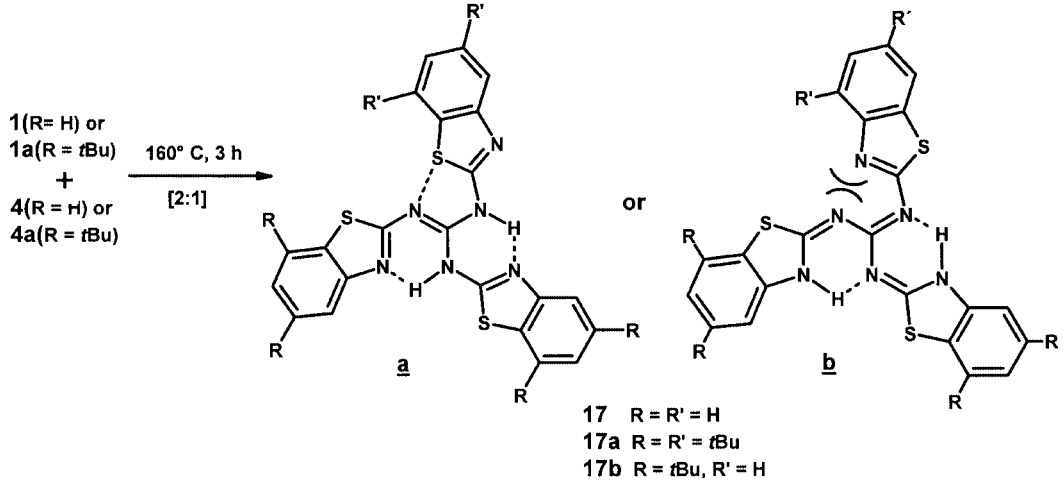


Figure 10. Molecular structure of compound **16**



Scheme 6

similar signals that were not completely assigned. It is deduced that, at this temperature, tautomer a with a preferred conformation is frozen; effectively two different N−H components were detected at δ = 13.37 and 14.08 ppm.

X-ray Analyses

Compound **3-Na** has a polymeric arrangement (Figure 1) with only one sodium atom per dithiocarbamate molecule. Each sodium is bonded to two dithiocarbamate molecules and each dithiocarbamate is bonded to two sodium atoms; one is coordinated by the thione group and the other by the N3 atom of the benzothiazole ring. The sodium atom is hexacoordinate with a distorted octahedral geometry. Each sodium atom is linked to four water molecules, two of them bridging two sodium atoms in a four-membered ring with a Na···Na distance of 3.623(2) Å.[37−39] The distance between sulfur atoms C8−S1···S13 is 3.022 Å, and the angle is 165.53°.

Compound **3-Li** was crystallized from a DMF/$CHCl_3$ mixture (50:50). The structure shows a distorted tetrahedral geometry for the lithium atom, which is bonded through the benzothiazole nitrogen, as observed in similar heterocycles,[40−43] and to the carbonyl groups of two *N*,*N*-dimethylformamide molecules; a fourth coordination is provided by a water molecule, which forms an intermolecular hydrogen bond with one sulfur atom from another molecule (Figure 2). The lithium does not interact with the sulfur atoms, contrary to what has been observed in analogous systems.[44−46] The two formamide and two water molecules determine the intra- and intermolecular interactions in the cell. An intramolecular hydrogen bond is found for O19−HN10 [2.01 Å, 166.1°]. The S1−C2−N10−C11−S13 fragment adopts a U-conformation allowing a short sulfur···sulfur contact, with the S1···S13 distance 2.975 Å (Σr_{vdW} 3.70 Å) and the C8−S1···S13 angle 166.83°. The bond length difference between C11−S13 [1.660(4) Å] and C11−S12 [1.720(3) Å] is due to coordination of S12 with two water molecules.

Compounds **4** and **5** were crystallized from methanol and ethanol, respectively, and both are planar with U-shaped arms in which S13 and N3 approach one another in **4** (dis-

tance 2.839 Å, Σr_{vdW} 3.35 Å) and S13 and S1 (2.947 Å) do the same in **5** (Figures 3 and 4). Compound **4** is a polymer in which S13 atom is connected through donor and acceptor interactions to two other S13 atoms (distance between S13 atoms is 3.47 Å and S13C···S13A···S13B angle is 71.47°; Figure 3).

In compound **5** the labile N−H proton was found by Fourier difference at N3, which allows intermolecular interactions through hydrogen bonds with N10 [2.33 Å, 163.7°]. The bond lengths C2−N10 [1.330(3) Å] and N10−C11 [1.355(3) Å] indicate an electronic delocalized system (Figure 4).

Compound **7** (Figure 5) has a structure similar to that of **5**, Its intramolecular O···S1 distance being 2.637 Å (Σr_{vdW} 3.25 Å), and intermolecular hydrogen bonds being observed between oxygen and H4 (2.50 Å) and between S12 and H7B (2.92 Å).

Compounds **8**, **10**, and **11** present planar structures with U-conformations and short distances between S1···S13 in their X-ray diffraction analysis (Figures 6 and 8); these distances and C8−S1−S13 angles are 2.908 Å and 167.10° in **8**, 3.044 Å and 165.86° in **10**, and 3.003 Å and 166.69° in **11**. The C−N bond lengths are characteristic of a delocalized system, while the C11−S13 bonds are typical double bonds. In compound **8** an intramolecular hydrogen bond between CH14c and N10 was found (distance 2.19 Å), and an intermolecular contact between N3−H···S13a was observed (2.70 Å).

In **10** and **11**, ADAD-DADA-type dimers are formed through H4···O (2.78 and 2.86 Å) and H10···N3 (2.04 and 2.17 Å) interactions; this is shown for **11** in Figure 8. In compound **11** other dimeric interactions exist through S1···S13A and S1A···S13 contacts (3.53 Å). The steric hindrance produced by the alkyl groups makes the molecules of **11** form diagonal arrangements (50°).

The X-ray structures for **9** and **13** (Figures 7 and 9) show intramolecular hydrogen bonds (data for **9**: H13·· N3 1.94 Å and 139.98°, **13**: 2.13 Å and 131.35°), which is in agreement with their ^{1}H NMR high-frequency chemical shifts.

