JOC Article

From Cyclopentanone Oximes to Bis[1,2,3]dithiazolo-*s*-indacenes, Cyclopenta[*c*][1,2]thiazine, Pentathiepino-, Tetrathiino-, and Thienocyclopenta[1,2,3]dithiazoles as a Rich Source of New Materials

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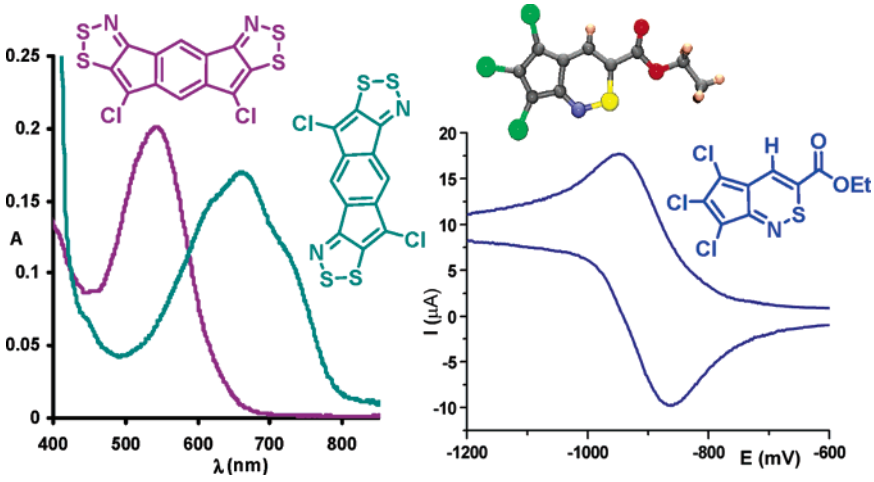

The 1,5- and 1,7-*s*-hydrindacenedione dioximes reacted with S_2Cl_2 and $^iBu_3N$ to give the first examples of bis[1,2,3]dithiazolo-*s*-indacenes; one of them was a near-infrared dye. In contrast, the silylated bicyclo[3.3.0]octan-2,6-dione dioxime reacted with S_2Cl_2 and Et_3N to give a bicyclic 4-cyanoethylcyclopenta[1,2,3]dithiazole or, after addition of Li_2S, a tricyclic 4-cyanoethyl-5,6-pentathiepinocyclopenta[1,2,3]dithiazole, also obtained from 2-cyanoethylcyclopentanone oxime, S_2Cl_2, and Hünig's base. In related reactions, 2-oxocyclopentylpropionate oxime gave the expected cyclopenta[1,2,3]dithiazole, in addition to an unexpected cyclopenta[*c*][1,2]thiazine that showed a reversible reduction wave in its CV at −0.95 V. Ethyl 2-oxocyclopentanecarboxylate oxime reacted with S_2Cl_2, Hünig's base, and Li_2S to give a 5,6-tetrathiinocyclopenta[1,2,3]dithiazole derivative. Cyclopentathiophen-4-one oximes reacted with S_2Cl_2 and $^iBu_3N$ to give thienocyclopenta[1,2,3]-dithiazoles that showed UV−vis spectral bands that depended on the positions of the ring fusion.

Introduction

Benzo-bridged bis[1,2,3]dithiazoles have been intensely studied as starting materials for the preparation of radical cations and charge-transfer salts in the search for novel radical ion conductors.[1] These compounds were synthesized by cyclization from the corresponding diaminobenzenedithioles and disulfur dichloride (S_2Cl_2) because the usual approach by using the Herz reaction[2] (i.e., the condensation of aromatic amines and S_2Cl_2 to give the corresponding 1,2,3-benzodithiazolium chlorides) only gave traces of the chlorinated benzobis[1,2,3]dithiazoles.[1] Notwithstanding, a naphthobis[1,2,3]dithiazole has been successfully obtained by using a Herz reaction, through

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(2) Koutentis, P. A.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **2002**, 315−319.

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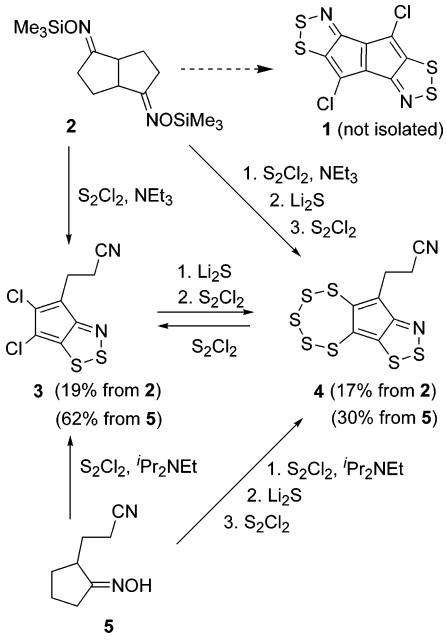
a double cyclocondensation of 2,6-diaminonaphthalene with S_2Cl_2, and then was electro-oxidized to a conductive, π-stacked mixed valence salt.[3] Both synthetic approaches have been successfully employed for the preparation of antiaromatic pyridine-bridged bis[1,2,3]dithiazoles with zwitterionic ground states.[4] Therefore, reactions of 2,6-diaminopyridine or 2,6-diaminopyridine-3,5-dithiol and S_2Cl_2 were common procedures for the synthesis of chlorinated zwitterionic bis[1,2,3]dithiazolopyridine derivatives that have been successively alkylated and reduced to the corresponding resonance-stabilized dithiazolo−dithiazolyl radicals.[4] The nonchlorinated derivatives have also been prepared by double Herz condensations from N-alkylated 2,6-diaminopyridinium salts with S_2Cl_2 and characterized as prototypal dithiazolo−dithiazolyl radicals.[5] The substituent effects on solid-state structures and properties of these neutral radicals have been studied, and several new magnetic and conducting materials have been reported in this series.[6] Despite the importance of all these compounds in the preparation of new molecular conductors and radical-based magnets, the number of bis[1,2,3]dithiazole derivatives hitherto known is so far very scarce. A small number of aryl- and heteroaryl-fused 1,2,3-dithiazoles are also known.[2,7] In view of the increasing importance of mono- and bis[1,2,3]-dithiazoles not only as new materials but also by their potential agricultural applications,[8] new synthetic methods are needed. We have developed several new methods for the preparation of cyclopenta[1,2,3]dithiazoles,[9] benzo-[1,2,3]dithiazol-6-ones,[10] cyclopenta[1,2]dithioles, and cyclopenta[1,2]thiazines[11] by the reaction of cyclic oximes with S_2Cl_2 and cyclopenta[1,2,6]thiadiazines by the reaction of cyclic enaminonitriles and sulfur dichloride (SCl_2).[12] In 2001, we reported that in the search for tetracyclic bis-dithiazole **1** we instead discovered an unusual and unexpected one-pot synthesis of a new polycyclic pentathiepin by an extensive domino sequence, including a vinylogous sulfur-assisted Beckmann fragmentation, that

SCHEME 1



was involved in the one-pot conversion of the bicyclo-[3.3.0]octan-2,6-dione[13] dioxime by S_2Cl_2 into two dithiazole derivatives, the cyanoethyl[1,2,3]dithiazole **3** and the tricyclic pentathiepin **4** (Scheme 1).[14] Pentathiepins have attracted much attention recently because of their remarkable stability and their potent biological activity.[15] Therefore, the possibility to synthesize polyheterocyclic 1,2,3-dithiazoles as well as the initial purpose of synthesizing bis[1,2,3]dithiazoles were both attractive goals to be thoroughly developed. In this paper, we report the synthesis of new bis[1,2,3]dithiazolo-*s*-indacenes as well as pentathiepino, tetrathiino, and thieno[1,2,3]dithiazole derivatives, and also several new polysubstituted dithiazoles, by the reactions of monocyclic and polycyclic cyclopentanone oximes with S_2Cl_2.

Results and Discussion

In an attempt to synthesize tetracyclic bis-dithiazole **1**, we treated the silylated bicyclo[3.3.0]octan-2,6-dione[16] dioxime **2** (Scheme 1) with S_2Cl_2 (20 equiv) and Et_3N (20 equiv) at 4 °C for 3 days. Chromatography gave the purple product **3** (19%) and a very minor mauve product **4** (1−3%). Compound **3** was shown by HRMS spectroscopy and microanalysis to have two chlorine atoms but only two sulfur atoms and also showed a cyanoethyl group in its IR and $^1H/^{13}C$ NMR spectral data; therefore, structure **3** was assigned to the purple product that was confirmed by single crystal X-ray diffraction. Half of the expected biscyclopenta[1,2,3]dithiazole was formed, but the second carbocyclic ring unexpectedly opened to give rise to the cyanoethyl group.

