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Cyclopentathiadiazines, Cyclohepta- and Cyclopentadithiazoles: New Materials and a Rich Heterocyclic Chemistry of Cyclic Enaminonitriles

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Dedicated to Professor Charles W. Rees

Keywords: Sulfur–nitrogen heterocycles / Materials science / Liquid crystals / Radicals / Fused-ring systems

3-Amino-1*H*-indene-2-carbonitrile and 2-amino-3*H*-indene-1-carbonitrile reacted with SCl_2, *i*Bu_3N and NCS to give benzocyclopenta[1,2,6]thiadiazines, and whilst 2-aminocyclopent-1-enecarbonitrile gave, under the same conditions, a cyclopenta[1,2,6]thiadiazine, its reaction with mixtures of S_2Cl_2, SCl_2 and *i*Bu_3N under different conditions gave, selectively, an isothiazolo[3,4-*d*]cyclopenta[1,2,3]dithiazole and new cyclopenta[1,2,3]dithiazole derivatives. Similarly, 2-aminocyclohept-1-enecarbonitrile reacted with SCl_2, *i*Bu_3N and NCS to give a formally antiaromatic cyclohepta[1,2,3]dithiazole. Some of the compounds obtained showed characteristics useful as new materials, for example, as liquid crystals and near-infrared dyes.

Introduction

Polycyclic 1,2,6-thiadiazine 2,2-dioxides have been intensively studied because of their practical use and economic interest.[1] Bentazone [3-isopropyl-1*H*-2,1,3-benzothiadiazine-4(3*H*)-one 2,2-dioxide] is a well-known, highly active and selective herbicide of long-standing that has been routinely used as a post-emergence herbicide for the control of broad-leaf weeds and some grasses.[2] The 1*H*-pyrazino[2,3-*c*][1,2,6]thiadiazine 2,2-dioxide system,[3] which is structurally related to pteridine, is of considerable pharmaceutical interest since some of its derivatives have shown interesting properties as diuretics, platelet aggregation inhibitors,[4] and bronchodilator agents[5] whilst benzyl derivatives of benzothieno[3,2-*a*]thiadiazine 2,2-dioxides act as phosphodiesterase 7 inhibitors.[6] In contrast, very few unoxidized polycyclic 1,2,6-thiadiazines are known,[1] probably because convenient synthetic approaches to these compounds are lacking. All the reported polycyclic 1,2,6-thiadiazines, except for the naphtho- and naphthobis[1,2,6]thiadiazines,[8] have been prepared from preformed 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one or its 4-dicyanomethylene derivative.[7] Cyclopenta[1,2,3]dithiazoles,[9] cyclopenta[1,2]dithioles and cyclopenta[1,2]thiazines[10] have been prepared by several methods that involve the reaction of simple saturated ketoximes with disulfur dichloride. We have reported a related procedure that is suitable for the one-pot preparation of the first cyclopenta[1,2,6]thiadiazines by the reaction of indene and cyclopentene enaminonitriles and sulfur dichloride (SCl_2).[11] Shortly afterwards we discovered that cyclic enaminonitriles are also a good source of several heterocyclic systems. In this paper we report the selective preparation of benzocyclopenta- and cyclopentathiadiazines, as well as a new isothiazolocyclopentadithiazole, a cycloheptadithiazole and some cyclopentadithiazoles from five- and seven-membered cyclic enaminonitriles.

Results and Discussion

We selected several cyclic enaminonitriles as starting materials. First, the cyclopentyl derivatives 3-amino-1*H*-indene-2-carbonitrile[12] (**1**), 2-amino-3*H*-indene-1-carbonitrile[13] (**2**) and 2-aminocyclopent-1-enecarbonitrile[14] (**3**) were employed. SCl_2 (20 equiv.) was added at –20 °C under nitrogen to a solution of one equivalent of **1**, **2** or **3**, *N*-chlorosuccinimide (NCS, 40 equiv.) and triisobutylamine (7.5 equiv.) in tetrahydrofuran (THF, 100 mL per equiv. of **1**, **2** or **3**), then the cooling bath was removed and the mixture was refluxed for 12 h (for **1**), 18 h (for **2**) or 14 h (for **3**), the solvent was evaporated under reduced pressure and

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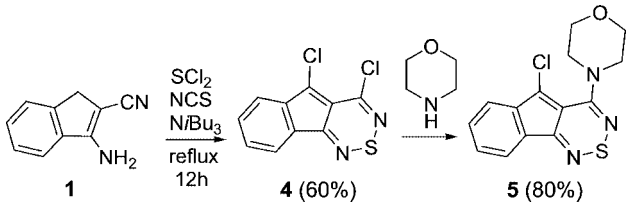
the residue subjected to flash column chromatography (silica, hexane or hexane/CH_2Cl_2 0→35%). Under these conditions compound **1** afforded the crystalline orange-red solid **4** (60%) whose spectroscopic data were consistent with the formation of a 1,2,6-thiadiazine ring accompanied by dehydrogenation and chlorination of the cyclopentathiazine moiety (Scheme 1). The structure of **4** was confirmed by single-crystal X-ray diffraction. The molecules in the crystal have short contacts (3.24 Å) between the sulfur and nitrogen atoms of opposite molecules that lie in parallel planes separated by 3.49 Å in such a way that each molecule is inverted with respect to the ones situated in the planes above and below with no interactions between them (Figure 1).



Scheme 1.

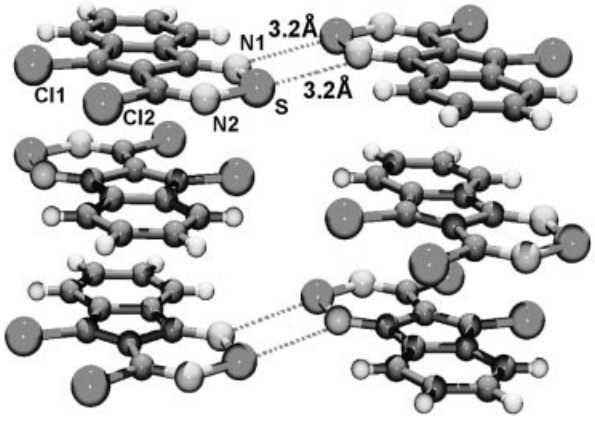
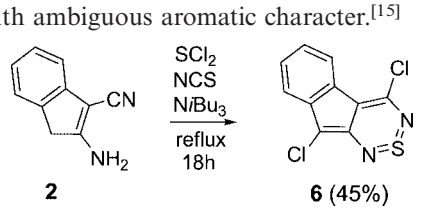


Figure 1. Packing of **4** in parallel layers of alternate molecules.

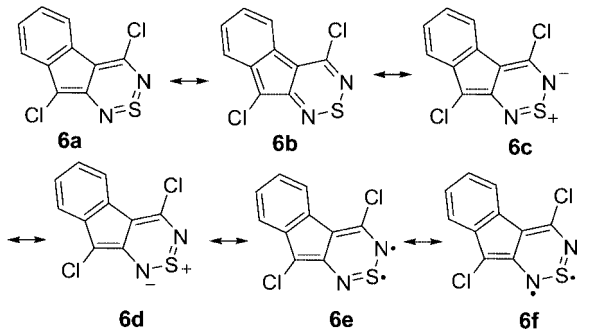
The chlorine atom on the thiadiazine ring is expected to be reactive.[7] Thus, the reaction of **4** with two equivalents of morpholine in Cl_2CH_2 at reflux for 20 h gave exclusively the crystalline orange-red solid **5** (80%). Compound **5** was fully characterized by spectroscopy, microanalysis and single-crystal X-ray diffraction,[11] which showed that only the 3-chloro atom was selectively substituted. We had expected that substitution of a halogen atom by a nitrogen atom would give rise to some bathochromic displacement of the absorption bands in the visible spectrum, but the UV spectra of **4** (λ_{max} = 453 nm, ε = 1809 $mol^{-1}\,dm^3\,cm^{-1}$) and **5** (λ_{max} = 469 nm, ε = 3917 $mol^{-1}\,dm^3\,cm^{-1}$) in CH_2Cl_2 exhibited similar bands, probably because steric barriers prevented conjugation (see the Supporting Information).