Figure 7 shows a dimer for **9** with four contacts: two hydrogen bonds (S12 and H10; 2.47 Å, 162.98°) and two short contacts (S12···S1; 3.48 Å), S12 participating in a tricentric contact. In **13** a dimer is formed with molecules in perpendicular planes and with two hydrogen bonds between N3 and H4 (distances 2.644 and 2.667 Å).

The structure of compound **16** presents six planar aromatic fused rings, with a delocalized system existing between all C−N bonds. The C11−S12 bond length [1.777(4) Å] is slightly longer than a single C−S bond (1.75 Å). The N3−S12 [2.051(2) Å] and N3a−S12 [1.868(2) Å] bonds are of different length, and longer than a N−S single bond (1.77 Å), but far from the sums of the van der Waals radii (S−N 3.35 Å). This indicates strong nitrogen−sulfur coordination and hence Lewis acid behavior of the hypervalent sulfur atom. In the cell, compound **16** is in a two-shells arrangement, one perpendicular to another and with N10···H7 intermolecular interactions (2.53 Å).

Conclusion

We have prepared a series of polyfunctional compounds, which display very complex tautomeric and conformational behavior, from 2-aminobenzothiazole. The reported molecules are quite reactive and can be used as precursors for more complex molecules. In molecules **3**−**7** the endocyclic sulfur atom behaves as a Lewis acid and is coordinated by oxygen, nitrogen, and sulfur atoms. These stabilizing contacts determine their preferred conformation. Compounds **8**−**15** and **17** have labile acidic N−H protons, which participate in strong hydrogen bonds. A new dibenzothiazolyltetraazathiapentalene **16** bearing a T-shaped hypervalent sulfur atom bonded to a carbon and to two nitrogen atoms and presenting a "single bond-no bond" resonance structure is reported. All the studied compounds are planar and highly delocalized molecules with carbon heteroatom alternating frameworks. We are currently investigating their coordination behavior with metals, and research into their biological activity is also in progress.

Experimental Section

An FT IR spectrometer (Perkin−Elmer 1600) was used for obtaining IR spectra of solid samples in KBr pellets (4000−400 cm^{-1}). The UV/Visible spectra (diffuse reflectance, were recorded on a Cary-5E (Varian) spectrometer. The MS spectra were obtained by direct insertion at 20 eV in an HP 5989 spectrometer. X-ray diffraction studies were performed with a Siemens SMART Area-detector, CAD4, Kappa CCD. The crystal structures were determined and refined with the SHELXTL [x,y] system. Aromatic H atoms were placed on idealized positions for (**3-Na**, **4**, **7**, **9**−**11**, and **13**), and were refined with a riding model.[47] Hydrogen atoms were found by Fourier difference in **3-Li**, **5**, **8**, and **16**. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC: 229330 (for **3-Na**), 229328 (for **3-Li**), 229327 (for **4**), 229326 (for **5**), 229325 (for **7**), 229320 (for **8**), 229322 (for **9**), 229323 (for **10**), 229324 (for **11**), 229321 (for **13**), and 229329 (for **16**). Copies of the data can be obtained, free of charge, on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk].

(5,7-Di-*tert*-butylbenzothiazol-2-yl)amine (1a): Bromine (0.78 g, 4.87 mmol) was slowly added to a mixture of 3,5-di-*tert*-butylaniline (1 g, 4.87 mmol) and KSCN (0.95 g, 9.74 mmol) dissolved in glacial acetic acid (7.74 mL). The mixture was stirred for 1 h at room temp. After that, the solvent was evaporated, and the solid was washed with methanol and filtered. The methanolic solution was neutralized with an aq. solution of KOH (30%) and a colorless solid was formed; this was filtered off and washed with cool methanol (0.94 g, 74%), m.p. 162−164 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3449, 3403, 3290, 3095, 2963, 1639, 1536, 1393, 1325. UV/Vis: λ (nm) = 378, 348 and 312. MS: *m*/*z* = 262 (64) [M^+]; 247 (100). $C_{15}H_{22}N_2S$ (266.24): calcd. C 68.66, H 8.45, N 10.68; found C 69.12, H 8.79, N 10.68. ^{13}C NMR ($CDCl_3$): δ (ppm) = 34.9 and 31.7 (*t*Bu-7); 35.6 and 29.6 (*t*Bu-5); 114.5 (C-6); 117.2 (C-4); 125.1 (C-8); 143.3 (C-7); 149.3 (C-5); 153.2 (C-9); 166.7 (C-2) ppm. ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.36 (s, 9 H, 7-*t*Bu); 1.44 (s, 9 H, 5-*t*Bu); 5.53 (s br, 2

H, N-H); 7.19 (d, ^4J = 1.8 Hz, 1 H, 6-H); 7.48(d, ^4J = 1.8 Hz, 1 H, 4-H).

Sodium Compounds 2-Na and 3-Na: NaOH solution (3.0 mL, 20 M) was added to a solution of **1** (7.5 g, 50 mmol) in DMF (50 mL). The mixture was stirred for 45 min in an ice/water bath. After that, CS_2 (6.0 mL, 50 mmol) was added and stirring was continued for 60 min. The reaction product was poured into $CHCl_3$. A yellow crystalline solid was formed, was filtered off and washed, and was found to be a mixture (40:60) of **2-Na/3-Na**.

Sodium Benzothiazol-2-yldithiocarboimidate (2-Na): ^{13}C NMR ([D$_6$]DMSO): δ (ppm) = 117.8 (C-4); 120.6 (C-7); 120.8 (C-6); 124.9 (C-5); 131.7 (C-8); 149.1 (C-9); 169.8 (C-2); 193.5 (C-11) ppm. ^{1}H NMR ([D$_6$]DMSO): δ (ppm) = 6.97 (s br, 1 H, 6-H); 7.16 (s br, 1 H, 5-H); 7.36 (s br, 1 H, 7-H); 7.58 (s br, 1 H, 4-H).

Sodium Benzothiazol-2-yldithiocarbamate (3-Na): ^{13}C NMR ([D$_6$]DMSO): δ (ppm) = 120.8 (C-4); 121.2 (C-7); 122.7 (C-6); 125.7 (C-5); 131.1 (C-8); 148.1 (C-9); 161.6 (C-2); 213.7 (C-11) ppm. ^{1}H NMR ([D$_6$]DMSO): δ (ppm) = 7.22 (s br, 1 H, 6-H); 7.36 (s br, 1 H, 5-H); 7.69 (s br, 1 H, 7-H); 7.84 (s br, 1 H, 4-H); 11.59 (s br, 1 H, N10-H).