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(4) (a) Beer, L.; Oakley, R. T.; Mingie, J. R.; Preuss, K. E.; Taylor, N. J.; Cordes, A. W. *J. Am. Chem. Soc.* **2000**, *122*, 7602−7603. (b) Beer, L.; Brusso, J. L.; Cordes, A. W.; Haddon, R. C.; Itkis, M. E.; Kirschbaum, K.; MacGregor, D. S.; Oakley, R. T.; Pinkerton, A. A.; Reed, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 9498−9509.
(5) (a) Beer, L.; Brusso, J. L.; Cordes, A. W.; Godde, E.; Haddon, R. C.; Itkis, M. E.; Oakley, R. T.; Reed, R. W. *Chem. Commun.* **2002**, 2562−2563. (b) Beer, L.; Britten, J. F.; Brusso, J. L.; Cordes, A. W.; Haddon, R. C.; Itkis, M. E.; MacGregor, D. S.; Oakley, R. T.; Reed, R. W.; Robertson, C. M. *J. Am. Chem. Soc.* **2003**, *125*, 14394−14403.
(6) Beer, L.; Britten, J. F.; Clements, O. P.; Haddon, R. C.; Itkis, M. E.; Matkovich, K. M.; Oakley, R. T.; Reed R. W. *Chem. Mater.* **2004**, *16*, 1564−1572.
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(9) (a) Plater, M. J.; Rees, C. W.; Roe, D. G.; Torroba, T. *Chem. Commun.* **1993**, 293−294. (b) Plater, M. J.; Rees, C. W.; Roe, D. G.; Torroba, T. *J. Chem. Soc., Perkin Trans. 1* **1993**, 769−774.
(10) Polo, C.; Ramos, V.; Torroba, T.; Rakitin, O. A.; Rees, C. W. *Tetrahedron* **1998**, *54*, 223−232.
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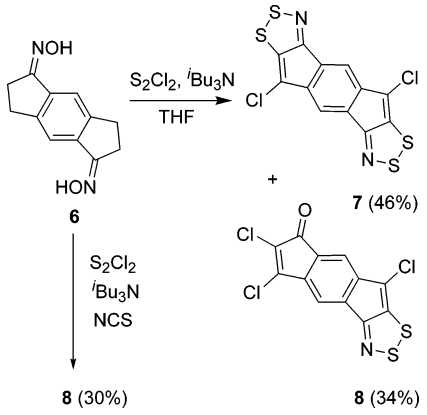
(13) Hagedorn, A. A.; Farnum, D. G. *J. Org. Chem.* **1977**, *42*, 3765−3767; Pérard-Viret, J.; Rassat, A. *Tetrahedron: Asymmetry* **1994**, *5*, 1−4.
(14) Macho, S.; Rees, C. W.; Rodríguez, T.; Torroba, T. *Chem. Commun.* **2001**, 403−404.
(15) Konstantinova, L. S.; Rakitin, O. A.; Rees, C. W. *Chem. Rev.* **2004**, *104*, 2617−2630.
(16) (a) Hagedorn, A. A.; Farnum, D. G. *J. Org. Chem.* **1977**, *42*, 3765−3767. (b) Pérard-Viret, J.; Rassat, A. *Tetrahedron: Asymmetry* **1994**, *5*, 1−4.

The single-crystal X-ray diffraction of **3** afforded two independent orthogonal dispositions for the molecule, giving four molecules in the crystal cell around the center of symmetry. Two main interactions of molecules in the crystal could be found. First, mutual interactions between the nitrile groups and both dithiazole sulfur atoms of two molecules placed the heterocyclic systems in parallel dimeric dispositions. Second, interactions between two antiparallel nitrogen−sulfur groups from two close molecules placed the heterocyclic systems of both molecules in the same plane (see Figure S1 in the Supporting Information).

The mauve product was shown, from analytical and spectral data, to have five extra sulfur atoms in place of the two chlorine atoms in **3** and also showed a cyanoethyl group, but now one of the methylenes gave a complex signal in the ^{1}H NMR spectrum compounded of two quintets; each quintet was the sum of two overlapping triplets, suggesting the presence of conformational isomers. Therefore, structure **4**, having a slowly inverting chairlike pentathiepin ring fused to a cyclopentadithiazole, was assigned. The pentathiepin ring in **4** was presumably formed by substitution of the chlorine atoms in **3** by some nucleophilic sulfur species, then the seven-membered ring could then be completed by S_2Cl_2 in a reaction related to the known formation of benzopentathiepins from aromatic dithioles and S_2Cl_2.[15] We proved this hypothesis by performing the reaction of dioxime **2** with S_2Cl_2 as before, but after 3 days we added Li_2S (20 equiv), stirred the mixture for 6 h at 4 °C, and then added more S_2Cl_2 (20 equiv) at −20 °C and stirred for 45 min at room temperature. Chromatography gave a higher yield (17%) of **4** as the only isolable product. A starting material possessing the hydrocarbon framework of **3** should be more suitable for a rational synthesis of dithiazoles **3** and **4**, so we started from 2-(2-cyanoethyl)-cyclopentanone oxime[17] **5** to improve the yields. Oxime **5** was treated at −20 °C with S_2Cl_2 (10 equiv) and *N*-ethyldiisopropylamine (Hünig's base, 10 equiv) in THF, and then the mixture was left to warm at 4 °C and stirred for 3 days to give **5** (62%). Some minor byproducts, apparently chlorinated and dehydrogenated derivatives of **5**, by EIMS, were also obtained, as well as **4** as traces. In the same way, oxime **5** was treated at −20 °C with S_2Cl_2 (10 equiv) and Hünig's base (10 equiv) in THF, then the mixture was left to warm at 4 °C and stirred for 3 days, treated with Li_2S (20 equiv) in THF at 4 °C for 8 h, and then treated again with S_2Cl_2 (20 equiv) at −20 °C and left to warm at room temperature for 30 min, all in one pot to give the pentathiepin **4** (30%) as the only product. Additionally, compound **4** was transformed into **5** when treated with an excess of S_2Cl_2 for 1 day at 4 °C; therefore, longer reaction periods in the last part of the reaction were avoided. Compounds **3** and **4** are the first cyclopentadithiazole derivatives having a functionalized aliphatic chain; the inertness of the cyanoethyl group in the reaction with S_2Cl_2 is in strong contrast to the reactivity of the oxime group and the cyclopentane moiety, which is completely chlorinated and dehydrogenated in the reaction conditions, leaving the lateral chain untransformed.

SCHEME 2



A way to avoid the vinylogous sulfur-assisted Beckmann fragmentation that gave **3** could be by inserting an additional benzo-fused ring between the two cyclopentane rings. In this way, the aromaticity of the expected products should be kept intact, and the steric hindrance between functional groups should be prevented. The 1,5- and 1,7-*s*-hydrindacenediones,[18] which were obtained together in a convenient procedure from *s*-hydrindacen-1-one[19] in turn obtained from 5-(3-chloropropionyl)Indane,[20] were found suitable for this purpose. Therefore, 1,5-*s*-hydrindacenedione dioxime **6** was treated at −20 °C with S_2Cl_2 (10 equiv) and triisobutylamine (10 equiv) in THF, and then the mixture was left to warm at 4 °C and stirred for 3 days. Column chromatography of the residue gave two green products, **7** (45%) and **8** (34%) (Scheme 2). The main product **7** showed only a singlet signal at δ 8.4 in its ^{1}H NMR spectrum and six signals in its ^{13}C NMR spectrum, therefore corresponding to a highly symmetric structure that was characterized by HRMS and microanalysis as **7**. The second product **8** showed instead two singlet signals in its ^{1}H NMR spectrum and more than six signals in its ^{13}C NMR spectrum, one of them at δ 196, indicating the presence of a ketone group, confirmed by IR. HRMS and microanalysis pointed to a structure **8**, in which an initial cyclopentanone oxime moiety was transformed into a dithiazole group and the other one was hydrolyzed and chlorinated to give the dichlorocyclopentenone moiety.