The reaction of **2**, SCl_2, NCS and iBu_3N in THF under the conditions described above afforded the crystalline green solid **6** (45%) (Scheme 2). Compound **6** exhibited similar peaks in its ^1H, ^{13}C NMR and HRMS spectra to those of its isomer **4** except for the fact that in the ^1H NMR spectrum of compound **6**, one proton appeared at δ = 8.8 ppm, a lower field than expected. To explain the chemical shift of this signal we performed ab initio calculations (unrestricted Hartree–Fock, 6-31G*) in order to obtain the most plausible geometry for structure **6** (see the Supporting Information). The structure determined showed that the distance between the chlorine atom in the 8-position and the next hydrogen atom in the 7-position was 2.56 Å. It was therefore expected that the hydrogen atom would appear at a lower field in the ^1H NMR spectrum than the rest of the hydrogen atoms in the molecule, which confirmed the structure of **6**. The UV spectrum of **6** exhibited a broad spectral absorption in the near-infrared region (λ_{max} = 823 nm, ε = 797 $mol^{-1}\,dm^3\,cm^{-1}$ and λ_{max} = 741 nm, ε = 879 $mol^{-1}\,dm^3\,cm^{-1}$ in CH_2Cl_2) that did not appear in the UV spectrum of **4** (see the Supporting Information). In addition, compound **6** exhibited a broad signal of low intensity in its EPR spectrum, both in a solution of benzene and in the solid state, which could not be resolved.[11] Under the same conditions, compound **4** did not exhibit any EPR signals. Structure **6** can be formulated as **6a**, a cyclic sulfurdiimide containing an oxidized sulfur(IV) atom (Scheme 3), and **6b** an unusual *o*-quinodimethane thiadiazine with a reduced sulfur(II) atom. However, compound **6** did not cycloadd to dimethyl acetylenedicarboxylate (as **6b** should do) and its reaction with morpholine led to the decomposition of **6**; therefore neither of these structures defines compound **6**. The charged forms **6c** and **6d** are likely to be more stable than **6a**,**b** because they have an aromatic fused benzene ring and a less oxidized sulfur atom although they have separate charges. In this case the sulfur atom is clearly the donor atom and the nitrogen atoms are the acceptor atoms. But noncharged structures are also possible. Structures **6e** and **6f** are biradical species with the same bonding as **6c** and **6d** and all of them are 14π aromatic species. What is the most plausible structure that explains all the experimental features of compound **6** is a challenging question. A partial biradical system mainly localized between the sulfur and the nitrogen atoms is the most plausible structure of **6** and is confirmed by a large and diffuse absorption in its near-infrared spectrum (see the Supporting Information). This type of structure is expected to have little influence on the nuclear spins of the far hydrogen atoms and so on the NMR spectra of **6**, which has no enlargement due to the presence of radical species. Very few cyclic sulfurdiimides have been described,[8] but all those that have are blue compounds with ambiguous aromatic character.[15]



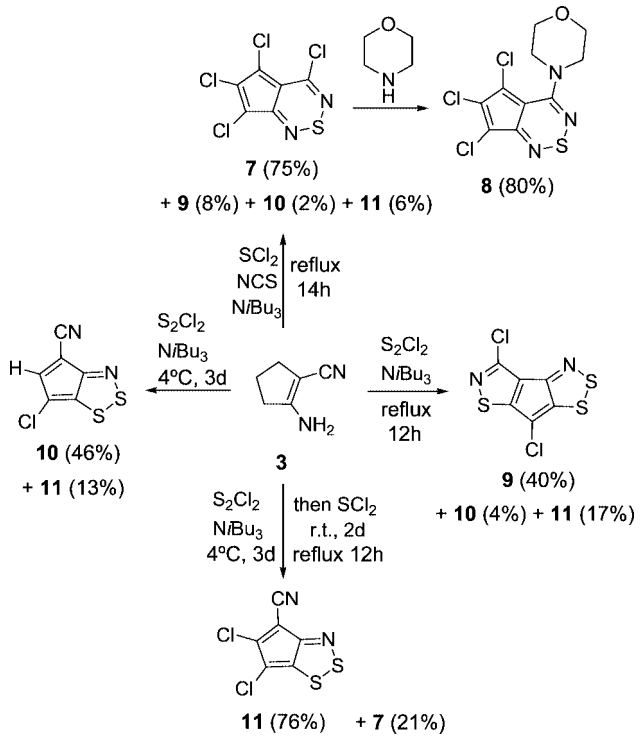
Scheme 2.

The reaction of **3**, SCl_2, NCS and iBu_3N in THF under the conditions described above gave the crystalline red solid



Scheme 3.

7 (75%) which did not exhibit any proton signals in its ^{1}H NMR spectrum, but did exhibit six signals in its ^{13}C NMR spectrum and a molecular formula of $C_6Cl_4N_2S$ was determined by HRMS and microanalysis, all consistent with a cyclopenta[1,2,6]thiadiazine structure **7** (Scheme 4).



Scheme 4.

Upon cooling after melting on a hot-stage polarizing microscope, compound **7** exhibited strong birefringence indicative of liquid crystallinity. Differential scanning calorimetry (DSC) exhibited a mesophase between 111 and 70 °C on cooling.[11] Therefore, compound **7** is a new example of a rare class of liquid-crystal pseudoazulene.[16] The structure of **7** was further confirmed by its chemistry. The reaction of **7** with two equivalents of morpholine in Cl_2CH_2 at reflux for 5.5 h gave exclusively the crystalline orange-red solid **8** (80%). Fully characterized by spectroscopy, microanalysis and single-crystal X-ray diffraction,[11] it was shown that only the 4-chloro atom of compound **7** was selectively substituted (Scheme 4). The UV spectra of **7** (λ_{max} = 504 nm, ε = 573 mol^{-1} dm^3 cm^{-1}) and **8** (λ_{max} = 501 nm, ε = 3443 mol^{-1} dm^3 cm^{-1}) in CH_2Cl_2 exhibited similar absorption bands, probably because steric barriers prevented conjugation, as was found for **4** and **5** (see the Supporting Information).

In some attempts to prepare **7**, three new additional colored products, **9** (8%), **10** (2%) and **11** (6%). were isolated in very low yields. Compounds **9** and **11** exhibited no hydrogen atoms in their ^{1}H NMR spectra, but **10** exhibited an intriguing aromatic proton at δ = 8.1 ppm. Their corresponding molecular formulae determined by HRMS and microanalyses, $C_6Cl_2N_2S_3$ (**9**), $C_6HClN_2S_2$ (**10**) and $C_6Cl_2N_2S_2$ (**11**), indicated new structural possibilities. The fact that the new structures contained up to three sulfur atoms indicated that a reagent capable of forming disulfur links could increase the yields of these products. Therefore we performed several experiments using disulfur dichoride (S_2Cl_2) and mixtures of SCl_2 and S_2Cl_2 under different conditions in order to isolate selectively each one of them (Scheme 4). The red compound **9** (40%) was prepared by the reaction of **3** (1 equiv.) with S_2Cl_2 (10 equiv.) and *i*Bu_3N (7.5 equiv.) in THF at 4 °C for 3 days, then refluxing for 2.5 h, then additional S_2Cl_2 (10 equiv.) was added and the reaction refluxed for an additional 12 h. Work-up and medium-pressure column chromatography of the residue afforded **9**. Compounds **10** (4%), **11** (17%) and traces of **7** (1%) were also obtained. The absence of the C≡N absorption in the IR spectrum and the presence of three sulfur atoms suggested that more than one heterocycle was present in the structure of **9**. The presence of a chlorinated isothiazole and a 1,2,3-dithiazole, both fused to the chlorinated cyclopentadiene ring, could therefore satisfy all the spectral features. Single-crystal X-ray diffraction confirmed the structure of **9** as the first example of an isothiazolo[3,4-*d*]cyclopenta[1,2,3]dithiazole, a new heterocyclic system (Figure 2). The molecules in the solid state showed close contacts between the three sulfur atoms and one nitrogen atom in one direction, and between one of the chlorine atoms and one of the nitrogen atoms in the orthogonal direction, but there are no close contacts with the remaining chorine atom. Consequently the molecules form linear strands composed of two strings of molecules packed closely in independent parallel layers with virtually no interaction between the neighboring strands. The close contacts found are: N2–S4, 3.00 Å; N2–S3, 3.06 Å; S1–S4, 3.39 Å; and in the orthogonal direction: N1–Cl2 and Cl2–N1, 3.18 Å. The molecules form parallel sheets through π-stacking, the distance between the sheets being 3.87 Å.

The purple bluish compound **10** (46%) was prepared by the reaction of **3** (1 equiv.) with S_2Cl_2 (10 equiv.) and *i*Bu_3N (10 equiv.) in THF at 4 °C for 3 days, followed by work-up and medium-pressure column chromatography of the residue. Compound **11** (13%) and traces of **9** (1%) were also obtained. This time the presence of one aromatic proton in the ^{1}H NMR spectrum of **10**, confirmed by ^{13}C NMR spectroscopy, the presence of a strong absorption due to a cyano group in its IR spectrum and the MS and analytical data, showed the presence of the partially chlorinated 4-cyanocyclopenta[1,2,3]dithiazole system. Therefore this

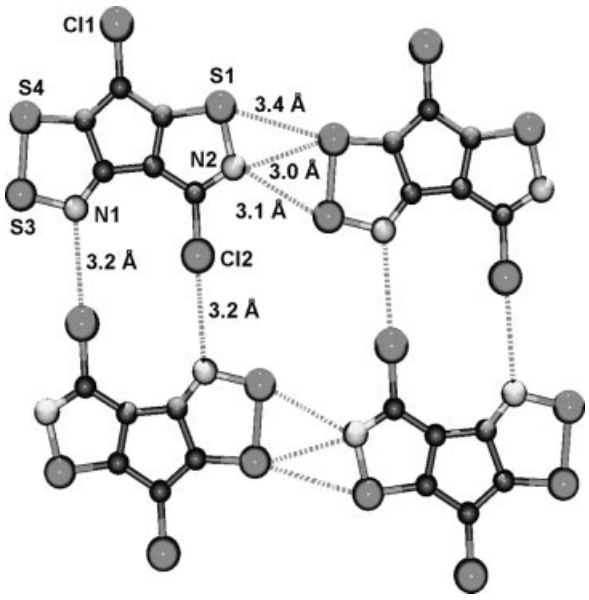


Figure 2. Single-crystal X-ray structure of compound **9** showing the close contacts between molecules.