Potassium Benzothiazol-2-yldithiocarboimidate (2-K): KOH (0.7 g, 12.5 mmol) was added to a solution of **1** (1.87 g, 12.5 mmol) in DMF (15 mL), and the mixture was stirred for 45 min in an ice/water bath. After that, CS_2 (1.5 mL, 12.5 mmol) was added and stirring was continued for 60 min. A second equivalent of KOH (0.7 g, 12.5 mmol) was added, and after 1 h the mixture was poured into $CHCl_3$. The yellow precipitate was filtered off and washed (1.32 g, 35%), m.p. 280 °C dec. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1726, 1632, 1499. UV/Vis: λ (nm) = 387, 338. MS: *m*/*z* = 224 (2) [M$^+$], 150 (100). $C_8H_4N_2S_3K_2$ (306.42), C 31.76, H 1.33, N 9.26; found C 31.32, H 1.37, N 8.77. ^{13}C NMR ([D$_6$]DMSO): δ (ppm) = 119.9 (C-4); 121.2 (C-7); 122.5 (C-6); 125.0 (C-5); 131.7 (C-8); 148.7 (C-9); 170.0 (C-2); 193.3 (C-11). ^{1}H NMR ([D$_6$]DMSO): δ (ppm) = 7.21 (dd, ^3J = 8.6, 7.7 Hz, 1 H, 6-H); 7.35 (t, ^3J = 7.7 Hz, 1 H, 5-H); 7.69 (d, ^3J = 8.6 Hz, 1 H, 7-H); 7.80 (d, ^3J = 7.7 Hz, 1 H, 4-H).

Lithium Benzothiazol-2-yldithiocarbamate (3-Li): $LiOH·H_2O$ (0.84 g, 40 mmol) was added to a solution of **1** (3.0 g, 20 mmol) in DMF (25 mL), and the mixture was stirred for 0.5 h and cooled in an ice/water bath. CS_2 (1.20 mL, 20 mmol) was then added, and stirring was continued for 45 min. The mixture was poured into $CHCl_3$. Yellow crystals were formed, filtered off, and washed. (3.15 g, 52%), m.p. 70 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1672, 1657, 1531, C=S 1211. UV/Vis: λ (nm) = 422, 332. MS: *m*/*z* = 236 (1) [M$^+$], 150 (100). $C_{14}H_{23}N_4S_3Li$ (358.31): calcd. C 40.57, H 5.59, N 13.52; found C 40.56, H 4.86, N 13.29.^{13}C NMR ([D$_6$]DMSO, HETCOR, COLOC): δ (ppm) = 119.6 (C-4); 121.2 (C-7); 122.6 (C-6); 125.6 (C-5); 131.1 (C-8); 148.1 (C-9); 161.8 (C-2); 213.7 (C-11). ^{1}H NMR ([D$_6$]DMSO, HETCOR, COSY): δ (ppm) = 7.21 (dd, ^3J = 7.6, 7.9 Hz, 1 H, 6-H); 7.35 (t, ^3J = 7.9 Hz, 1 H, 5-H); 7.69 (d, ^3J = 7.6 Hz, 1 H, 7-H); 7.84 (d, ^3J = 7.9 Hz, 1 H, 4-H).

***N*-(Benzothiazol-2-yl)-*S*,*S*′-dimethyldithiocarboimine (4):** CH_3I (1.3 mL, 20 mmol) was added to a solution of **2-K** (3.0 g, 10 mmol) in DMF (40 mL) in an ice/water bath. The mixture was stirred for 2 h and poured into water. The yellow solid was filtered off, washed, and recrystallized from methanol (2.0 g, 75%), m.p. 72−73 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1509, 1464, 1429, 1180. UV/Vis: λ (nm) = 380, 338 nm. MS: *m*/*z* = 254 (20) [M$^+$], 192 (100). $C_{10}H_{10}N_2S_3$ (258.27): calcd. C 47.24, H 3.94, N 11.02; found C 47.05, H 3.95, N 11.13. ^{13}C NMR (C_6D_6): δ (ppm) = 121.3 (C-4); 122.8 (C-7); 124.2 (C-6); 126.0 (C-5); 135.1 (C-8); 152.3 (C-9); 15.4 (C-13); 167.4 (C-2); 174.7 (C-11). ^{1}H NMR (C_6D_6): δ (ppm) = 2.06 (s, 1 H, SCH_3); 6.99 (dd, ^3J = 8.0, 7.7 Hz, 1 H, 6-H); 7.15 (t, ^3J = 7.7 Hz, 1 H, 5-H); 7.40 (d, ^3J = 8.0 Hz, 1 H, 4-H); 8.05 (d, ^3J = 7.7 Hz, 1 H, 7-H).

***N*-(5,7-Di-*tert*-Butylbenzothiazol-2-yl)-*S*,*S*′-dimethyldithiocarboimine (4a):** NaH (0.02 g, 0.936 mmol) was added to a solution of compound **1a** (0.12 g, 0.468 mmol) in THF (8 mL), and the mixture was stirred for 4 h at room temp. CS_2 (0.03 mL, 0.468 mmol) was then added at 5 °C, the reaction mixture was stirred overnight, and a solid precipitated. The suspension was cooled to 5 °C, CH_3I (0.06 mL, 9.36 mmol) was added, and the mixture was stirred for 2 h at room temp. Water (10 mL) was then added and the mixture was stirred overnight. A yellow solid was filtered off and washed with water (0.12 g, 72%). IR (cm^{-1}): $\tilde{\nu}_{max}$ = 2963, 1536, 1507, 1181. UV/Vis: λ (nm) = 448, 338 nm. MS: *m*/*z* = 366 (57) [M$^+$], 351 (84), 293 (100). $C_{18}H_{26}N_2S_3$ (370.41): calcd. C 58.97, H 7.15, N 7.64; found C 58.70, H 7.22, N 7.54. ^{13}C NMR ($CDCl_3$): δ (ppm) = 15.9 (C-13); 35.8 and 29.6 (7-*t*Bu); 35.0 and 31.7 (5-*t*Bu); 117.2 (C-6); 119.0 (C-4); 128.3 (C-8); 143.7 (C-7); 149.1 (C-5); 152.6 (C-9); 168.2 (C-2); 173.8 (C-11). ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.38 (s, 9 H, 7-*t*Bu); 1.48 (s, 9 H, 5-*t*Bu); 2.59 (s, 6 H, SCH_3); 7.34 (d, ^4J = 1.6 Hz, 1 H, 6-H); 7.81(d, ^4J = 1.6 Hz, 1 H, 4-H).