Product **8** was obtained as the only reaction product by treating 1,5-*s*-hydrindacenedione dioxime **6** with S_2Cl_2 (20 equiv), triisobutylamine (20 equiv), and *N*-chlorosuccinimide (NCS, 40 equiv) in THF at 4 °C for 3 days and then at room temperature for an additional 3 days but in lower yield (30%). A purple product that was shown by EIMS to be a thioketone related to **8**, whose IR evolved on standing for a few days to an IR similar to the one of **8**, was also obtained as traces. A mechanism that explains the formation of compounds **7** and **8** is shown in Scheme 3. The sequence of nucleophilic attack of an oxime group to S_2Cl_2 (**6** → **i**), followed by deprotonation (**i** → **ii**), ring closing (**ii** → **iii**), deprotonation (**iii** → **iv**), dehydration (**iv** → **v**), and chlorination (**v** → **vi**),

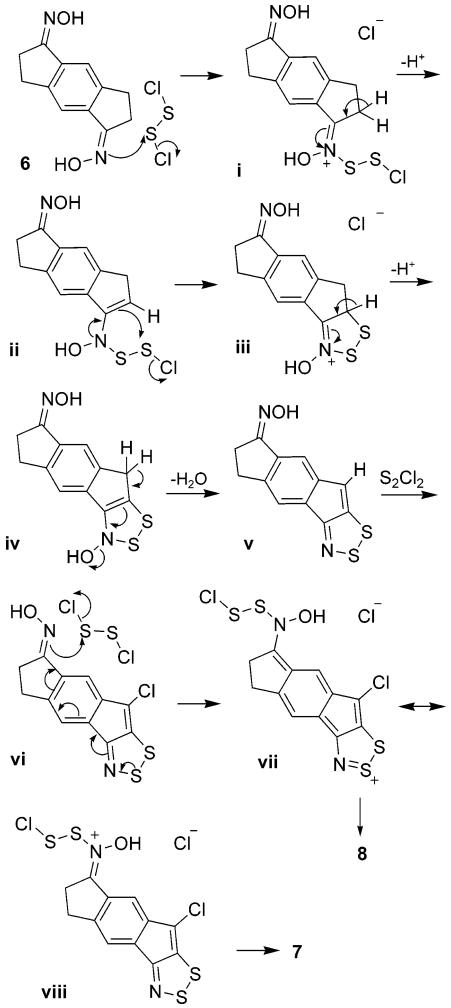
(17) Vijn, R. J.; Arts, H. J.; Maas P. J.; Castelijns, A. M. *J. Org. Chem.* **1993**, *58*, 887−891.

(18) Seeger, D. E.; Lathi, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1996**, *108*, 1251−1265.

(19) Woodward, R. B.; Hoye, T. R. *J. Am. Chem. Soc.* **1977**, 99, *24*, 8007−8014.

(20) Urban, F. J.; Jasys, V. J.; Raggon, J. W.; Buzon, R. A.; Hill, P. D.; Eggler, J. F.; Weaver, J. D. *Synth. Commun.* **2003**, *33*, 2029−2043.

SCHEME 3



followed by nucleophilic attack to S_2Cl_2, should give a delocalized intermediate having two main canonical forms **vii** and **viii**. Form **viii** is suitable for an analogous sequence of reactions to give **7**, but **vii** is not suitable for a ring closing reaction, therefore being chlorinated and hydrolyzed to give **8**.

The isolation of compound **8** as a reaction product clearly indicated that under the reaction conditions, the formation of the second dithiazole group was as probable as the chlorination and hydrolysis of the expected intermediate **vii** ↔ **viii**. In fact, under highly chlorinating conditions, the second reaction pathway is favored. Here, steric factors are not relevant, so the most probable reason is a lower reactivity of the second cyclopentanone oxime due to the para-conjugation of both oxime groups. These circumstances do not apply to the 1,7-*s*-hydrindacenedione dioxime **9**, in which the ortho-conjugation of oximes does not deactivate the groups; therefore, we should find a more predictable behavior. In fact, treating **9** with S_2Cl_2 (10 equiv) and triisobutylamine (10 equiv) in THF at 4 °C for 3 days, we obtained, after column chromatography, the purple product **10** (75%) shown by spectroscopy and microanalysis to be an isomer of **7** (Scheme 4). Notwithstanding the similarity of the usual spectra of **7** and **10**, the UV spectra of both compounds were very different, reflecting the different color of each one (Figure 1). It is apparent that the initial metha-

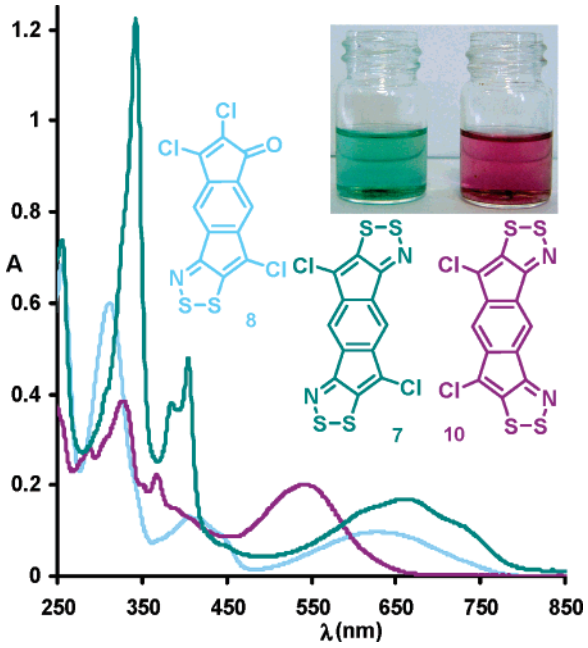
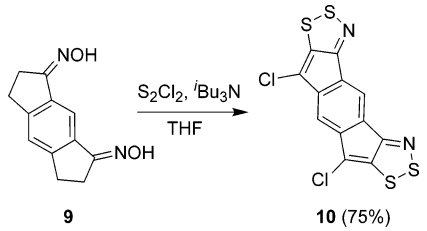


FIGURE 1. UV spectra of compounds **7**, **8**, and **10** and image of solutions of **7** and **10** in CH_2Cl_2.

SCHEME 4



disubstitution of oximes in **9** does not deactivate them in the cyclization reaction to give the dithiazole rings. In addition, the color of **10** (λ_{max} 545 nm, ϵ 2513), similar to the color of **3**, shows that there is no electronic interaction between both dithiazole groups due to the cross-conjugation between them (Figure 1). Instead, the bluish green **7** (λ_{max} 659 nm, ϵ 2650), which is a near-infrared dye, reflects a dipolar interaction between both dithiazole groups along the benzo ring (Figure 2). The same kind of charge-transfer band is found in the UV spectrum of **8** (λ_{max} 628, ϵ 1412), also a near-infrared dye; here, the dithiazole ring acts as the electron donor and the dichlorocyclopentenone moiety as the electron acceptor (Figure 1). Previous examples of different UV spectral absorption of naphtho[1,2,3]dithiazolone isomers are known,[10] showing the great sensitivity of the 1,2,3-dithiazole nucleus to electronic interactions.

We then turned to the study of reactions of ethyl 2-oxocyclopentylpropionate[21] oxime **11**, which is structurally similar to **5**, in reactions with S_2Cl_2. Thus, treatment of **11** with S_2Cl_2 (10 equiv) and triisobutylamine (10 equiv) in THF at 4 °C for 3 days, following a similar procedure employed for **5**, afforded after workup and chromatography of the reaction residue, the expected ethyl 3-(5,6-dichlorocyclopenta[1,2,3]dithiazol-4-yl)pro-

(21) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207−222.