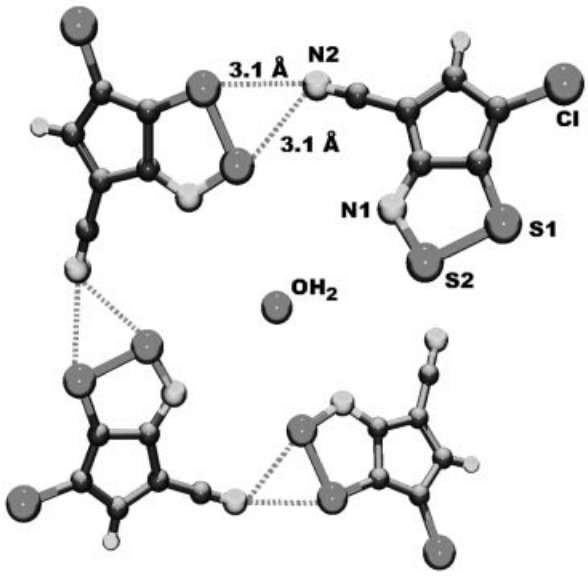


Figure 3. Single-crystal X-ray structure of compound **10** showing the close contacts between molecules. The hydrogen atoms of the disordered water molecule have been omitted.

method offers a new alternative route to the preparation of cyclopenta[1,2,3]dithiazoles, which are usually obtained from oximes.[9] The low field of the proton signal, found at δ = 8.0 ppm, suggested that the hydrogen atom is at the β-position with respect to the cyano group, and thus the chlorine atom was assigned to the 6-position. Single-crystal X-ray diffraction confirmed the structure of **10** (Figure 3). The packing of molecules of **10** is dominated by close contacts between the C≡N nitrogen of one molecule and the two sulfur atoms of a vicinal molecule such that the molecules form infinite parallel helices. The empty space inside the helices is filled with disordered water molecules captured from the dichloromethane used as crystallization solvent. This unusual packing system appears to be caused by the presence of a hydrogen atom that perturbs the usual near-circular form found in other molecules that favor layered quasihexagonal stacking. The close contacts found (excluding those of the disordered water) are: N2–S1, 3.07 Å; N2–S2, 3.08 Å. Also an H–S1 contact of 2.98 Å was found between the molecules of different helices.

The purple compound **11** (76%) was prepared by the reaction of **3** (1 equiv.) with S_2Cl_2 (10 equiv.) and iBu$_3$N (7.5 equiv.) in THF at 4 °C for 3 days, followed by refluxing for 2.5 h. SCl_2 (20 equiv.) was then added and the reaction mixture stirred for 2 days at room temp. and then refluxed for 12 h. Compound **7** (21%) was also obtained after work-up and medium-pressure column chromatography of the residue. The conditions used for the selective preparation of compound **11** are essentially the same as those used for the preparation of compound **10** followed by treatment under highly chlorinating conditions using SCl_2 as the chlorinating reagent. In fact, compound **11** could be obtained by chlorination of **10** with SCl_2 in THF at reflux for 12 h. The absence of protons in the ^{1}H NMR spectrum of **11** and the presence of a strong absorption due to a cyano group in the IR spectrum, confirmed by ^{13}C NMR spectroscopy and the MS and analytical data, showed the presence of the fully chlorinated 4-cyanocyclopenta[1,2,3]dithiazole system. Single-crystal X-ray diffraction confirmed the structure of **11** (Figure 4). The packing of molecules is dominated by close contacts between the C≡N nitrogen of one molecule and the two sulfur atoms of two vicinal molecules. Thus a tridimensional network is formed caused by the tilted disposition of each molecule with respect to its vicinal molecules. The molecules are packed in tilted columns by π-stacking. The close contacts found are: N2–S1, 3.05 Å; N2–S2, 2.94 Å; N2–S2′, 3.10 Å.

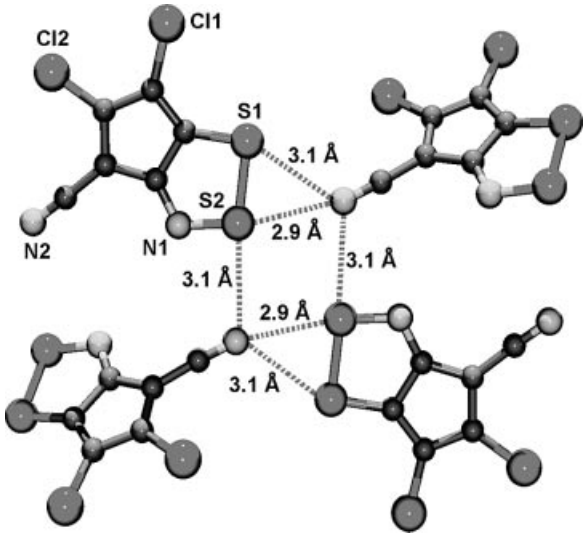
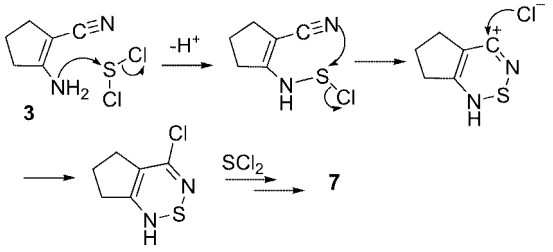


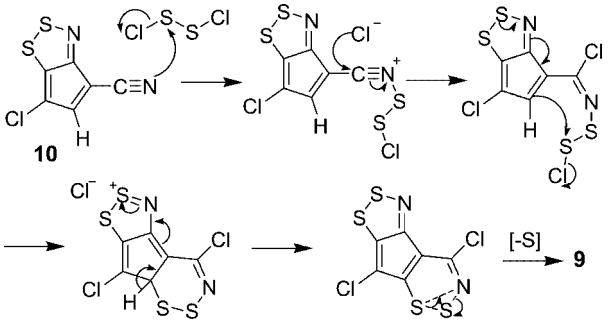
Figure 4. Single-crystal X-ray sructure of compound **11** showing the close contacts between molecules.

Therefore compounds **10** and **11** are new examples of partially or fully chlorinated cyano-substituted cy-

clopenta[1,2,3]dithiazoles obtained from enaminonitriles. The sensitivity of 2-aminocyclopent-1-enecarbonitrile (**3**) to the reaction conditions is remarkable. By using the abilities of SCl_2 and S_2Cl_2 to transfer one or two sulfur atoms to the amine or the nitrile group at the appropriate temperature in the presence or absence of strong chlorinating reagents, the reaction conditions can be controlled to obtain the desired product. In this way, SCl_2 in refluxing THF attacks both the amino and the nitrile groups to give the 1,2,6-thiadiazine ring and subsequent chlorination and dehydrochlorination steps form the main reaction pathway (Scheme 5). On the other hand, S_2Cl_2 at a low temperature selectively gives the dithiazole ring following a mechanism similar to that found for its synthesis from oximes,[9] but in refluxing THF it is also able to attack the nitrile group to give the isothiazole ring (Scheme 6).

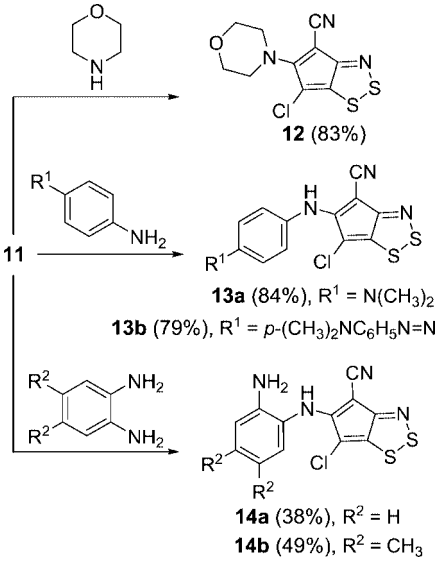


Scheme 5.



Scheme 6.

The products of all these reactions were used to study new reactions. To test the reactivity of **11**, we allowed this compound to react with morpholine (2 equiv.) in THF at room temp. for 75 min, expecting that the two chlorine atoms would be substituted. After work-up and column chromatography of the reaction residue we obtained a crystalline orange solid **12** (83%) which was found by MS to have a chlorine atom in the molecule (Scheme 7). Its ^1H NMR spectrum exhibited signals characteristic of morpholine protons and therefore we concluded that only one chlorine atom was substituted by the starting amine. For this reason we assigned the structure **12** to the product, which was confirmed by HRMS and microanalysis. The UV spectrum of **12** (λ_{max} = 412 nm, ε = 23928 $mol^{-1}\,dm^3\,cm^{-1}$) in CH_2Cl_2 contrasted the UV spectrum of **11** (λ_{max} = 546 nm, ε = 2618 $mol^{-1}\,dm^3\,cm^{-1}$) (Figure 5). Apparently, the morpholine group in **12** disrupts the charge-transfer band between the two rings by conjugation between the amine and cyano groups. For comparison, compound **10** was refluxed with the same amine in different solvents, from THF to chlorobenzene, but we always recovered the starting compounds unchanged. We concluded that the 6-chlorine atom is inert to nucleophilic substitution reactions and hence only the 5-chorine atom in **11** is reactive with amines. To prove this, compound **11** was allowed to react with substituted anilines in THF at reflux for 12–34 hours. In this way, the reactions of **11** and 4-dimethylaminoaniline or 4-dimethylamino-4′-aminoazobenzene gave, respectively, the orange compounds **13a** (84%) and **13b** (79%) in good yields (Scheme 7). Analogously, the reactions of compound **11** with 1,2-phenylenediamine or 4,5-dimethyl-1,2-phenylenediamine gave, respectively, the orange compounds **14a** (38%) and **14b** (49%) in much lower yields. In all the products obtained only the 5-chlorine atom of **11** was substituted. The selectivity of these substitution reactions was probably due to the activation of the β-position by the cyano group of **11**, which is a unique feature of this compound.



Scheme 7.