***N*-(Benzothiazol-2-ylidene) *O*-Methyl Dithiocarbamate (5):**[26] CH_3I (1.52 mL, 10 mmol) was added to a solution of **3-Li** (2.5 g, 10 mmol) in DMF (40 mL), cooled in an ice/water bath. The mixture was stirred for 2 h and poured into water. The yellow crystals were filtered off, washed, and recrystallized from ethanol. (1.5 g, 64%), m.p. 187−188 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3440, 1527, 1442, 1384 1274, C=S 1212. UV/Vis: λ (nm) = 448, 340 nm. MS: *m*/*z* = 240 (40) [M$^+$], 192 (100). $C_9H_8N_2S_3$ (244.25): calcd. C 44.97, H 3.35, N 11.65; found C 45.19, H 3.39, N 11.70. ^{13}C NMR ([D$_6$]DMSO, HETCOR, COLOC): δ (ppm) = 18.7 (C-13); 115.4 (C-4); 122.9 (C-7); 124.6 (C-6); 126.9 (C-8); 127.4 (C-5); 138.3 (C-9); 165.2 (C-2); 207.0 (C-11). ^{1}H NMR ([D$_6$]DMSO, HETCOR, COSY): δ (ppm) = 2.612 (s, 3 H, SCH_3); 13.76 (s br, 1 H, N-H); 7.36 (dd, ^3J = 7.0, 7.9 Hz, 1 H, 5-H); 7.46 (t, ^3J = 7.9 Hz, 1 H, 6-H); 7.50 (d, ^3J = 7.0 Hz, 1 H, 4-H); 7.91 (d, ^3J = 7.9 Hz, 1 H, 7-H).

***S*-Methyl *N*-(3-Methylbenzothiazol-2-ylidene) Thiocarbamate (7);** Yellow crystals were obtained from the mother liquors produced in the reaction between **2-Na** and CH_3I (0.5 g, 13%), m.p. 173−174 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1643, 1528, 1446. UV/Vis: λ (nm) = 390, 338, 279 nm. MS: *m*/*z* = 238 (75) [M$^+$]. $C_{10}H_{11}N_3S_2$ (243.21): calcd. C 50.39, H 4.23, N 11.75; found C 50.69, H 4.10, N 11.89. ^{13}C NMR ($CDCl_3$): δ (ppm) = 12.6 (C-13); 30.0 (NCH_3); 34.2 (C-14); 112.1 (C-4); 122.5 (C-7); 123.7 (C-6); 124.5 (C-8); 126.9 (C-5); 136.9 (C-9); 163.7 (C-2); 177.5 (C-11). ^{1}H NMR ([D$_6$]DMSO): δ (ppm) = 2.32 (s, 3 H, SCH_3); 3.01 (s br, 3 H, NCH_3); 7.35 (s br, 1 H, 5-H); 7.51 (s br, 1 H, 6-H); 7.80 (s br, 1 H, 4-H); 7.83 (s br, 1 H, 7-H).

1-(Benzothiazol-2-yl)-3,3-dimethylthiourea (8): Aq. $NH(CH_3)_2$ (40%, 1.6 mL, 0.01 mol) was added at room temp to a solution of **5** (2.50 g, 0.01 mol) in ethanol (50 mL). The mixture was heated at reflux for 6 h, giving yellow pale crystals, which were filtered off, washed, and recrystallized from methanol (1.65 g, 70%), m.p. 180−184 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3196, 1555, 1507, 1468, C=S 1130. UV/Vis: λ (nm) = 386, 356 nm. MS: *m*/*z* = 237 (80). $C_{10}H_{11}N_3S_2$ (243.21): calcd. C 50.60, H 4.67, N 17.70; found C 50.17, N 4.61 N, 17.70. ^{13}C NMR ([D$_6$]DMSO): δ (ppm) = 41.6 (C-14); 117.0 (C-7); 122.7 (C-4); 123.0 (C-6); 125.9 (C-8); 126.7 (C-5); 135.8 (C-9); 167.3 (C-2); 185.3 (C-11). ^{1}H NMR ([D$_6$]DMSO, HETCOR, COSY): δ (ppm) = 3.27 (s, 6 H, NCH_3); 7.10 (s br, 2 H, 4-H and

7-H); 7.20 (s br, 1 H, 5-H); 7.46 (s br, 1 H, 6-H); 10.86 (s br, 1 H, N3-H).

1-(Benzothiazol-2-ylidene)-3-methylthiourea (9): Aq. NH_2CH_3 (40%, 0.860 mL, 0.01 mol) was added at room temp to a solution of **5** (2.40 g, 0.01 mol) in ethanol (40 mL). The mixture was heated at reflux for 6 h, giving a colorless solid that was recrystallized from methanol (1.80 g, 81%), m.p. 210 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3168, 2974, 1570, 1524, 1460, 1440, C=S 1210. UV/Vis: λ (nm) = 370, 338 nm. MS: *m*/*z* = 223 (82) [M^+]. $C_9H_9N_3S_2$ (229.19): calcd. C 48.40, H 4.06, N 18.82; found C 47.71, H 4.09, N 18.82. ^{13}C NMR ([D_6]DMSO, HETCOR, COLOC): δ (ppm) = 31.5 (C-13); 118.7 (C-4); 121.7 (C-7); 123.6 (C-6); 126.3 (C-5); 129.5 (C-8); 146.9 (C-9); 161.7 (C-2); 180.4 (C-11). ^1H NMR ([D_6]DMSO, HETCOR, COSY): δ (ppm) = 3.07 (s br, 1 H, 3 H, NCH_3); 7.21 (dd, ^3J = 7.8, 7.9 Hz, 1 H, 6-H); 7.35 (t, ^3J = 7.9 Hz, 1 H, 5-H); 7.62 (d, ^3J = 7.9 Hz, 1 H, 4-H); 7.85 (d, ^3J = 7.8 Hz, 1 H, 7-H); 9.83 (s br, 1 H, N13-H) 12.04 (s br, 1 H, N10-H).