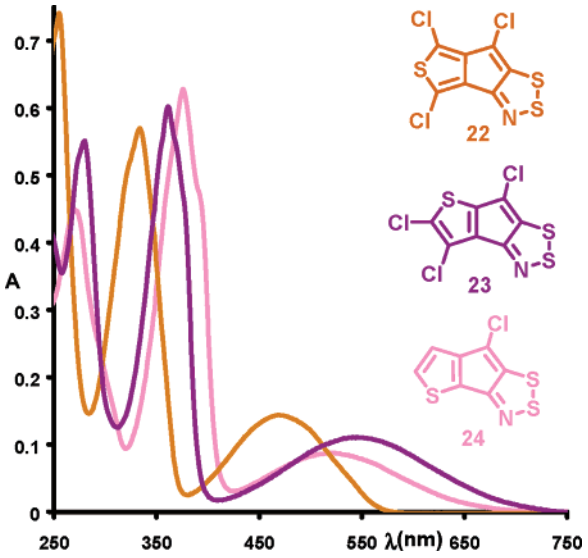
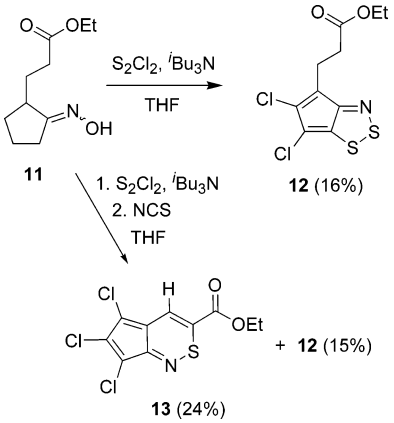


FIGURE 2. UV spectra of compounds **22**–**24**.

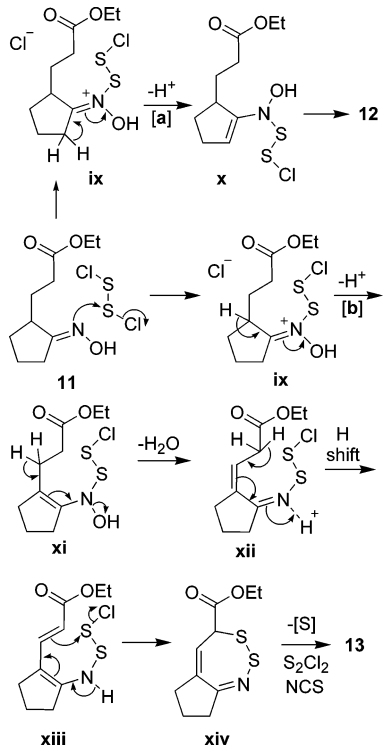
SCHEME 5



pionate **12** as a purple solid but in low yield (16%) (Scheme 5). Several attempts to improve the yield by modifying the reaction conditions did not give any improvement in the yield but afforded a new reaction pathway. Therefore, **11** was treated with S_2Cl_2 (10 equiv) and triisobutylamine (10 equiv) in THF at room temperature for 4 h and under reflux for 15 h, then NCS (20 equiv) was added, and the reaction mixture was heated under reflux for 1 day. Workup and chromatography of the reaction residue gave the purple compound **13** in low yield (24%) as the main product. Product **12** was also obtained in similar yield (15%) to that obtained under previous conditions.

Compound **13** showed an aromatic proton signal at δ 8.6 in its ^{1}H NMR spectrum, an unusual feature in this type of reaction, in addition to the ethoxy group signals. Analytical and HRMS spectral data agreed with the presence of three chlorine atoms and one sulfur atom. This fact, and the lack of aliphatic hydrogen atoms, suggested the presence of a new type of heterocyclic system formed by cyclization of the aliphatic chain and the oxime group through a sulfur bridge between the nitrogen and the carbon atom close to the carboxylic function, giving rise to the ethyl 5,6,7-trichlorocyclopenta-[*c*][1,2]thiazine-3-carboxylate **13**. This structure was later confirmed by single-crystal X-ray diffraction. The molecules of **13** are perfectly planar, with the ethoxycarbonyl group located in the same plane of the heterocyclic system. The molecules are situated in infinite parallel sheets but occupying antiparallel positions in the plane. The sheets are supported by close contacts in the plane between nitrogen and sulfur atoms of two different molecules from one side and close contacts between one chlorine atom of the same molecule and the carbonyl group of a neighboring molecule. The sheets are separated by an average distance of 3.45 Å (see Figure S2 in the Supporting Information).

SCHEME 6

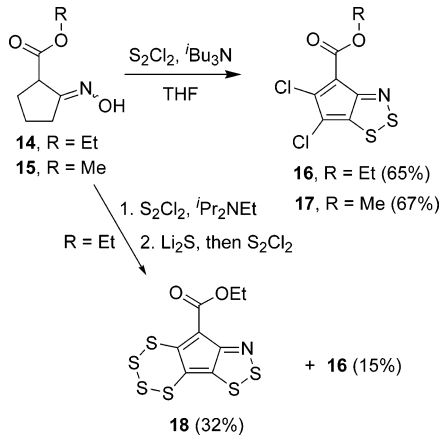


A mechanism that explains the formation of compounds **12** and **13** is shown in Scheme 6. The nucleophilic attack of oxime **11** to S_2Cl_2 (**11** → **ix**) may be followed by deprotonation of the methylene group (**ix** → **x**, path **a**) or the methyne group (**ix** → **xi**, path **b**). Intermediate **x** may undergo a ring closing that eventually should afford **12** by a mechanism similar to the explained in Scheme 3. Intermediate **xi** may undergo deprotonation (**xi** → **xii**), tautomerization (**xii** → **xiii**), and ring closing (**xiii** → **xiv**) to give the intermediate dithiazepine **xiv**, which can easily extrude sulfur to give product **13** after deprotonation and chlorination by the combined action of S_2Cl_2 and NCS.

The cyclopenta[1,2]thiazine family of aromatic heterocycles is scarcely known. In addition to this new 5,6,7-trichlorocyclopenta[*c*][1,2]thiazine **13**, reported examples are the 3,4,5,6,7-pentachlorocyclopenta[*d*][1,2]thiazine,[22] the related benzo-fused 3,4,9-trichloroindeno[2,1-*d*][1,2]-thiazine (a discotic liquid crystal compound),[22] and three four-substituted 3,9-dichloroindeno[1,2-*e*][1,2]thiazine de-

(22) (a) Rakitin, O. A.; Rees, C. W.; Williams, D. J.; Torroba, T. *J. Org. Chem.* **1996**, *61*, 9178–9185. (b) Barberá, J.; Rakitin, O. A.; Ros, M. B.; Torroba, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 296–299.

SCHEME 7



rivatives,[23] although aliphatic examples are known.[24] The example **13** disclosed fills the gap in the knowledge of this type of pseudoazulene heterocycles.

The fact that the ethoxycarbonyl function survived in the reaction conditions, without sulfuration or chlorination, prompted us to study the reactions of simpler ketone oximes having a carboxylic function. Therefore, alkyl 2-hydroxyminocyclopentanecarboxylates **14**−**15**, readily obtained from commercial alkyl 2-oxocyclopentanecarboxylates, were selected to be studied in reactions with S_2Cl_2. In this way, treatment of oximes **14** or **15** with S_2Cl_2 (10 equiv) and triisobutylamine (10 equiv) in THF at 4 °C for 3 days, following a similar procedure employed for **11**, afforded after workup and chromatography of the reaction residue, the expected ethyl or methyl 3-(5,6-dichlorocyclopenta[1,2,3]dithiazol-4-yl)carboxylates **16** (65%) or **17** (67%) as purple solids (Scheme 7). Under these conditions, we did not find traces of byproducts; moreover, the procedure gave clean reaction mixtures of purple color that were easily worked up, being the most general procedure so far described for the preparation of functionalized cyclopenta[1,2,3]dithiazoles from cyclic oximes.

By treating oxime **14** with S_2Cl_2 (10 equiv) and Hünig's base (10 equiv) in THF at 4 °C for 3 days, then with Li_2S (20 equiv) for 8 h at 4 °C, and then followed by S_2Cl_2 (20 equiv) at room temp for 30 min, we obtained, after workup and chromatography of the residue, again compound **16** (15%) in addition to a new reddish purple solid product **18** (32%) that showed ^{1}H and ^{13}C NMR spectral data closely related to the data from **16** but afforded by HRMS an elemental composition of the molecular peak $C_8H_5NO_2S_6$, confirmed by elemental analysis. The highest peak signal in the HRMS spectrum corresponded to an elemental composition $C_8H_5NO_2S_5$; therefore, one sulfur atom was easily lost from the molecule. The data pointed to a structure containing a rare tetrathiine ring bonded to the cyclopenta[1,2,3]dithiazole. In the polysulfane series,[25] [1,2,3,4]tetrathianes are much less common than [1,2,3,4,5]pentathiepanes or [1,2,3]trithiolanes, although some stable derivatives have been reported.[26] To verify the purity and homogeneity of the material (an equilibrated mixture of the pentathiepin and trithiolane derivatives could give the same analytical data), we performed repeated flash column chromatography of the product, checking the result by EIMS, HRMS, and ^{13}C NMR spectroscopy. After every purification step, the mass spectrum of the product gave the same spectral pattern of peaks. The peak corresponding to the pentathiepin derivative was never detected, and the ratio of intensities of the molecular peak to the most abundant peak in MS was constant, as the corresponding lines in the ^{13}C NMR spectrum of the product. Therefore, the 5,6-tetrathiinocyclopenta[1,2,3]dithiazole structure, a new heterocyclic system, was assigned to **18**.