In view of the rich heterocyclic chemistry of compound **3**, we next selected a related cyclic enaminonitrile, the 2-aminocyclohept-1-enecarbonitrile[14] (**15**), as a starting material (Scheme 6). SCl_2 (20 equiv.) was added at –20 °C under nitrogen to a solution of **15** (1 equiv.), *N*-chlorosuccinimide (NCS, 20 equiv.) and triisobutylamine (7.5 equiv.) in THF. The cooling bath was then removed and the mixture was allowed to warm to room temp., then refluxed for 4.5 h and subsequently stirred for 12 h at room temperature. The solvent was then evaporated under reduced pressure and the residue subjected to flash column chromatography (silica, hexane or hexane/CH_2Cl_2, 0→35%). Under these conditions compound **15** afforded the crystalline green solid **16** (40%) as the only recognizable product (Scheme 8). The ^1H NMR spectrum of **16** exhibited two doublet signals at δ = 5.9 and 5.7 ppm, each with a coupling constant of 1.9 Hz and the same intensity. The low value of the coupling con-

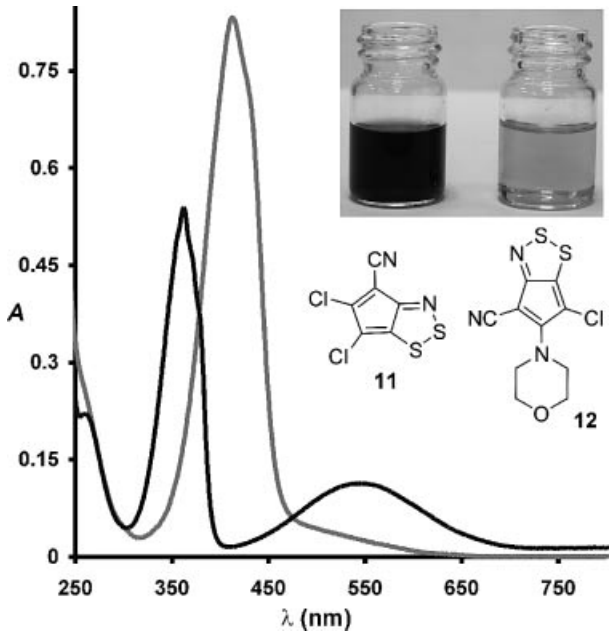
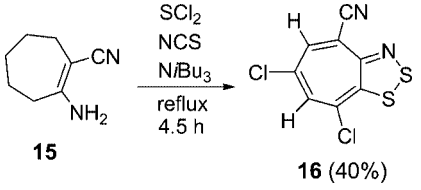


Figure 5. Comparison between structures and UV spectra of **11** (black) and **12** (grey).

stants indicates that the protons are not situated on vicinal carbon atoms. The ^{13}C NMR spectrum exhibited eight peak signals, the one at δ = 115 ppm corresponding to the nitrile group, which was confirmed by IR spectroscopy (2217 cm^{-1}). The molecular peak system revealed by HRMS agreed with the molecular formula of $C_8H_2N_2S_2Cl_2$, having two chlorine and two hydrogen atoms. Single-crystal X-ray diffraction confirmed the structure of **16**, proving unambiguously the alternate positions of the chlorine and hydrogen atoms (Figure 6).



Scheme 8.

The packing of molecules of **16** is dominated by close contacts between all the nitrogen and sulfur atoms and one chlorine atom of one molecule and all the nitrogen and sulfur atoms and one chlorine atom of three vicinal molecules, but there are no close contacts with the remaining chorine atom (Figure 6). The molecules lie in perfectly planar layers, but within the layers the molecules are associated by close contacts so forming infinite linear strings. The most remarkable feature is the close interaction between the disulfur links that connect all the sulfur atoms in the crystal to form infinite rows of closely packed sulfur atoms. The close contacts found are: N2–S2, 3.19 Å; N2–Cl2, 3.15 Å; N1–S1, 3.25 Å; S1–S2, 3.50 Å. The distance between parallel layers is 3.47 Å.

Despite the large number of experiments performed by reacting compound **15** with SCl_2 and S_2Cl_2 under different

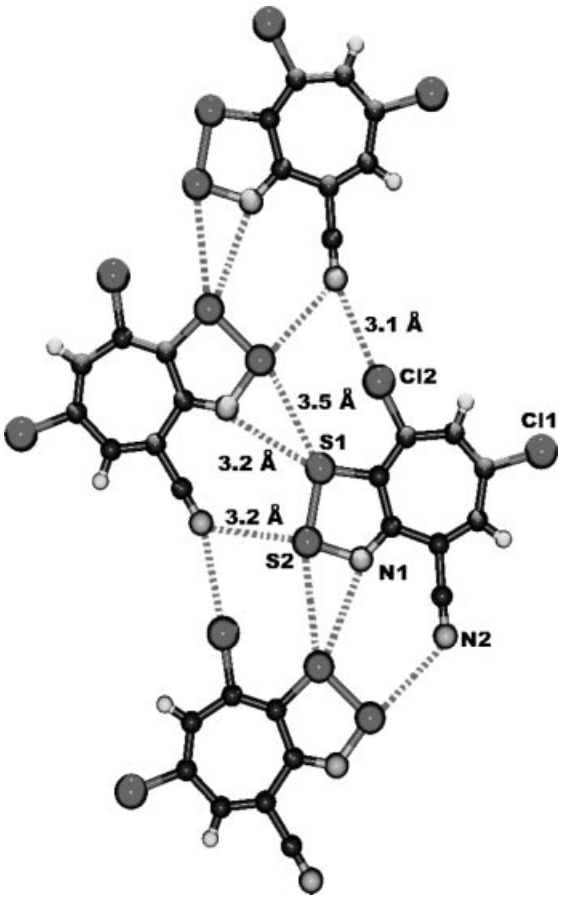


Figure 6. Single-crystal X-ray structure of compound **16** showing the close contacts between molecules.

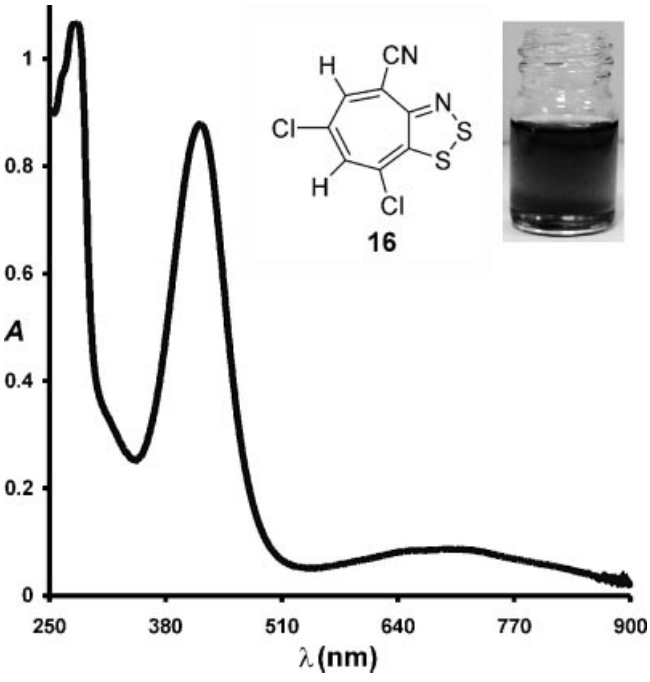


Figure 7. Structure and UV spectrum of compound **16**.

conditions, compound **16** was obtained as the only product but in lower yields. The UV spectrum of **16** in CH_2Cl_2 showed a broad spectral absorption in the near-infrared region (λ_{max} = 700 nm, ε = 864 $mol^{-1}\,dm^3\,cm^{-1}$) (Figure 7).

Electrochemical Study

We performed cyclic voltammetry experiments on 5×10^{-4} M solutions of compounds **4**–**12** and **16** in dichloromethane at 20 °C using Bu_4NPF_6 as the supporting electrolyte in an approximate 0.1 M concentration, a platinum ball as the working electrode, platinum wire as the auxiliary electrode and saturated calomelanes as the reference electrode. The cyclic voltammograms were registered at different scan rates and exhibited reversible and irreversible processes, as shown in Table 1. Most of the compounds studied exhibited irreversible oxidation waves near the limits of the range of study, but compounds **5** and **16** exhibited reversible or quasireversible oxidation waves at 1.16 and 1.18 V, respectively (Figure 8 and Table 1). All the compounds gave reduction waves between –0.63 and –1.45 V except for compound **6**, which exhibited a second reduction wave at –1.52 V. Two compounds, **6** and **7**, exhibited reversible reduction waves at –0.63 and –0.73 V, respectively. All the cyclopentadithiazoles exhibited irreversible waves, but three cyclopentathiadiazine derivatives, in addition to the only cycloheptadithiazole studied, exhibited reversible oxidation or reduction waves, showing that these new heterocyclic systems may be potential redox materials.

Table 1. Peak potentials for cyclic voltammograms registered at 100 $mV\,s^{-1}$.