***O*-Ethyl *N*-(Benzothiazol-2-yl) Thiocarbamate (10):** Compound **4** (240 mg, 1 mmol) was dissolved in hot ethanol (30 mL) and added to an ethanol (5 mL) solution of mercury(II) acetate (32 mg, 0.1 mmol). The solution was heated and stirred for 4 h. A colorless precipitate was formed, and this was filtered off and recrystallized from methanol (0.15 g, 63%), m.p. 135 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3175, 1602, 1568, 1449, 1386, C=S 1204. UV/Vis: λ (nm) = 370, 285 nm. MS: *m*/*z* = 238 (44) [M^+]. $C_{10}H_{10}N_2OS_2$ (242.21): calcd. C 50.39, H 4.23, N 11.75; found C 50.73, H 4.26, N 11.79. ^{13}C NMR ([D_6]DMSO, HETCOR, COLOC): δ (ppm) = 163.9 (C-2); 119.1 (C-4); 127.4 (C-5); 124.8 (C-6); 122.9 (C-7); 130.2 (C-8); 145.2 (C-9); 190.6 (C-11); 67.3 (C-13); 14.8 (C-14). ^1H NMR ([D_6]DMSO, HETCOR, COSY): δ (ppm) = 7.65 (d, ^3J = 7.9 Hz, 1 H, 4-H); 7.45 (t, ^3J = 7.9 Hz, 1 H, 5-H); 7.33 (t, ^3J = 7.9 Hz, 1 H, 6-H); 7.97 (d, ^3J = 7.9 Hz, 1 H, 7-H); 13.43 (s br, 1 H, N10-H); 4.50 (q, ^3J = 7.0 Hz, 2 H, OCH_2); 1.35 (t, ^3J = 7.0 Hz, 3 H, CH_3).

***O*-Isopropyl *N*-(Benzothiazol-2-yl) Thiocarbamate (11):** Compound **11** was prepared by the same procedure as for **10**; colorless crystals were obtained (20 mg, 80%), m.p. 162 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3466, 1601, 1572, 1441, C=S 1202. UV/Vis: λ (nm) = 384 nm. MS: *m*/*z* = 252 (30) [M^+]. $C_{11}H_{12}N_2OS_2$ (256.22): calcd. C 52.35, H 4.79, N 11.10; found C 51.78, H 4.77, N 11.37. ^{13}C NMR ([D_6]DMSO, HETCOR, COLOC): δ (ppm) = 21.4 (C-14); 74.3 (C-13); 118.7 (C-4); 122.0 (C-7); 123.9 (C-6); 126.5 (C-5); 128.4 (C-8); 144.9 (C-9); 162.5 (C-2); 188.6 (C-11). ^1H NMR ([D_6]DMSO, HETCOR, COSY): δ (ppm) = 1.34 (d, ^3J = 7.0 Hz, 3 H, CH_3) 5.51 (quint, ^3J = 7.0 Hz, 1 H, O-CH); 7.67 (d, ^3J = 7.9 Hz, 1 H, 4-H); 7.32 (dd, ^3J = 7.6, 7.9 Hz, 1 H, 6-H); 7.45 (t, ^3J = 7.9 Hz, 1 H, 5-H); 7.96 (d, ^3J = 7.6 Hz, 1 H, 7-H); 13.34 (s br, 1 H, N10-H).

General Procedure for Compounds 12−14: The appropriate amine (10 or 20 mmol, vide infra) was added to a solution of **4** (2.54 g, 10 mmol) in ethanol (10 mL), and the solution was heated at reflux for 8 h. The solvent was evaporated at room temp.

1-(Benzothiazol-2-yl)-2,3-dimethylisothiourea (12): This compound was obtained by treatment with aq. CH_3NH_2 (40%, 775 mg, 10 mmol), yellow powder (2.0 g, 90%), m.p. 61 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3445, 3193, 1608, 1567, 1470, 1437. UV/Vis: λ (nm) = 4022, 360, 338 nm. MS: *m*/*z* = 237.25 (29) [M^+], 190.25 (100). $C_{10}H_{11}N_3S_2$ (243.21): calcd. C 50.63, H 4.64, N 17.72; found C 50.58, H 4.71, N 17.82. ^{13}C NMR ([D_6]DMSO): δ (ppm) = 13.9 (C-13); 30.0 (C-14); 120.1 (C-4); 121.0 (C-7); 123.1 (C-6); 125.7 (C-5); 131.4 (C-8); 151.1 (C-9); 166.0 (C-2); 171.0 (C-11). ^1H NMR ($CDCl_3$): δ (ppm) = 2.32 (s, 3 H, SCH_3); 2.49 (s, 3 H, NCH_3); 7.21 (t, ^3J = 7.9 Hz, 1 H, 6-H); 7.36 (t, ^3J = 7.9 Hz, 1 H, 5-H); 7.67 (d, ^3J = 7.9 Hz, 1 H, 4-H); 7.80 (d, ^3J = 7.9 Hz, 1 H, 7-H); 10.64 (s br, 1 H, N13-H).

1-(Benzothiazol-2-yl)-2-isopropyl-3-methylisothiourea (3): This compound was obtained by treatment with isopropylamine (590 mg, 10 mmol), colorless crystals (2.3 g, 86.2%) with m.p. 52−53 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1636, C=N *endo*, 1652, C=N *exo*; 3179, 1558, 1472, 1436. UV/Vis: λ (nm) = 360, 338 nm. MS: *m*/*z* = 265 (29) [$M]^+$, 218 (36), 176(100). $C_{12}H_{15}N_3S_2$ (271.24): calcd. C 54.34; H 5.66; N 15.85; found C 54.36; H 5.57; N 15.88. ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.5 (C-14); 23.1 (2 CH_3); 23.1 (C-13); 45.9 (CH); 119.9 (C-7); 120.7 (C-4); 122.7 (C-6); 125.2 (C-5); 131.7 (C-8); 151.0 (C-9); 163.8 (C-2); 171.9 (C-11). ^1H NMR ($CDCl_3$,): δ (ppm) = 1.27 (d, ^3J = 6.6 Hz, 6 H, CH_3); 2.46 (s, 3 H, SCH_3); 3.85 (hept, ^3J = 6.6 Hz, 1 H, CH); 7.13 (dd, ^3J = 7.2, 6.6 Hz, 1 H, 6-H); 7.28 (t, ^3J = 7.2 Hz, 1 H, 5-H); 7.61 (d, ^3J = 6.6 Hz, 1 H, 7-H); 7.63 (d; ^3J = 7.2 Hz, 1 H, 4-H); 10.70 (s br, 1 H, N13-H).