The stability in air of the polycyclic systems obtained was remarkable, in comparison to the nonaromatic counterparts reported in the literature (see Introduction). We initially considered that the presence of several chlorine atoms was a necessary requisite for the stability of the cyclopentadithiazole group, but the products obtained in these reactions show that the presence of electron-donating heterocycles can be compatible with stability in several polycyclic cyclopentadithiazole structures. Seeking new, substituted, and stable heterocyclic derivatives, we studied the reactions of well-known fused thienyl cyclopentanone oximes with S_2Cl_2. Therefore, we can obtain new derivatives bearing donor groups that could give stable products. Therefore, 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one oxime[27] **19**, 5,6-dihydrocyclopenta[*b*]thiophen-4-one[28] oxime **20**, and 4,5-dihydrocyclopenta[*b*]thiophen-6-one[29] oxime **21** were subjected to reaction with S_2Cl_2 (10 equiv) and triisobutylamine (10 equiv) in THF at 4 °C for 3 days, following a similar procedure employed for **5**, **11**, and **14**−**15**. After workup and chromatography of the reaction residue, oxime **19** afforded the expected 4,6,7-trichlorothieno[3,4-*e*]cyclopenta[1,2,3]dithiazole **22** (68%) as an orange solid. Similarly, oxime **23** afforded 4,5,7-trichlorothieno[4,5-*e*]-cyclopenta[1,2,3]dithiazole **23** (73%) as purple crystals, but oxime **22** afforded the monochlorinated 7-chlorothieno-[2,3-*e*]cyclopenta[1,2,3]dithiazole **24** (42%) as purple crystals (Scheme 8). The absence of signals in the ^{1}H NMR spectra of **22** and **23**, their related ^{13}C NMR spectra, and their similar HRMS and microanalytical data clearly indicated that **22** and **23** were all-chlorinated isomeric structures, but **24** showed two coupled aromatic protons in its ^{1}H NMR spectrum, and the rest of data pointed to the monochlorinated structure **24**. The lower yield of this last compound, in comparison to the fair yields obtained for the related structures, could be due to steric or

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(24) See, for example: (a) Hanessian, S.; Sailes, H.; Therrien, E. *Tetrahedron* **2003**, *59*, 7047−7056. (b) Piatek, A.; Chapuis, C.; Jurczak, J. *J. Phys. Org. Chem.* **2003**, *16*, 700−708. (c) Piatek, A.; Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **2002**, *85*, 1973−1988. (d) Doi, J. T.; Bharadwaj, P. K.; Musker, W. K. *J. Org. Chem.* **1987**, *52*, 2581−2584.

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(26) Sauve, A. A.; Groves, J. T. *J. Am. Chem. Soc.* **2002**, *124*, 4770−4778 and references therein.

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(29) (a) Blanchard, P.; Brisset, H.; Illien, B.; Riou, A.; Roncali, J. *J. Org. Chem.* **1997**, *62*, 2401−2408. (b) Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 8310−8319.

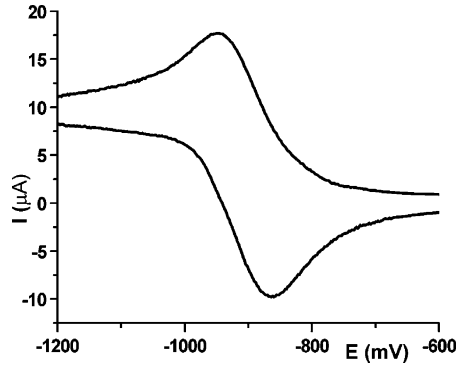
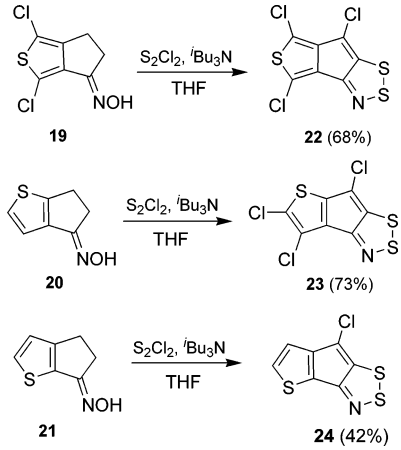


FIGURE 3. Cyclic voltammogram of **13**.

SCHEME 8

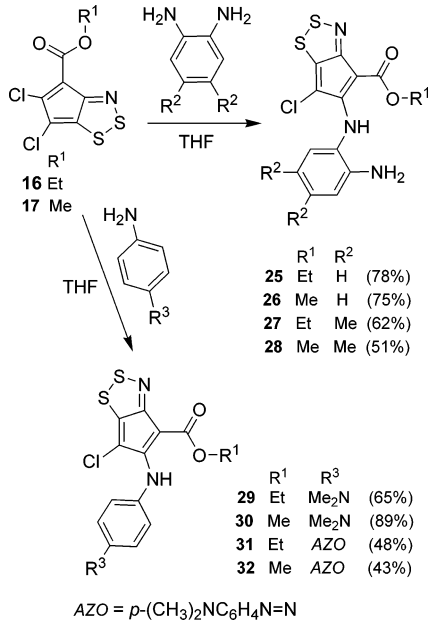


electronic interactions of the sulfur atom close to the oxime group.

The different color of isomers **22** and **23** was surprising. The UV spectra of both isomers and the monochloro derivative **24** are represented in Figure 3. Compound **23** (λ_{max} 549 nm, ϵ 2204) showed a maximum of absorption at a longer wavelength than **22** (λ_{max} 469 nm, ϵ 2885) and related to **24** (λ_{max} 515 nm, ϵ 1742) that showed similar spectral bands in the rest of the UV region. The maximum wavelength of every compound reflects the degree of conjugation in the tricyclic system, especially the cross-conjugation of compound **22** and the more efficient conjugation of compounds **23** and **24** (Figure 2).

Reactivity of Dithiazoles 16−17. With the aim of obtaining new dithiazole derivatives, we subjected ethyl and methyl dithiazolylcarboxylates **16** and **17** to reaction with aromatic amines. We selected phenylenediamine derivatives to test the reactivity of the two chlorine atoms in **16**−**17** with amines. In a typical experiment, compound **16** (1 equiv) was treated with 1,2-phenylenediamine (1 equiv) at room temperature for 3 h in THF. Workup and chromatography of the reaction residue gave a new compound **25** (78%) as an orange solid. Compound **25** showed by HRMS to have one chlorine atom in its structure; consequently, **16** underwent the substitution of one single chlorine atom (Scheme 9). All spectral and analytical data agreed with the monosubstituted derivative **25**, in which the chlorine atom near the ethoxycarbonyl group was substituted by an amine group as the most probable structure. Single-crystal X-ray diffraction of **25** confirmed the assigned structure and proved

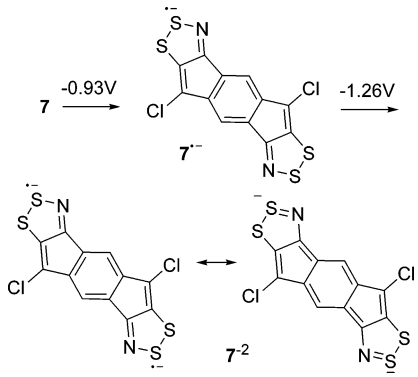
SCHEME 9



unequivocally the substitution position. The X-ray diffraction structure of **25** shows that the ethoxycarbonyl group is coplanar with the heterocyclic ring, which itself forms an angle with the phenyl ring of 32°. The C−N−C angle is 127°, giving rise to an almost planar amine group; therefore, a strong conjugation between the nitrogen and the two aromatic rings exists. The proton bonded to the amine linkage between rings is placed at distances of 2.3 and 2.5 Å from the carbonyl oxygen and the second amine group, respectively. In fact, the ^{1}H NMR spectrum of **25** shows an amine proton at δ 9.9 and the other two amine protons at δ 3.9, indicating that the differences in the electronic environments of every amine group are kept in solution. The crystal is supported by interactions between the two sulfur atoms and the carbonyl oxygen and between the chlorine atom and one aryl hydrogen in the para-position from the amine linkage. The molecules are disposed in antiparallel strings of coplanar cyclopentadithiazole rings supported by the sulfur−oxygen interactions (see Figure S3 in the Supporting Information).