Compound	E_p^{ox} [V]	E_p^{red} [V]
4	1.75	–1.45
5	1.16 (reversible)	–1.45
6	1.30	–0.63 (reversible), –1.52
7	1.65	–0.73 (reversible)
8	1.37	–1.00
9	1.73	–1.45
10	1.70	–0.69
11	1.65	–0.64
12	1.41	–1.01
16	1.18 (quasireversible)	–0.72

In summary, we have developed one-pot syntheses of cyclopentathiadiazines and studied the chemistry of these compounds. We have also achieved the one-pot syntheses of several polycyclic cyclopentadithiazoles from a single cyclic enaminonitrile as starting material by varying the reaction conditions and extended the synthesis to a new cycloheptadithiazole. In addition, we have described the physicochemical characteristics of all the new compounds, which are suitable as remarkable new materials, and these characteristics are summarized here. All the compounds obtained are heteroaromatic pseudoazulenes[17] with notable exceptions, such as compound **16**, which is formally a 12π antiaromatic compound, or compound **6**, which has resonance structures that include sulfur atoms in more than one oxidation state. With most of the heterocycles in these compounds being planar with few or no hydrogen atoms, the crystal packing trends give rise to planar sheets of mole-

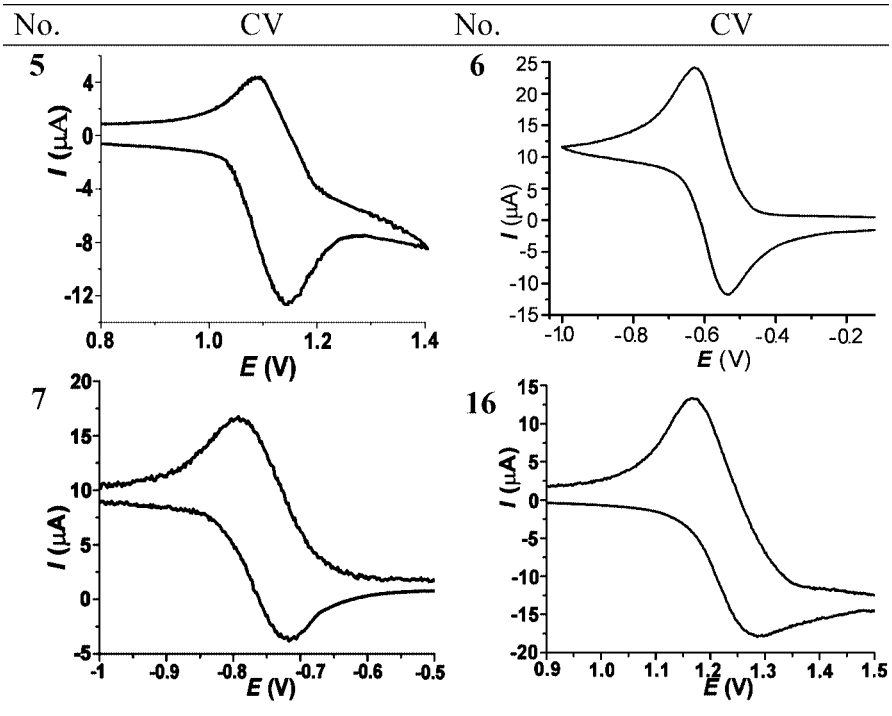


Figure 8. Reversible waves in the CV plots of compounds **5**–**7** and **16**.

cules supported by interactions between electron-acceptor and electron-donor groups. The interactions between the molecules give rise to a monotropic mesophase in the case of 7 and to infinite strings of sulfur–sulfur contacts in the solid state of **16**. A remarkable exception is the packing of **10** in helices, supported by hydrogen-bond contacts with adventitious water included in the crystal packing. The abnormally high number of heteroatoms included in the structures confers electronic properties to the reported compounds that are far from normal. The pseudoazulene structures give rise to colored compounds such as the purple-blue dithiazoles **9** and **10**. Two green compounds, **6** and **16**, absorb in the near-infrared region as a result of large intramolecular charge-transfer bands that stabilize the structures. One of them, compound **6**, also exhibited radical characteristics. In addition, the reversible reduction waves seen in the CVs of **6** (–0.63 V) and **7** (–0.73 V) are probably due to stabilization of the anion radical by the cyclopentadiene moiety. On the other hand, the reversible oxidation waves seen in the CVs of **5** (+1.16 V) and **16** (+1.18 V) indicate the stabilization of the radical cation by the morpholine nitrogen in **5** and by the cycloheptatriene moiety in **16**, giving rise in the latter case to a more aromatic structure. Very few nonfused 1,2,3-dithiazoles[18] and only some aryl-fused 1,2,3-dithiazoles[19] have been studied as new materials and their synthesis is based mainly on the Apple's salt chemistry[20] and the Herz reaction.[21] The methodology reported in this paper provides a new approach to air-stable, crystalline pseudoheteroazulenes that are useful new materials.

Experimental Section

Techniques: ^{1}H and ^{13}C NMR spectra were recorded with Varian Unity Inova 400 MHz and Varian Mercury 300 MHz spectrometers; chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) in Hz. IR spectra were recorded with a Nicolet Impact 410 instrument in KBr pellets; wavenumbers ($\tilde{\nu}$) are given in cm^{-1}. UV spectra were recorded with a Varian Cary 300 Bio instrument in 1 cm quartz cells at 25 °C. Low- and high-resolution mass spectra were recorded with a Micromass AutoSpec instrument using electron-impact ionization. Microanalyses were performed with a Leco CHNS-932 instrument. Cyclic voltammetry was performed with an EG&G VersaStat instrument in anhydrous CH_2Cl_2 using a three-electrode cell: a platinum ball was used as the working electrode, a platinum wire as the auxiliary electrode and saturated calomelane as the reference electrode with 0,1 M Bu_4NPF_6 as the supporting electrolyte. Chlorinated solvents were distilled from phosphorus pentaoxide, THF was distilled from sodium using benzophenone as the indicator. Melting points are uncorrected. TLC was carried out on silica gel Merck 60 GF-254 plates. Flash column chromatography was carried out on silica gel Merck C60 (230–400 mesh). Medium-pressure liquid chromatography was carried out on a Wilson apparatus using silica gel Merck C60 (<230 mesh).

Synthesis: Compounds **1**,[12] **2**,[13] **3**,[14] **14**[14] and **15**[14] were prepared as previously reported.

4,5-Dichloro-6,7-benzocyclopenta[*c*][1,2,6]thiadiazine (4): SCl_2 (1.60 mL, 25.60 mmol) was added under N_2 to a stirred solution of 3-amino-1*H*-indene-2-carbonitrile (**1**) (0.20 g, 1.28 mmol), NCS (6.94 g, 51.20 mmol) and iBu$_3$N (2.30 mL, 9.60 mmol) in THF (100 mL) at –20 °C. This mixture was allowed to warm to room temp. and then refluxed for 12 h. Removal of the solvent and column chromatography (silica, hexane, mixture of isomers) of the residue gave **4** (196 mg, 60%) as orange crystals (hexane), m.p. 166–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, J = 7.75 Hz, 1 H, CH), 7.91–7.76 (m, 2 H, 2×CH), 7.66 (t, J = 7.75 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.16, 144.68, 138.99, 132.35, 127.92, 126.02, 122.23, 119.70, 107.99 ppm. IR (KBr): $\tilde{\nu}$ = 1612, 1553, 1472, 1317, 716 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 457 (1815), 441 (1767), 371 (6513), 356 (5664), 334 (9059), 278 (24778), 245 nm (9328 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 258 (13) [M + 4]$^+$, 256 (70) [M + 2]$^+$, 254 (100) [M]$^+$, 219 (45) [M – Cl]$^+$, 184 (21) [M – 2Cl]$^+$, 138 (17), 99 (14), 83 (20), 78 (37), 63 (44). HRMS (70 eV, EI): calcd. for $C_{10}H_4{}^{37}ClClN_2S$: 255.9443; found 255.9448; calcd. for $C_{10}H_4N_2SCl_2$: 253.9472; found 253.9478; $C_{10}H_4Cl_2N_2S$ (255.12): C 47.08, H 1.58, N 10.98; found C 47.15, H 1.44, N 10.80. Crystal data for **4**: $C_{10}H_4Cl_2N_2S$, M = 255.11, triclinic, $P\bar{1}$, a = 6.888(4), b = 8.696(5), c = 9.612(5) Å, α = 68.24(1), β = 83.00(1), γ = 70.33(1)°; V = 503.5(5) Å^3, Z = 2, $D_{calcd.}$ = 1.683 g cm^{-1}, μ(Mo-K_α) = 0.812 mm^{-1}, red needles, (0.45×0.08×0.03) mm^3, 2285 measured reflections, 1452 independent (R_{int} = 0.0217), 1090 observed [$I > 2\sigma(I)$]. R_1 = 0.0489, wR_2 = 0.1375 (all data). CCDC-250853.