1-(Benzothiazol-2-yl)-2,3-dimethylguanidine (14): This compound was obtained by treatment with aq. CH_3NH_2 (40%, 1.5 g, 20 mmol), viscous pungent yellow liquid was obtained (2.0 g, 90%). IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3440, 3270, 2924, 1602, 1574, 1477, 1441. UV/Vis: λ (nm) = 396 nm. MS: *m*/*z* = 220 (100), 189 (22) [M^+ − 31]. $C_{10}H_{12}N_4S$ (228.14): calcd. C 54.54, H 5.45, N 25.45; found C 54.80, H 5.49, N 24.24. ^{13}C NMR ($CDCl_3$): δ (ppm) = 27.7 (C-13 and C-14); 118.7 (C-7); 120.7 (C-4); 121.9 (C-6); 125.3 (C-5); 131.2 (C-8); 151.8 (C-9); 156.9 (C-2); 174.3 (C-11). ^1H NMR ($CDCl_3$): δ (ppm) = 2.78 (s, 6 H, 2 N-CH_3); 7.56 (d, ^3J = 7.6 Hz, 1 H, 4-H); 7.24 (t, ^3J = 7.6 Hz, 1 H, 5-H); 7.06 (dd, ^3J = 7.9, 7.6 Hz, 1 H, 6-H); 7.53 (d, ^3J = 7.9 Hz, 1 H, 7-H); 9.6 (s br, 2 H, N-H).

***N*,*N*′-Bis(Benzothiazol-2-yl)thiourea (15):** A mixture of **5** (240 mg, 1 mmol) and **1** (15 mg, 1 mmol) was heated at 160 °C for 3 h in a glass ampoule. The yellow solid **15** was purified by recrystallization from $CHCl_3$ (320 mg, 95%), m.p. 268−270 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3265, 1525, 1490, 1462, C=S 1240. UV/Vis: λ (nm) = 422, 358, 292 nm. MS: *m*/*z* = 342 (5) [M^+], 308 (11) [$M - H_2S]^+$, 192 (100) [$M - C_7H_4N_2S]^+$; 100]. $C_{15}H_{10}N_4S_3$ (350.27): calcd. C 52.61, H 2.94, N 16.36; found C 53.04, H 3.08, N 16.24. ^{13}C NMR ([D_6]DMSO, HETCOR, 120 °C): δ (ppm) = 163.8(C-2); 118.1 (C-4); 126.9 (C-5); 124.2 (C-6); 122.3 (C-7); 130.6 (C-8); 143.8 (C-9); 182.2 (C-11). ^1H NMR ([D_6]DMSO): δ (ppm) = 7.29 (t, ^3J = 7.9 Hz, 2 H, 6-H); 7.42 (t, ^3J = 7.9 Hz, 2 H, 5-H); 7.66 (d, ^3J = 7.9 Hz, 2 H, 7-H); 7.85 (d, ^3J = 7.9 Hz, 2 H, 4-H); 12.58 (s br, 2 H, N-H).

Sodium *N*,*N*′-Bis(benzothiazol-2-yl)thiourea (15-Na): Compound **15** (68 mg, 0.2 mmol) was dissolved in DMSO (0.5 mL) and heated at 110−120 °C. The solution was cooled to 25 °C, and NaH (24 mg, 1 mmol) was added. The mixture was stirred for 4 h at room temp., the precipitate was filtered off, and the solvent was evaporated to afford a yellow solid (70 mg, 90%), m.p. 342−346 °C dec. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1506, 1458, 1429. UV/Vis: λ (nm) = 437, 353 nm. ^{13}C NMR ([D_6]DMSO, 25 °C): δ (ppm) = 117.4 (C-7); 119.3 (C-6); 120.7 (C-4); 124.3 (C-5); 132.7 (C-8); 151.0 (C-9); 171.8 (C-2); 188.4 (C-11). ^1H NMR ([D_6]DMSO): δ (ppm) = 6.89 (t, ^3J = 7.4 Hz, 2 H, 6-H); 7.10 (t, ^3J = 7.4 Hz, 2 H, 5-H); 7.36 (d, ^3J = 7.4 Hz, 2 H, 7-H); 7.50 (d, ^3J = 7.4 Hz, 2 H, 4-H).

(Dibenzothiazol-2-yl)tetraazathiapentalene (16): *N*-Bromosuccinimide (89 mg, 0.5 mmol) was added at room temp. to a solution of **15** (171 mg, 0.50 mmol) in CH_2Cl_2 (20 mL) and stirring was maintained for 2 h, water (20 mL) was added, and the reaction mixture was extracted with CH_2Cl_2. The solvent was dried with $MgSO_4$, and removed under vacuum, and the solid residue was recrystallized from DMSO, giving yellow crystals (60 mg, 35%), m.p.

234−238 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 1494, 1457, 1400, 1320, 1277, 1270. UV/Vis: λ (nm) = 422, 338, 286. MS: *m*/*z* = 340 (100) [M^+], 192 (32) [M − $C_7H_4N_2S_1$]$^+$, 166 (30) [M − $C_7H_4N_3S$]$^+$. $C_{15}H_8N_4S_3$ (348.25): calcd. C 52.92, H 2.37, N 16.46; found C 52.77, H 2.46, N 16.05. ^{13}C NMR ([D$_6$]DMSO, HETCOR, 120 °C): δ (ppm) = 116.5 (C-7); 124.0 (C-4); 124.8 (C-6); 127.4 (C-5); 129.4 (C-8); 140.6 (C-9); 169.1 (C-2); 179.4 (C-11) ppm. ^{1}H NMR ([D$_6$]DMSO): δ (ppm) = 7.42 (d, ^3J = 6.5 Hz, 2 H, 7-H); 7.61 (dd, ^3J = 7.7, 6.5 Hz, 2 H, 6-H); 8.07 (dd, ^3J = 7.7 and 6.5 Hz, 2 H, 5-H); 8.09 (d, ^3J = 6.5 Hz, 2 H, 4-H).