Similarly, compound **19** was treated with 1,2-phenylenediamine (1 equiv) at room temp for 3 h in THF, giving the monosubstituted derivative **26** (75%) as an orange solid. The UV spectra of **25** taken in solvents of different polarities showed a small bathochromic shift from cyclohexane ($\lambda_{máx}$ 400 nm, ϵ 12654) to DMF ($\lambda_{máx}$ 434 nm, ϵ 3766). The corresponding UV spectra of **26** showed lesser variation from cyclohexane ($\lambda_{máx}$ 399 nm, ϵ 18091) to DMF ($\lambda_{máx}$ 412 nm, ϵ 11094); therefore, the solvent polarity showed very little influence in the stabilization of polar conjugated forms of these compounds (see Figures S4 and S5 in the Supporting Information). In turn, compounds **19** and **20** were treated with 4,5-dimethyl-1,2-phenylenediamine (1 equiv) in THF at reflux for 12 h, from which the orange solid products **27** (62%) and **28** (51%) were obtained. Forcing conditions of the reactions of **19** and **20** with 1,2-phenylenediamine or 4,5-dimethyl-1,2-phenylenediamine in high boiling point solvents for longer times always afforded mono-

SCHEME 10



substituted derivatives **25**−**28**. Treatment of **16** and **17** with *N*,*N*-dimethyl-1,4-phenylenediamine (1 equiv) in THF at room temperature for 3 days or with *N*,*N*-dimethyl-4,4′-azodianiline (1 equiv) in THF at reflux for 1 day gave the orange solid products **29**−**32** (43−89%). Despite the different conjugation degree of the anilines employed in these reactions, the physicochemical characteristics were always similar. All these compounds were air-stable crystalline solids whose orange color was in sharp contrast to the deep-purple color of the starting dithiazoles **16**−**17**. Apparently, the aniline group in compounds **25**−**32** disrupts the initial cyclopentadiene to dithiazole charge-transfer band, by conjugation between amine and ester groups. These compounds are derivatives possessing a heterocyclic amino acidic structure related to anthranylic acid, and compounds **31**−**32** hold a photoresponsive azo group that could be interesting for the preparation of photocontrollable self-assemblies.[30]

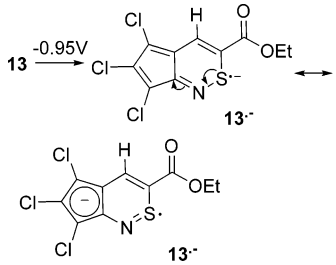
Electrochemical Study. We performed cyclic voltammetry experiments of 5×10^{-4} M solutions of **3**−**4**, **7**−**8**, **10**, **12**−**13**, **16**−**18**, and **22**−**26** in dichloromethane at 20 °C, using Bu_4NPF_6 as a supporting electrolyte in an approximate 0.1 M concentration, a platinum ball as working electrode, platinum wire as an auxiliary electrode, and saturated calomelanes as reference electrodes. The cyclic voltammograms were registered at different scanning velocities, showing irreversible processes for all 1,2,3-dithiazoles studied. Compound **17** did not show any signal in its CV. All compounds, whether mono- or dithiazoles, showed a single oxidation wave in the range of 1.1−1.7 V, except **26** that showed two close oxidation waves probably due to independent oxidations of the dithiazole and the *o*-phenylenediamine moieties. All compounds showed reduction waves in the range of −0.7 to −1.3 V, except for **10**, **18**, and **24**. Four compounds, **4**, **7**, **22**, and **23**, showed two different reduction waves in their CV plots, **4**, **22**, and **23** corresponding to polycyclic dithiazoles that may undergo different reduction processes either in the dithiazole or in the pentathiepino or thiophene moieties. But, the two different reduction waves in the CV of **7** were probably due to successive reductions of the *p*-phenyl-conjugated dithiazole rings to give a unstable quinonic structure (**7** → **7**•$^-$ → **7**$^{-2}$) (Scheme 10), a situation that did not happen in the cross-conjugated dithiazole rings of **10** that did not show any reduction wave in the measured range (Table 1).

(30) Yagai, S.; Karatsu, T.; Kitamura, A. *Chem.*−*Eur. J.* **2005**, *11*, 4054−4063 and references therein.

TABLE 1. Peak Potentials for Cyclic Voltammograms Registered at 100 mV/s

compound	E_p^{ox} (V)	E_p^{red} (V)
3	1.48	−1.03
4	1.55	−0.80, −1.20
7	1.10	−0.93, −1.26
8	1.42	−0.68
10	1.08	
12	1.40	−1.20
13	1.60	−0.95 (reversible)
16	1.70	−0.80
18	1.20	
22	1.27	−1.05, −1.33
23	1.28	−0.97, −1.28
24	1.55	
25	1.10	−1.15
26	0.90, 1.10	−1.10

SCHEME 11



The cyclopenta[1,2]thiazine **13**, the only compound that has no dithiazole nucleus, showed a reversible reduction wave at −0.95 V (Figure 3). This is probably due to an increased ability of the system to stabilize the intermediate cyclopentadienyl radical anion **13**•$^-$ (Scheme 11) in comparison to the lesser ability of the cyclopenta[1,2,3]-dithiazole ring to stabilize the corresponding radical anion, due to the easy opening of the S−S bond.

Conclusions

We have developed one-pot syntheses of several polycyclic cyclopentadithiazoles and one cyclopentathiazine and studied the chemistry of selected new compounds. In addition, we have described the physicochemical characteristics of all new compounds that make them suitable as remarkable new materials, as it is expected for compounds having a heteroaromatic pseudoazulene structure.[31] The abnormally high number of heteroatoms included in the structures confers unusual electronic properties to the reported compounds. The pseudoazulene structures give rise to colorful compounds whose main spectral bands depend on the conjugation between the different heterocycles that form every structure; for this reason, isomeric structures showed different spectral characteristics. For example, bisdithiazole **10** is purple, as are most of the reported dithiazoles, but its isomer **7** is bluish green, absorbing in the near-infrared region. The isomeric thienocyclopentadithiazoles **22**−**23** and the related **24** showed bathochromic displacements of the UV spectral bands depending on the positions of the thiophene ring fusion. Thiophene derivatives are important starting materials for the preparation of conducting polymers and

(31) de Meijere, A.; Schirmer, H.; Stein, F.; Funke, F.; Duetsch, M.; Wu, Y.-T.; Noltemeyer, M.; Belgardt, T.; Knieriem, B. *Chem.*−*Eur. J.* **2005**, *11*, 4132−4148.

electroluminescent materials.[32] The now reported compounds expand the range of monomeric starting materials with potential applications. The cyclopentathiazine **13** showed a reversible reduction wave in its CV at −0.95 V, probably due to stabilization of the anion radical between the cyclopentadiene and the thiazine ring, a feature that can be interesting in relation to redox-active materials. Very few heteroaryl-fused 1,2,3-dithiazoles have been studied as new materials, and their syntheses are based mainly on Apple's salt chemistry and the Herz reaction. The methodology reported in this paper largely expands the synthetic approach to air-stable, crystalline pseudo-heteroazulenes composed of cyclopenta[1,2,3]-dithiazoles fused to several types of heterocycles, and a new cyclopenta[*c*][1,2]thiazine, that are useful as new materials.

Experimental Procedures

Synthesis of Ketones. The 1,7- and 1,5-*s*-hydrindacenediones[18] were obtained together from *s*-hydrindacen-1-one,[19] in turn obtained from 5-(3-chloropropionyl)Indane,[20] following the reported method. Bicyclo[3.3.0]octan-2,6-dione,[16] 2-(2-cyanoethyl)cyclopentanone oxime **5**,[17] 2-oxocyclopentylpropionate,[21] 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one oxime **19**,[27] 5,6-dihydrocyclopenta[*b*]thiophen-4-one,[28] and 4,5-dihydrocyclopenta[*b*]thiophen-6-one[29] were prepared as reported. Ethyl and methyl 2-oxocyclopentanecarboxylates were commercial compounds.