5-Chloro-4-(morpholin-4-yl)-6,7-benzocyclopenta[*c*][1,2,6]thiadiazine (5): Morpholine (0.02 mL, 0.18 mmol) was added under N_2 to a solution of **4** (23 mg, 0.09 mmol) in CH_2Cl_2 (25 mL) at –5 °C. This solution was allowed to warm to room temp. and then refluxed for 20 h. Then water (25 mL) was added, the organic layer was collected, washed (aqueous saturated $NaHCO_3$, 20 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, hexane/CH_2Cl_2, 80:20) of the residue gave **5** (22 mg, 80%) as orange crystals (hexane), m.p. 268–269 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 7.60 Hz, 1 H, ArH), 7.76 (d, J = 7.60 Hz, 1 H, ArH), 7.69 (t, J = 7.60 Hz, 1 H, ArH), 7.56 (t, J = 7.60 Hz, 1 H, ArH), 3.94 (t, J = 4.50 Hz, 4 H, 2×CH_2O), 3.42 (t, J = 4.50 Hz, 4 H, 2×CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.96, 154.58, 137.75, 130.63, 126.65, 123.05, 121.24, 118.92, 105.94, 66.48, 50.10) ppm. IR (KBr): $\tilde{\nu}$ = 1530, 1476, 1437, 1266, 765, 734 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 469 (3917), 378 (6010), 361 (6453), 283 (15994), 242 nm (13365 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 307 (34) [M + 2]$^+$, 305 (100) [M]$^+$, 270 (20) [M – Cl]$^+$, 247 (21), 221 (24), 220 (47), 219 (43), 185 (38), 184 (26), 86 (53). HRMS (70 eV, EI): calcd. for $C_{14}H_{12}ClN_3OS$: 305.0390; found 305.0395; $C_{14}H_{12}ClN_3OS$ (305.78): C 54.83, H 3.96, N 13.74; found C 54.91, H 4.00, N 13.74. Crystal data for **5**: $C_{14}H_{12}ClN_3OS$, M = 305.78, monoclinic, $C2/c$, a = 16.356(6), b = 11.871(4), c = 15.296(5) Å, β = 114.333(7)°, V = 2706.0(17) Å^3, Z = 8, $D_{calcd.}$ = 1.50 g cm^{-1}, μ(Mo-K_α) = 0.435 mm^{-1}, orange-red prisms, (0.27×0.14×0.10) mm^3, 5954 measured reflections, 1957 independent (R_{int} = 0.0582), 1363 observed [$I > 2\sigma(I)$]. R_1 = 0.0509, wR_2 = 0.1368 (all data). CCDC-247923.

4,9-Dichloro-5,6-benzocyclopenta[*c*][1,2,6]thiadiazine (6): SCl_2 (1.60 mL, 25.60 mmol) was added under N_2 to a stirred solution of 2-amino-3*H*-indene-1-carbonitrile (**2**) (0.20 g, 1.28 mmol), NCS (6.94 g, 51.20 mmol) and iBu$_3$N (2.30 mL, 9.60 mmol) in THF (100 mL) at –20 °C. This mixture was allowed to warm to room temp. and then refluxed for 18 hours. Removal of the solvent and column chromatography (silica, cyclohexane to hexane) of the residue gave **6** (147 mg, 45%) as green crystals (hexanes), m.p. 155–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, J = 7.30 Hz, 1 H, ArH), 8.11 (d, J = 7.30 Hz, 1 H, ArH), 7.80 (t, J = 7.30 Hz, 1 H,

ArH), 7.61 (t, J = 7.30 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.78, 143.35, 141.50, 131.07, 125.49, 125.24, 125.11, 119.50, 104.87, 104.42 ppm. IR (KBr): $\tilde{\nu}$ = 1604, 1515, 1464, 1340, 703, 629 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 823 (797), 741 (879), 466 (2607), 441 (2403), 334 (35102), 321 (30237), 272 (12104), 231 nm (6971 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 258 (20) [M + 4]$^+$, 256 (92) [M + 2]$^+$, 254 (100) [M]$^+$, 219 (44) [M – Cl]$^+$, 184 (87) [M – 2Cl]$^+$, 175 (30), 138 (31), 99 (29), 79 (47). HRMS (70 eV, EI): calcd. for $C_{10}H_4Cl^{37}ClN_2S$: 255.9446; found 255.9453; calcd. for $C_{10}H_4Cl_2N_2S$: 253.9472; found 253.9483; $C_{10}H_4Cl_2N_2S$ (255.12): C 47.08, H 1.58, N 10.98; found C 47.21, H 1.39, N 10.74.

4,5,6,7-Tetrachlorocyclopenta[*c*][1,2,6]thiadiazine (7): SCl_2 (2.94 mL, 46.24 mmol) was added under N_2 to a stirred solution of 2-aminocyclopent-1-enecarbonitrile (**3**) (0.25 g, 2.31 mmol), NCS (12.35 g, 92.48 mmol) and iBu$_3$N (4.20 mL, 17.34 mmol) in THF (100 mL) at –20 °C. This mixture was allowed to warm to room temp. and then refluxed for 14 h. Removal of the solvent and medium-pressure column chromatography (silica, hexane to hexane/CH_2Cl_2, 65:35) of the residue gave **7** (475 mg, 75%) as red crystals (hexane/CH_2Cl_2), R_f = 0.79 (hexane/CH_2Cl_2, 1:1), m.p. 116–117 °C. DSC (10 K min^{-1}), T/°C [ΔH/[kJ mol^{-1}]: K 116.7 (peak), 112.2 (onset) [47.09] I; I 111.2 (peak), 112.3 (onset) [13.25] Col$_{plast}$ 70.1 (peak), 71.1 (onset) [24.18] I. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.73, 145.52, 141.57, 121.39, 112.45, 104.34 ppm. IR (KBr): $\tilde{\nu}$ = 1450, 1289, 759 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 501 (967), 398 (1122), 378 (1664), 360 (1484), 319 (17616), 306 (13766), 276 (22030), 269 nm (22949 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 276 (19) [M + 4]$^+$, 274 (38) [M + 2]$^+$, 272 (27) [M]$^+$, 202 (23) [M – 2Cl]$^+$, 141 (15), 132 (34), 100 (58), 79 (96). HRMS (70 eV, EI): calcd. for $C_6Cl_2{}^{37}Cl_2N_2S$: 275.8477; found 275.8503; calcd. for $C_6{}^{37}ClCl_3N_2S$: 273.8507; found 273.8499; calcd. for $C_6Cl_4N_2S$: 271.8536; found 271.8551; $C_6Cl_4N_2S$ (273.95): C 26.31, H 0.00, N 10.23; found C 26.41, H not detected, N 10.12. Compounds **9** (49 mg, 8%), **10** (9 mg, 2%) and **11** (33 mg, 6%) were also isolated.

5,6,7-Trichloro-4-(morpholin-4-yl)cyclopenta[*c*][1,2,6]thiadiazine (8): Morpholine (0.014 mL, 0.16 mmol) was added under N_2 to a solution of 7 (22 mg, 0.08 mmol) in CH_2Cl_2 (25 mL) at 0 °C. This mixture was allowed to warm to room temp. and then refluxed for 5.5 h. Then water (25 mL) was added, the organic layer was collected, washed (aqueous saturated $NaHCO_3$, 20 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, hexane/CH_2Cl_2, 65:35) of the residue gave **8** (21 mg, 80%) as orange crystals (hexane/CH_2Cl_2), m.p. 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (t, J = 4.60 Hz, 4 H, 2 × CH_2O), 3.51 (t, J = 4.60 Hz, 4 H, 2 × CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.73, 154.68, 148.08, 136.05, 116.09, 110.69, 66.44 (2 × CH_2O), 50.47 (2 × CH_2N) ppm. IR (KBr): $\tilde{\nu}$ = 1736, 1503, 1445, 1289, 1227, 1122, 781 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 504 (3443), 431 (2111), 283 (25426), 224 (7712 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 327 (6) [M + 4]$^+$, 325 (18) [M + 2]$^+$, 323 (18) [M]$^+$, 267 (13), 238 (27), 202 (13), 167 (21), 149 (75), 86 (77) [C_4H_8NO]$^+$, 58 (100). HRMS (70 eV, EI): calcd. for $C_{10}H_8Cl^{37}Cl_2N_3OS$: 326.9395; found 326.9417; calcd. for $C_{10}H_8Cl_2{}^{37}ClN_3OS$: 324.9424; found 324.9438; calcd. for $C_{10}H_8Cl_3N_3OS$: 322.9454; found 322.9463; $C_{10}H_8Cl_3N_3OS$ (324.61): C 37.00, H 2.48, N 12.94; found C 36.91, H 2.54, N 12.82. Crystal data for **8**: $C_{10}H_8Cl_3N_3OS$, M = 324.60, triclinic, $P\bar{1}$, a = 7.226(1), b = 8.913(1), c = 10.049(1) Å, α = 98.589(3), β = 93.045(3), γ = 99.426(2)°, V = 629.35(15) Å^3, Z = 2, $D_{calcd.}$ = 1.71 g cm^{-1}, μ(Mo-K_α) = 0.883 mm^{-1}, red prisms, (0.29 × 0.20 × 0.09) mm^3. 2820 measured reflections, 1768 independent (R_{int} = 0.0145), 1598 observed [$I > 2\sigma(I)$], R_1 = 0.0335, wR_2 = 0.0988 (all data). CCDC-247924.

4,7-Dichloroisothiazolo[4,5-*d*]cyclopenta[1,2,3]dithiazole (9): S_2Cl_2 (3.70 mL, 46.24 mmol) was added under N_2 to a stirred solution of 2-aminocyclopent-1-enecarbonitrile (**3**) (0.50 g, 4.62 mmol) and iBu$_3$N (8.40 mL, 13.87 mmol) in THF (70 mL) at –20 °C. This mixture was stirred at 4 °C for 3 days and then refluxed for 2.5 hours. The mixture was then cooled to –20 °C and further S_2Cl_2 (3.70 mL, 46.24 mmol) was added under N_2. This mixture was allowed to warm to room temp. and then refluxed for 12 hours. Removal of the solvent and medium-pressure column chromatography (silica, hexane to hexane/CH_2Cl_2, 70:30) of the residue gave **9** (494 mg, 40%) as red crystals (hexane/CH_2Cl_2), R_f = 0.53 (hexane/CH_2Cl_2, 1:1), m.p. 142–143 °C. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.53, 153.86, 142.13, 121.94, 107.63, 107.21 ppm. IR (KBr): $\tilde{\nu}$ = 1453, 1087, 749 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 500 (256), 376 (2153), 354 (1451), 275 nm (6559 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 270 (19) [M + 4]$^+$, 268 (76) [M + 2]$^+$, 266 (100) [M]$^+$, 231 (9) [M – Cl]$^+$, 190, (72), 155 (22), 129 (35), 94 (63), 70 (19). HRMS (70 eV, EI): calcd. for $C_6Cl^{37}ClN_2S_3$: 267.8571; found 267.8568; calcd. for $C_6Cl_2N_2S_3$: 265.8601; found 265.8596; $C_6Cl_2N_2S_3$ (267.18): C 26.97, H 0.00, N 10.48; found C 26.91, H not detected, N 10.32. Crystal data for **9**: $C_6Cl_2N_2S_3$, M = 267.16, triclinic, $P\bar{1}$, a = 3.868(2), b = 8.239(5), c = 14.872(9) Å, α = 74.14(1), β = 86.63(1), γ = 87.10(1)°, V = 454.8(4) Å^3, Z = 2, $D_{calcd.}$ = 1.95 g cm^{-1}, μ(Mo-K_α) = 1.346 mm^{-1}, red needles, (0.21 × 0.05 × 0.02) mm^3, 2876 measured reflections, 1305 independent (R_{int} = 0.0216), 1048 observed [$I > 2\sigma(I)$], R_1 = 0.0303, wR_2 = 0.0819 (all data). CCDC-271053. Compounds **10** (37 mg, 4%), **11** (185 mg, 17%) and traces of **7** (8 mg, <1%) were also isolated.