***N*,*N*′,*N*′′-Tris(benzothiazol-2-yl)guanidine (17):** In a oil bath, **1** (354 mg, 2.36 mmol) was stirred and slowly heated at 180 °C, and **4** (300 mg, 1.18 mmol) was added. The mixture was stirred for 30 min at 180 °C, and a yellow solid was filtered off and washed with THF to give **17** (500 mg, 90%), m.p. 274−278 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3437, 1644, 1607, 1573, 1461, 1436. UV/Vis: λ (nm) = 410, 283 nm. MS: *m*/*z* = 458 (48) [M^+], 425 (1.5), 309 (100). $C_{22}H_{14}N_6S_3$ (470.29): calcd. C 57.62, H 3.08, N 18.33; found C 57.31, H 3.09, N 17.89. ^{13}C NMR ([D$_6$]DMSO, 120 °C): δ (ppm) = 165.5 (C-2); 118.5 (C-4); 126.9 (C-5); 124.0 (C-6); 122.1 (C-7); 131.3 (C-8); 151.9 (C-9); 187.4 (C-11). ^{1}H NMR ([D$_6$]DMSO): δ (ppm) = 7.72 (d, ^3J = 7.9 Hz, 3 H, 4-H); 7.45 (t, ^3J = 7.9 Hz, 3 H, 5-H); 7.30 (t, ^3J = 7.9 Hz, 3 H, 6-H); 7.87 (d, ^3J = 7.9 Hz, 3 H, 7-H); 13.23 (s br, 1 H, N-H); 13.49 (s br, 1 H, N-H).

***N*,*N*′,*N*′′-Tris(5,7-di-*tert*-butylbenzothiazol-2-yl)guanidine (17a):** Compounds **4a** (52 mg, 14.8 mmol) and **1a** (78 mg, 29.69 mmol) were heated in a sealed glass ampoule in an oil bath for 3 h at 165 °C, and the ampoule was then cooled in a dry ice bath and opened. The yellow solid was washed with hexane, filtered off, and dried under vacuum (90 mg, 77%), m.p. 304−306 °C, IR (cm^{-1}): $\tilde{\nu}_{max}$ = 3436, 2962, 1643, 1579 and 1468. UV/Vis: λ (nm) = 384 nm. MS: *m*/*z* = 794 (3) [M^+]; 533 (15), 262 (100). $C_{46}H_{62}N_6S_3$ (806.69): calcd. C 69.48, H 7.79, N 10.57; found C 68.34, H 7.79, N 10.39. ^{13}C NMR ($CDCl_3$, −60 °C): δ (ppm) = 29.9 and 36.0 (5-*t*Bu); 31.8 and 35.2 (7-*t*Bu) 117.0, 115.7, and 115.5 (3 C-6); 119.7, 118.9, and 118.8 (3 C-4); 127.4, 125.5, and 123.9 (3 C-8); 144.3, 143.9, and 143.8 (3 C-7); 146.0, 159.7, and 158.5 (3 C-2); 150.0, 149.4, and 149.3 (3 C-5); 150.3 151.0, and 150.9 (3 C-9); 170.5 (C-11). ^{1}H NMR ($CDCl_3$, −60 °C): δ (ppm) = 1.46 (s, 27 H, 7-*t*Bu); 1.58 and 1.67 (s, 27 H, 5-*t*Bu); 7.42 (s, 3 H, 4-H); 7.80, 7.86 and 7.97 (s, 3 H, 6-H); 13.37 (s br, 1 H, N-H); 14.08 (s br, 1 H, N-H).

***N*,*N*′-Di(5,7-di-*tert*-butylbenzothiazol-2-yl)-*N*′′′-(benzothiazol-2-yl)guanidine (17b):** Compounds **4** (137 mg, 0.54 mmol) and **1a** (244 mg, 0.11 mmol) were heated in a sealed glass ampoule in an oil bath at 165 °C for 3 h. The ampoule was cooled in a dry ice bath and opened. Compound **17b** was washed with hexane, filtered off, dried in vacuo, and obtained as a yellow solid (155 mg, 85%), m.p. 266−268 °C. IR (cm^{-1}): $\tilde{\nu}_{max}$ = 2962, 1571 and 1640. UV/Vis: λ (nm) = 383 nm. MS: *m*/*z* = 682 (7.1) [M^+]; 533 (4.8), 262 (100). $C_{36}H_{46}N_6S_3$ (670.56): calcd. C 66.88, H 7.12, N 12.30; found C 66.65, H 6.79, N 11.81. ^{13}C NMR ($CDCl_3$): δ (ppm) = 116.1 (C-4); 126.1 (C-5); 123.8 (C-6); 121.1 (C-7); 150.8 (C-9); 119.1 (C-4); 146.4 (C-5); 115.8 (C-6); 144.0 (C-7); 149.9 (C-9).

Acknowledgments

We thank Conacyt-Mexico (Grant 34714-E) for financial support and F. T.'s scholarship. We thank Ing. Marco Antonio Leyva Ramírez for technical assistance.