4-Cyanoethyl-5,6-dichlorocyclopenta[1,2,3]dithiazole 3. Method A: Me_3SiCl (1.5 mL, 11.90 mmol) in THF (10 mL) was added under nitrogen to a mixture of bicyclo[3.3.0]-octan-2,6-dione[16] dioxime (0.50 g, 2.97 mmol) and Et_3N (1.7 mL, 11.90 mmol) in THF (15 mL), and the mixture was refluxed for 1 h and stirred at room temperature for an additional 1 h. Then, Et_3N (10.5 mL, 82.75 mmol) in THF (45 mL) was added, the mixture was cooled at −20 °C, and S_2Cl_2 (4.8 mL, 60.27 mmol) was added dropwise. The mixture was then left to warm at 4 °C and stirred for 3 days. Then, the solvent was evaporated under reduced pressure, the residue was suspended in CH_2Cl_2 and filtered on silica gel, the solvent was evaporated again, and the residue was subjected to medium-pressure liquid chromatography (MPLC) (silica gel <230 mesh, hexane, mixture of isomers, to hexane/CH_2Cl_2 65:35 v/v) to obtain **3** (150 mg, 19%). Method B: S_2Cl_2 (2.8 mL, 32.90 mmol) was added under nitrogen to a mixture of 2-(2-cyanoethyl)cyclopentanone oxime[19] **5** (0.50 g, 3.29 mmol) and $^iPr_2NEt$ (5.8 mL, 32.90 mmol) at −20 °C, and then the mixture was left to warm at 4 °C and was stirred for 3 days. Then, the solvent was evaporated under reduced pressure, the residue was suspended in CH_2Cl_2 and filtered on silica to remove insoluble salts, the solvent was evaporated again, and the residue was subjected to MPLC (hexane to hexane/CH_2Cl_2 65:35 v/v) to obtain **3** (535 mg, 62%) as purple crystals (hexane/CH_2Cl_2), mp 108−109 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.17 (t, J = 7.4 Hz, 2H, CH_2), 2.78 (t, J = 7.4 Hz, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.0, 146.6, 129.5, 118.8, 115.0, 110.0, 22.1 (CH_2), 17.2 (CH_2); IR (KBr) $\tilde{\nu}$ 2955, 2249(C≡N), 1555 cm^{-1}; EIMS *m/z* 266 (M^+ + 4, 4), 264 (M^+ + 2, 17), 262 (M^+, 22), 226 (22), 224 (81), 222 (100); HRMS (EI) calcd for $C_8H_4Cl^{37}ClN_2S_2$: 263.9163; found 263.9161; calcd for $C_8H_4Cl_2N_2S_2$: 261.9193; found 261.9188; Anal. Calcd for $C_8H_4Cl_2N_2S_2$: C, 36.51; H, 1.53; N, 10.65. Found C, 36.69; H, 1.38; N, 10.42. Crystal data for **3**, $C_8H_4Cl_2N_2S_2$, M = 263.15, triclinic, $P\bar{1}$, a = 5.699(4) Å, b = 11.841(7) Å, c = 16.163(11) Å, α = 72.67(1)°, β = 89.88(1)°, γ = 88.61(1)°; V = 1040 (1) Å^3, Z = 4, D_{calc} = 1.68 g cm^{-1}, μ(Mo Kα) = 0.981 mm^{-1}. Black needle (0.37 × 0.14 × 0.05) mm^3. 4618 measured reflections, 2986 independent (R_{int} = 0.0178), 2389 observed ($I > 2\sigma(I)$). R_1 = 0.0372, wR_2 = 0.1126 (all data). CCDC 277136.

4-Cyanoethyl-5,6-pentathiepinocyclopenta[1,2,3]-dithiazole 4. Method A: Me_3SiCl (1.5 mL, 11.90 mmol) in THF (10 mL) was added under nitrogen to a mixture of bicyclo-[3.3.0]octan-2,6-dione[16] dioxime (0.50 g, 2.98 mmol) and Et_3N (1.7 mL, 11.90 mmol) in THF (15 mL), and the mixture was refluxed for 1 h and stirred at room temperature for an additional 1 h. Then, Et_3N (10.5 mL, 82.75 mmol) in THF (45 mL) was added, the mixture was cooled at −20 °C, and S_2Cl_2 (4.8 mL, 60.27 mmol) was added dropwise. The mixture was then left to warm at 4 °C and was stirred for 3 days. Then, Li_2S (2.74 g, 59.52 mmol) in THF (25 mL) was added, and the mixture was stirred at 4 °C for 6 h. Then, the mixture was cooled at −20 °C and S_2Cl_2 (4.8 mL, 59.97 mmol) in THF (20 mL) was added and stirred for 10 min at −20 °C, and then the mixture was left to warm at room temperature and was stirred for 45 min. Workup was as stated previously, and MPLC of the residue gave **4** (180 mg, 17%). Method B: S_2Cl_2 (2.8 mL, 32.90 mmol) was added under nitrogen to a mixture of 2-(2-cyanoethyl)cyclopentanone oxime **5**[19] (0.50 g, 3.29 mmol) and $^iPr_2NEt$ (5.8 mL, 32.90 mmol) at −20 °C and then the mixture was left to warm to 4 °C and was stirred for 3 days. Then, Li_2S (3.02 g, 65.80 mmol) in THF (30 mL) was added, and the mixture was stirred at 4 °C for 8 h. Then, the mixture was cooled at −20 °C, and S_2Cl_2 (5.5 mL, 65.80 mmol) in THF (25 mL) was added, and the mixture was left to warm to room temperature and was stirred for 30 min. Workup was as stated previously, and MPLC of the residue gave **4** (348 mg, 30%) as a mauve solid (hexane/CH_2Cl_2), mp 153−154 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.40 (dt, J_1 = 14.6 Hz, J_2 = 7.40 Hz, 1H, 1/2CH_2), 3.24 (dt, J = 14.6 Hz, J = 7.4 Hz, 1H, 1/2CH_2), 2.78 (t, J = 7.4 Hz, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.8, 145.9, 124.8, 120.1, 119.1, 118.6, 23.4 (CH_2), 18.3 (CH_2); IR (KBr) $\tilde{\nu}$ 2923, 2240 (C≡N), 1462 cm^{-1}; EIMS *m/z* 352 (M^+, 16), 288 (79), 248 (100); HRMS calcd for $C_8H_4N_2S_7$: 351.8419; found 351.8423; Anal. Calcd for $C_8H_4N_2S_7$: C, 27.25; H, 1.14; N, 7.95. Found: C, 27.59; H, 1.29; N, 7.68.

5,10-Dichlorobis[1,2,3]dithiazolo[4,5-*a*][4′,5′-*g*]-*s*-indacene 7. S_2Cl_2 (3.70 mL, 46.30 mmol) was added under nitrogen to a mixture of 1,5-*s*-hydrindacenedione[18] oxime **6** (0.50 g, 2.31 mmol) and $^iBu_3N$ (11.20 mL, 46.30 mmol) in THF (75 mL) at −20 °C and then the mixture was left to warm at 4 °C and was stirred for 3 days. Workup was as stated previously, and MPLC (hexane to hexane/CH_2Cl_2 70:30 v/v) of the residue gave **7** (397 mg, 46%) as a bluish green solid (hexane/CH_2Cl_2), mp >300 °C; ^1H NMR (400 MHz, pyridine-d_5) δ 8.44 (s, 2H, ArH); ^{13}C NMR (100 MHz, pyridine-d_5) δ 161.6, 137.6, 126.1, 125.8, 118.9, 113.1; IR (KBr) $\tilde{\nu}$ 1534, 1445, 1190, 725 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 659 (2650), 405 (7494), 385 (5948), 343 (19117), 255 (11548), 232 nm (11894); EIMS *m/z* 376 (M^+ + 4, 32), 372 (M^+, 82), 337 (M^+ − Cl, 12), 308 (M^+ − 2S, 13), 293 (21), 261 (39), 236 (17), 229 (22), 211 (19), 197 (21), 165 (17), 155 (26), 137 (22), 125 (35), 111 (65), 83 (88), 69 (98), 55 (100); HRMS (EI) calcd for $C_{12}H_2N_2S_4{}^{37}Cl_2$: 375.8419; found 375.8442; calcd for $C_{12}H_2N_2S_4Cl^{37}Cl$: 373.8448; found 373.8459; calcd for $C_{12}H_2N_2S_4Cl_2$: 371.8478; found 371.8473. Anal. Calcd for $C_{12}H_2N_2S_4Cl_2$: C, 38.61; H, 0.54; N, 7.50. Found: C, 38.84; H, 0.42; N, 7.37. 5,6,9-Trichloro-[1,2,3]dithiazolo[4,5-*a*]-*s*-indacen-7-one **8** (273 mg, 34%) was also obtained.