6-Chlorocyclopenta[1,2,3]dithiazole-4-carbonitrile (10): S_2Cl_2 (1.48 mL, 18.49 mmol) was added under N_2 to a stirred solution of 2-aminocyclopent-1-enecarbonitrile (**3**) (0.20 g, 1.85 mmol) and iBu$_3$N (4.48 mL, 18.49 mmol) in THF (30 mL) at –20 °C and then this mixture was stirred at 4 °C for 3 days. Removal of the solvent and medium-pressure column chromatography (silica, hexane to hexane/CH_2Cl_2, 85:15) of the residue gave **10** (171 mg, 46%) as purple-bluish crystals (hexane/CH_2Cl_2), R_f = 0.24 (hexane/CH_2Cl_2, 1:1), m.p. 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.34, 153.96, 130.81, 128.91, 113.73, 111.08 ppm. IR (KBr): $\tilde{\nu}$ = 2219 (C≡N), 1426, 810 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 563 (1980), 349 (8836), 260 (4184), 244 nm (6832 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 202 (42) [M + 2]$^+$, 200 (100) [M]$^+$, 165 (31) [M – Cl]$^+$, 149 (26), 121 (44), 109 (42), 95 (42), 71 (42), 69 (57). HRMS (70 eV, EI): calcd. for $C_6HClN_2S_2{}^{37}$: 201.9240; found 201.9261; calcd. for $C_6HClN_2S_2$: 199.9270; found 199.9271; $C_6HClN_2S_2$·0.25H_2O (205.17): C 35.12, H 0.74, N 13.65; found C 35.20, H 0.69, N 13.68. Crystal data for **10·0.25H$_2$O**: $C_6HClN_2S_2$·0.25H_2O, M = 205.16, tetragonal, $P4/n$, a = b = 20.571(9), c = 3.916(2) Å, V = 1657.0(14) Å^3, Z = 8, $D_{calcd.}$ = 1.64 g cm^{-1}, μ(Mo-K_α) = 0.898 mm^{-1}, black needles, (0.45 × 0.03 × 0.03) mm^3, 9373 measured reflections, 1207 independent (R_{int} = 0.0201), 698 observed [$I > 2\sigma(I)$], R_1 = 0.0878, wR_2 = 0.2795 (all data). CCDC-271054. Compound **11** (56 mg, 13%) and traces of **9** (3 mg, <1%) were also isolated.

5,6-Dichlorocyclopenta[1,2,3]dithiazole-4-carbonitrile (11): S_2Cl_2 (3.69 mL, 46.24 mmol) was added under N_2 to a stirred solution of 2-aminocyclopent-1-enecarbonitrile (**3**) (0.50 g, 4.62 mmol) and iBu$_3$N (8.39 mL, 34.68 mmol) in THF (70 mL) at –20 °C and then this mixture was stirred at 4 °C for 3 days. The mixture was then cooled to –20 °C and SCl_2 (5.87 mL, 92.46 mmol) was added under N_2. This mixture was allowed to warm to room temp. and refluxed for 12 hours. Removal of the solvent and medium-pressure column chromatography (silica, hexane to hexane/CH_2Cl_2, 65:35) of the

residue gave **11** (836 mg, 76%) as purple crystals (hexane/CH_2Cl_2), R_f = 0.26 (hexane/CH_2Cl_2, 1:1), m.p. 217–218 °C. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.75, 156.98, 137.32, 136.45, 112.10, 110.52 ppm. IR (KBr): $\tilde{\nu}$ = 2219 (C≡N), 1426, 755 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 546 (2618), 362 (12461), 260 (5109), 244 nm (7021 $mol^{-1}\,dm^3\,cm^{-1}$). MS (70 eV, EI): *m*/*z* (%) = 238 (8) $[M + 4]^+$, 236 (34) $[M + 2]^+$, 234 (49) $[M]^+$, 199 (15) $[M - Cl]^+$, 167 (12), 149 (40), 137 (24), 123 (51), 109 (61), 95 (73), 83 (66), 78 (73), 63 (100). HRMS (70 eV, EI): calcd. for $C_6Cl^{37}ClN_2S_2$: 235.8850; found 235.8840; calcd. for $C_6Cl_2N_2S_2$: 233.8880; found 233.8886; $C_6Cl_2N_2S_2$ (235.12): C 30.65, H 0.00, N 11.91; found C 30.58, H < 0.10, N 11.81. Crystal data for **11**: $C_6Cl_2N_2S_2$, M = 235.10, monoclinic, $P2_1/c$, a = 13.313(11), b = 3.894(3), c = 17.116(14) Å, β = 98.55(1)°, V = 877.5(13) $Å^3$, Z = 4, $D_{calcd.}$ = 1.78 $g\,cm^{-1}$, μ(Mo-K_α) = 1.152 mm^{-1}, black prisms, (0.13 × 0.12 × 0.06) mm^3, 5057 measured reflections, 1278 independent (R_{int} = 0.0972), 907 observed [$I > 2\sigma(I)$], R_1 = 0.0570, wR_2 = 0.1406 (all data). CCDC-271055. Compound **7** (266 mg, 21%) was also isolated.

6-Chloro-5-(morpholin-4-yl)cyclopenta[1,2,3]dithiazole-4-carbonitrile (12): Morpholine (0.19 mL, 2.12 mmol) was added under N_2 to a solution of **11** (250 mg, 1.06 mmol) in THF (25 mL) at 0 °C. This mixture was then allowed to warm to room temp. and stirred for 75 min. Then the solvent was evaporated, CH_2Cl_2 (25 mL) was added and the solution was washed (aqueous saturated $NaHCO_3$, 3 × 25 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, CH_2Cl_2/EtOAc, 35:65) of the residue gave **12** (252 mg, 83%) as an orange solid (CH_2Cl_2/EtOAc), m.p. 189–190 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.99–3.93 (m, 4 H, 2 × CH_2O), 3,92–3,85 (m, 4 H, 2 × CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.56, 162.62, 144.10, 116.46 (intense), 105.10, 66.84 (2 × CH_2O), 50.55 (2 × CH_2N) ppm. IR (KBr): $\tilde{\nu}$ = 2986, 2190 (C≡N), 1565, 1406 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 412 (23928), 224 nm (13715 $mol^{-1}\,dm^3\,cm^{-1}$). MS (70 eV, EI): *m*/*z* (%) = 287 (40) $[M + 2]^+$, 285 (100) $[M]^+$, 250 (16) $[M - Cl]^+$, 227 (72), 200 (25), 91 (24), 57 (28). HRMS (70 eV, EI): calcd. for $C_{10}H_8{}^{37}ClN_3OS_2$: 286.9768; found 286.9785; calcd. for $C_{10}H_8ClN_3OS_2$: 284.9797; found 284.9803; $C_{10}H_8ClN_3OS_2$ (285.77): C 42.03, H 2.82, N 14.70; found C 41.95, H 2.71, N 14.63.

6-Chloro-5-(4-dimethylaminophenylamino)cyclopenta[1,2,3]dithiazole-4-carbonitrile (13a): *N*,*N*-Dimethyl-1,4-phenylenediamine (10 mg, 0.07 mmol) was added under N_2 to a solution of **11** (17 mg, 0.07 mmol) in THF (15 mL) at 0 °C. This mixture was allowed to warm to room temp. and then refluxed for 13 h. Then the solvent was evaporated, CH_2Cl_2 (25 mL) was added and the solution was washed (aqueous saturated $NaHCO_3$, 3 × 10 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, hexane/CH_2Cl_2, 75:25, to CH_2Cl_2) of the residue gave **13a** (20 mg, 84%) as an orange solid (hexane/CH_2Cl_2), m.p. 141–142 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, J = 9.00 Hz, 2 H, ArH), 7.07 (s, 1 H, NH), 6.75 (d, J = 9.00 Hz, 2 H, ArH), 3.00 (s, 6 H, 2 × CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.73, 159.95, 155.28, 150.58, 126.64, 124.35, 114.37, 112.09, 104.68, 94.37, 40.52 ppm. IR (KBr): $\tilde{\nu}$ = 3342 (N–H), 2197 (C≡N), 1521, 820, 600 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 334 (0.5) $[M]^+$, 58 (100). HRMS (70 eV, EI): calcd. for $C_{14}H_{11}{}^{37}ClN_4S_2$: 336.0084; found 336.0068; calcd. for $C_{14}H_{11}ClN_4S_2$: 334.0114; found 334.0122; $C_{14}H_{11}ClN_4S_2$ (334.85): C 50.22, H 3.31, N 16.73; found C 50.46, H 3.19, N 16.61. Some starting material **11** (2 mg) was also recovered.