[1] N. Andrade-López, A. Ariza-Castolo, R. Contreras, A. Vázquez-Olmos, N. Barba-Behrens, H. Tlahuext, *Heteroatom Chem.* **1997**, *8*, 397−410.
[2] N. Andrade-López, R. Cartas-Rosado, E. García-Baéz, R. Contreras, H. Tlahuext, *Heteroatom Chem.* **1998**, *9*, 399−409.
[3] M.-P. Fialon, N. Andrade-López, N. Barba-Behrens, R. Contreras, *Heteroatom Chem.* **1998**, *9*, 637−641.
[4] M.-P. Fialon, E. García-Baéz, N. Andrade-López, G. Osorio-Monreal, G. Canseco-Melchor, I. Velázquez-Montes, N. Barba-Behrens, R. Contreras, *Heteroatom Chem.* **1999**, *10*, 577−584.
[5] [5a] P. Gund, *J. Chem. Educ.* **1972**, *49*, 100−103. [5b] A. Gobbi, G. Frenking, *J. Am. Chem. Soc.* **1993**, *115*, 2362−2372.
[6] T. K. Venkatachalam, E. A. Sudbeck, F. M. Uckum, *Bioorg. Med. Chem. Lett.* **2001**, 523−528.
[7] M. Eda, T. Takemoto, S.-I.. Ono, T. Okada, K. Kosaka, M. Gohda, S. Matzno, N. Nakamura, C. Fukaya, *J. Med. Chem.* **1994**, *37*, 1983−1990.
[8] K. Feichtinger, H. L. Sings, T. J. Baker, K. Matthews, M. Goodman, *J. Org. Chem.* **1998**, *63*, 8432−8439.
[9] R. G. S. Berlinck, *Nat. Prod. Rep.* **2002**, *19*, 617−649.
[10] A. Tanatani, K. Yamaguchi, I. Azumaya, R. Fukutomi, K. Shudo, H. Kagechika, *J. Am. Chem. Soc.* **1998**, *120*, 6433−6442.
[11] N. Andrade-López, Ph.D. Thesis, BQ-4464, Cinvestav-Mexico **1997**.
[12] F. Bernardi, *Organic Sulfur Chemistry*, Elsevier **1985**, pp. 192−245.
[13] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.
[14] R. Parthasarathy, T. N. Guru Row, *J. Am. Chem. Soc.* **1981**, *103*, 477−479.
[15] R. E. Rosenfield, Jr., R. Parthasarathy, J. D. Dunitz, *J. Am. Chem. Soc.* **1977**, *99*, 4860−4862.
[16] S. Oae, *Organic Sulfur Chemistry, Structure and Mechanism*, Florida, CRC-Press **1991**, pp. 19−35.
[17] B. M. Goldstein, F. Takusagawa, H. Berman, P. C. Srivastava, R. K. Robins, *J. Am. Chem. Soc.* **1983**, *105*, 7416−7422.
[18] F. T. Burling, B. M. Goldstein, *J. Am. Chem. Soc.* **1992**, *114*, 2313−2320.
[19] [19a] V. I. Minikin, R. M. Minyaev, *Chem. Rev.* **2001**, 1247−1265. [19b] K. Ohkata, M. Ohsugi, K. Yamamoto, M. Ohsawa, K.-Y. Akiba, *J. Am. Chem. Soc.* **1996**, *118*, 6355−6369.
[20] G. Vermeulen, G. Verhelst, G. L′abbé, *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 403−404.
[21] F. Iwasaki, S. Yoshida, S. Kakuma, T. Watanabe, M. Yasui, *J. Mol. Struc.* **1995**, *352/353*, 203−212.
[22] M. Yasui, S. Yoshida, S. Kakuma, S. Shimamoto, N. Matsumura, F. Iwasaki, *Bull. Chem. Soc., Jp.* **1996**, *69*, 2739−2747.
[23] R. L. N. Harris, *Austr. J. Chem.* **1972**, *25*, 993−1001.
[24] S. J. Coles, D. Douheret, M. B. Hursthouse, J. D. Kilburn, *Acta Crystallogr., Sect. C* **2000**, *56*, 687−688.
[25] R. B. Huang, X. Lu, N. Zheng, Y. Zou, S. Deng, H. Zhong, S. Xie, L. Long, L. Zheng, *J. Mol. Struct.* **2002**, *610*, 265−270.
[26] F. Merchán, J. Garín, E. Meléndez, *Synthesis* **1982**, 590−591.
[27] R. Neidlein, H. Reuter, *Synthesis* **1971**, 540−541.
[28] F. Merchán, J. Garín, E. Meléndez, T. Tejero, *Synthesis* **1982**, 1066−1067.
[29] J. Garín, E. Meléndez, F. Merchán, D. Ortiz, T. Tejero, *Synthesis* **1987**, 368−370.
[30] F. Merchán, J. Garín, V. Martínez, E. Meléndez, *Synthesis* **1982**, 482−484.
[31] J. Garín, E. Meléndez, F. Merchán, P. Merino, J. Orduña, T. Tejero, *Synthetic Commun.* **1989**, *19*, 2389−2399.
[32] J. Garín, E. Meléndez, F. Merchán, P. Merino, J. Orduna, T. Tejero, *J. Heterocyclic Chem.* **1990**, *27*, 1341−1344.
[33] J. Garín, E. Meléndez, F. Merchán, P. Merino, J. Orduna, T. Tejero, *J. Heterocyclic Chem.* **1990**, *27*, 1345−1349.
[34] J. Garín, E. Meléndez, F. Merchán, P. Merino, J. Orduna, T.

Tejero, M. Viñegra, *J. Heterocyclic Chem.* **1990**, *27*, 1351−1354.
[35] A. E. Ceniceros-Gómez, A. Ramos-Organillo, J. Hernández-Díaz, J. Nieto-Martinez, R. Contreras, S. E. Castillo-Blum, *Heteroatom Chem.* **2000**, *11*, 392−398.
[36] R. J. S. Beer, N. H. Holmes, A. Naylor, *J. Chem. Soc., Perkin I* **1979**, 2909−2913.
[37] M.-J. Crawford, T. M. Klapötke, P. Klüfers, P. Mayer, P. S. White, *J. Am. Chem. Soc.* **2000**, *122*, 9052−9053.
[38] H. U. Hummel, *Acta Crystallogr., Sect. C* **1987**, *43*, 41−43.
[39] T. C. W. Mak, K. S. Jasim, C. Chieh, *Can. J. Chem.* **1984**, *62*, 808−813.
[40] C. Lambert, F. Hampel, P. von R. Schleyer, *J. Organomet. Chem.* **1993**, *455*, 29−35.
[41] D. R. Armstrong, D. Barr, P. R. Raithby, R. Snaith, D. S. Wrigth, P. von R. Schleyer, *Inorg. Chim. Acta* **1991**, *185*, 163−167.
[42] D. R. Armstrong, F. A. Banbury, M. G. Davidson, P. R. Raithby, R. Snaith, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1992**, *20*, 1492−1494.
[43] P. C. Andrews, G. A. Koutsantonis, C. L. Raston, *J. Chem. Soc., Dalton Trans.* **1995**, 4059−4065.
[44] A. Oskarsson, I. Ymen, *Acta Crystallogr., Sect. C* **1984**, *40*, 30−32.
[45] S. C. Ball, I. Cragg-Hine, M. G. Davidson, R. P. Davies, A. J. Edwards, I. López-Solera, P. R. Raithby, R. Snaith, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 921−923.
[46] K. Tatsumi, I. Matsubara, Y. Inoue, A. Nakamura, R. E. Cramer, G. J. Tagoshi, J. A. Golen, J. W. Gilje, *Inorg. Chem.* **1990**, *29*, 4928−4938.
[47] G. M. Sheldrick, *SHELX 97-2 Users Manual*, University of Göttingen, Germany **1977**.

Received May 4, 2004