6-Chloro-5-[4-(4-dimethylaminophenylazo)phenylamino]cyclopenta-[1,2,3]dithiazole-4-carbonitrile (13b): 4,4′-Bis(dimethylamino)azobenzene (17 mg, 0.07 mmol) was added under N_2 to a solution of **11** (17 mg, 0.07 mmol) in THF (15 mL) at 0 °C. This mixture was allowed to warm to room temp. and then refluxed for 34 h. Then the solvent was evaporated, CH_2Cl_2 (25 mL) was added and the solution was washed (aqueous saturated $NaHCO_3$, 3 × 10 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, hexane/CH_2Cl_2, 75:25, to CH_2Cl_2) of the residue gave **13b** (25 mg, 79%) as an orange solid (hexane/CH_2Cl_2), m.p. 266–267 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 9.00 Hz, 2 H, ArH), 7.88 (d, J = 8.80 Hz, 2 H, ArH), 7.48 (d, J = 8.80 Hz, 2 H, ArH), 6.76 (d, J = 9.00 Hz, 2 H, ArH), 3.10 (s, 6 H, 2 × CH_3), 3.01 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.73, 169.85, 164.57, 156.18, 153.93, 152.56, 146.05, 140.11, 125.07, 124.44, 123.49, 111.47, 109.08, 94.38, 45.73 (2 × CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3437 (N–H), 2197 (C≡N), 1603, 1445, 820 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 438 (0.5) $[M]^+$, 137 (34), 136 (32), 109 (20), 94 (11), 77 (12), 63 (25), 49 (100). HRMS (70 eV, EI): calcd. for $C_{20}H_{15}{}^{37}ClN_6S_2$: 440.0459; found 440.0523; calcd. for $C_{20}H_{15}ClN_6S_2$: 438.0488; found 438.0518; $C_{20}H_{15}ClN_6S_2$ (438.96): C 54.72, H 3.44, N 19.15; found C 54.83, H 3.50, N 19.03. Some starting material **11** (8.1 mg) was also recovered.

5-(2-Aminophenylamino)-6-chlorocyclopenta[1,2,3]dithiazole-4-carbonitrile (14a): 1,2-Phenylenediamine (20 mg, 0.18 mmol) was added under N_2 to a solution of **11** (20 mg, 0.09 mmol) in THF (15 mL) at 0 °C. This mixture was allowed to warm tot room temp. and then stirred for 17 h. Then the solvent was evaporated, CH_2Cl_2 (25 mL) was added and the solution was washed (aqueous saturated $NaHCO_3$, 3 × 20 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, hexane/CH_2Cl_2, from 85:15 to 40:60) of the residue gave **14a** (10 mg, 38%) as an orange solid (hexane/CH_2Cl_2), m.p. 227–228 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.21 (m, 2 H, 2 × ArH), 6.88–6.85 (m, 2 H, 2 × ArH), 3.50 (br. s, 3 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.13, 143.07, 130.85, 130.22, 128.77, 128.07, 124.95, 121.74, 120.26, 119.13, 116.73, 113.32 ppm. IR (KBr): $\tilde{\nu}$ = 3155 (N–H), 2203 (C≡N), 1578, 774 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 308 (40) $[M + 2]^+$, 306 (100) $[M]^+$, 279 (14), 270 (61), 266 (88). HRMS (70 eV, EI): calcd. for $C_{12}H_7{}^{37}ClN_4S_2$: 307.9771; found 307.9786; calcd. for $C_{12}H_7ClN_4S_2$: 305.9801; found 305.9801; $C_{12}H_7N_4S_2Cl$ (306.80): C 46.98, H 2.30, N 18.26; found C 46.91, H 2.21, N 17.93.

5-(2-Amino-4,5-dimethylphenylamino)-6-chlorocyclopenta[1,2,3]-dithiazole-4-carbonitrile (14b): 3,4-Dimethyl-1,2-phenylenediamine (25 mg, 0.18 mmol) was added under N_2 to a solution of **11** (20 mg, 0.09 mmol) in THF (15 mL) at 0 °C. This mixture was allowed to warm to room temp. and then stirred for 5 h and refluxed for 12 h. Then the solvent was evaporated, CH_2Cl_2 (25 mL) was added and the solution was washed (aqueous saturated $NaHCO_3$, 3 × 20 mL), dried (Na_2SO_4) and the solvent evaporated. Column chromatography (silica, hexane/CH_2Cl_2, from 85:15 to 40:60) of the residue gave **14b** (14 mg, 49%) as an orange solid (hexane/CH_2Cl_2), m.p. 196–197 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 1 H, ArH), 6.85 (s, 1 H, NH), 6.66 (s, 1 H, ArH), 3.65 (br. s, 2 H, NH_2), 2.21 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.00, 163.38, 162.73, 140.52, 140.24, 138.73, 128.22, 127.61, 119.57, 118.27, 113.49, 104.79, 19.78 (CH_3), 18.90 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3426 (N–H), 2198 (C≡N), 800 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 336 (7) $[M + 2]^+$, 334 (17) $[M]^+$, 294 (56), 149 (21), 118 (33), 91 (83), 77 (61), 69 (66), 64 (75), 55 (65), 41 (100). HRMS (70 eV, EI): calcd. for $C_{14}H_{11}{}^{37}ClN_4S_2$: 336.0084; found 336.0056; calcd. for $C_{14}H_{11}ClN_4S_2$: 334.0114; found 334.0094; $C_{14}H_{11}ClN_4S_2$ (334.85): C 50.22, H 3.31, N 16.73; found C 49.89, H 3.11, N 16.45.

6,8-Dichlorocyclohepta[1,2,3]dithiazole-4-carbonitrile (16): SCl_2 (1.90 mL, 29.40 mmol) was added under N_2 to a stirred solution of

2-aminocyclohept-1-enecarbonitrile (**15**) (0.20 g, 1.47 mmol), NCS (3.98 g, 29.40 mmol) and iBu$_3$N (2.70 mL, 11.03 mmol) in THF (100 mL) at –20 °C. This mixture was allowed to warm to room temp. and then refluxed for 4.5 h and stirred for 12 h at room temp. Removal of the solvent and medium-pressure column chromatography (silica, hexane to hexane/CH_2Cl_2, 65:35) of the residue gave **16** (153 mg, 40%) as green crystals (hexane/CH_2Cl_2), R_f = 0.56 (hexane/CH_2Cl_2, 1:1), m.p. 184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.94 (d, J = 1.90 Hz, 1 H, CH), 5.73 (d, J = 1.90 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.34, 155.98, 144.27, 138.99, 127.07, 118.75, 115.47, 114.70 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2217 (C≡N), 1558, 1404, 866, 645, 520 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 700 (864), 419 (8788), 282 (10650), 277 (10642), 223 nm (21216 mol^{-1} dm^3 cm^{-1}). MS (70 eV, EI): m/z (%) = 264 (10) [M + 4]$^+$, 262 (64) [M + 2]$^+$, 260 (96) [M]$^+$, 225 (70) [M – Cl]$^+$, 200 (100), 190 (79), 181 (75), 99 (70), 91 (88), 79 (78), 69 (90), 64 (95). HRMS (70 eV, EI): calcd. for $C_8H_2Cl^{37}ClN_2S_2$: 261.9007; found 261.9010; calcd. for $C_8H_2Cl_2N_2S_2$: 259.9036; found 259.9045; $C_8H_2Cl_2N_2S_2$ (261.15): C 36.79, H 0.77, N 10.73; found C 36.87, H 0.54, N 10.45. Crystal data for **16**: $C_8H_2Cl_2N_2S_2$, M = 261.14, orthorhombic, $Pnma$, a = 10.485(3), b = 6.807(2), c = 13.606(4) Å, V = 971.2(5) Å^3, Z = 4, $D_{calcd.}$ = 1.79 g cm^{-1}, μ(Mo-K_α) = 1.051 mm^{-1}, black plates, (0.26 × 0.15 × 0.06) mm^3, 4111 measured reflections, 770 independent (R_{int} = 0.0376), 634 observed [$I > 2\sigma(I)$], R_1 = 0.0435, wR_2 = 0.1270 (all data). CCDC-271056.

Crystal Structure Determination for Compounds 4, 5, 8, 9, 10·0.25H$_2$O, 11 and 16: A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer equipped with a CCD area detector. The crystal was irradiated with graphite-monochromated Mo-K_α radiation. Raw frame data were integrated using the SAINT[22] program. The structures were solved by direct methods using SHELXTL.[23] An empirical absorption correction was applied using the SADABS program.[24] The non-hydrogen atoms of each structure were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. In the structure of **10**, a peak was found at the tetragonal axis which corresponds to a disordered molecule of adventitious water (occupancy 0.25) taken up during the crystallization process. All calculations were made with SHELXTL.

CCDC-247923, -247924, -250853, -271053, -271054, -271055 and -271056, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Medium- and near-IR spectra of compounds **4** and **6**, conformational studies of the rotation of the morpholine ring in **5** and **8**, calculation of the singlet state of compound **6** and Brookhaven pdb structure file of **6** (HyperChem. 7.5 Pro, UHF 6-31G*). Figure S1 shows the packing of **4** in parallel layers of alternate molecules.

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