Alternative Synthesis of 5,6,9-Trichloro[1,2,3]dithiazolo-[4,5-*a*]-*s*-indacen-7-one 8. S_2Cl_2 (1.48 mL, 18.52 mmol) was added under nitrogen to a mixture of 1,5-*s*-hydrindacenedione[18] oxime **6** (0.20 g, 0.93 mmol), $^iBu_3N$ (4.48 mL, 18.52 mmol), and *N*-chlorosuccinimide (NCS, 4.95 g, 37.04 mmol) in THF (50 mL) at −20 °C, and then the mixture was left to warm at 4 °C and was stirred for 3 days at 4 °C and for an additional 3 days at room temp. Workup was as stated previously, and flash column chromatography (silica gel 230−400 mesh, hex-

(32) See, for example: Dohi, T.; Morimoto, K.; Kiyono, Y.; Maruyama, A.; Tohma, H.; Kita, Y. *Chem. Commun.* **2005**, 2930−2932 and references therein.

ane to hexane/CH_2Cl_2 70:30 v/v) of the residue gave **8** (96 mg, 30%) as a bluish green solid (hexane/CH_2Cl_2), mp >300 °C; ^{1}H NMR (400 MHz, pyridine-d_5) δ 8.45 (s, 1H, ArH), 8.13 (s, 1H, ArH); ^{13}C NMR (100 MHz, pyridine-d_5) δ 195.9, 168.0, 150.6, 149.3, 136.0, 135.0, 133.1, 131.5, 129.2, 114.9, 108.9; IR (KBr) $\tilde{\nu}$ 1709 (C=O), 1515, 1215, 1030, 720 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 628 (1412), 417 (1840), 413 (1842), 407 (1886), 311 (8699), 255 nm (9904); EIMS *m/z* 349 ($M^+ + 4$, 17), 347 ($M^+ + 2$, 46), 345 (M^+, 44), 310 ($M^+ - Cl$, 11), 282 (12), 238 (15), 131 (21), 119 (12), 94 (41), 83 (53), 69 (100); HRMS (IE) calcd for $C_{12}H_2NOS_2{}^{37}Cl_3$: 350.8555; found 350.8548; calcd for $C_{12}H_2NOS_2{}^{37}Cl_2Cl$: 348.8584; found 348.8574; calcd for $C_{12}H_2NOS_2{}^{37}ClCl_2$: 346.8614; found 346.8598; calcd for $C_{12}H_2NOS_2Cl_3$: 344.8643; found 344.8642; Anal. Calcd for $C_{12}H_2NOS_2Cl_3$: C, 41.58; H, 0.58; N, 4.04. Found: C, 41.76; H, 0.43; N, 3.79.

8,10-Dichlorobis[1,2,3]dithiazolo[4,5-*a*][5′,4′-*h*]-*s*-indacene 10. S_2Cl_2 (1.36 mL, 17.24 mmol) was added under nitrogen to a mixture of 1,7-*s*-hydrindacenedione[18] oxime **9** (0.20 g, 0.88 mmol) and ^{i}Bu$_3$N (4.16 mL, 17.24 mmol) in THF (50 mL) at −20 °C, and then the mixture was left to warm at 4 °C and was stirred for 3 days. Workup was as stated previously, and flash chromatography (hexane) of the residue gave **10** (260 mg, 75%) as a deep purple solid (hexane), mp >300 °C; ^{1}H NMR (400 MHz, pyridine-d_5) δ 7.85 (s, 1H, ArH), 7.84 (s, 1H, ArH); ^{13}C NMR (100 MHz, pyridine-d_5) δ 164.4, 140.6, 131.4, 129.3, 120.7, 118.0, 114.5; IR (KBr) $\tilde{\nu}$ 1600, 1540, 1460, 1260, 1100, 1012, 805 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 545 (2513), 368 (2789), 328 (4796), 288 (3546), 248 (4713), 224 nm (5883); HRMS (EI) *m/z* 376 ($M^+ + 4$, 6), 374 ($M^+ + 2$, 27), 372 (M^+, 90), 293 (18), 261 (39), 111 (65), 97 (78), 83 (87), 69 (97), 55 (100); HRMS (EI) calcd for $C_{12}H_2N_2S_4Cl^{37}Cl$: 373.8448; found 373.8492; calcd for $C_{12}H_2N_2S_4Cl_2$: 371.8478; found 371.8466. Anal. Calcd for $C_{12}H_2N_2S_4Cl_2$: C, 38.61; H, 0.54; N, 7.50. Found: C, 38.79; H, 0.46; N, 7.29.

Ethyl 3-(5,6-Dichlorocyclopenta[1,2,3]dithiazol-4-yl)-propionate 12. S_2Cl_2 (2.00 mL, 25.13 mmol) was added under nitrogen to a mixture of 2-oxocyclopentylpropionate[21] oxime **11** (0.50 g, 2.51 mmol) and ^{i}Bu$_3$N (6.10 mL, 25.13 mmol) in THF (100 mL) at −20 °C, and then the mixture was left to warm at 4 °C and was stirred for 3 days. Workup was as stated previously, and flash chromatography (hexane to hexane/CH_2Cl_2 70:30 v/v) of the residue gave **12** (125 mg, 16%) as purple crystals (hexane/CH_2Cl_2), mp 83−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (q, J = 7.2 Hz, 2H, CH_2), 3.06 (t, J = 7.8 Hz, 2H, CH_2), 2.70 (t, J = 7.8 Hz, 2H, CH_2), 1.21 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 164.4, 144.9, 128.4, 117.8, 109.9, 60.5 (CH_2), 33.5 (CH_2), 21.3 (CH_2), 14.1 (CH_3); IR (KBr) $\tilde{\nu}$ 1720 (C=O), 1569, 1216, 1173, 715 cm^{-1}; EIMS *m/z* 309 (M^+, 10), 274 ($M^+ - Cl$, 5), 222 (85), 120 (5), 103 (15), 64 (100); HRMS (EI) calcd for $C_{10}H_9NO_2S_2{}^{37}Cl_2$: 312.9393; found 312.9418; calcd for $C_{10}H_9NO_2S_2{}^{37}ClCl$: 310.9422; found 310.9467; calcd for $C_{10}H_9NO_2S_2Cl_2$: 308.9452; found 308.9483. Anal. Calcd for $C_{10}H_9NO_2S_2Cl_2$: C, 38.72; H, 2.92; N, 4.52. Found: C, 39.00; H, 3.00; N, 4.63.

Ethyl 5,6,7-Trichlorocyclopenta[*c*][1,2]thiazine-3-carboxylate 13. S_2Cl_2 (2.00 mL, 25.13 mmol) was added under nitrogen to a mixture of 2-oxocyclopentylpropionate[21] oxime **11** (0.50 g, 2.51 mmol) and ^{i}Bu$_3$N (6.10 mL, 25.13 mmol) in THF (100 mL) at −20 °C, and then the mixture was left to warm at room temperature, stirred for 4 h, and heated under reflux for 15 h. Then, NCS (6.81 g, 50.26 mmol) was added, and the mixture was heated under reflux for 1 day. Workup was as stated previously, and MPLC (hexane to hexane/CH_2Cl_2 70:30 v/v) of the residue gave **13** (187 mg, 24%) as purple crystals (hexane/CH_2Cl_2), mp 135−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (1H, ArH), 4.48 (q, J = 7.2 Hz, 2H, CH_2), 1.45 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 151.7, 141.4, 132.1, 124.7, 118.6, 112.1, 112.0, 62.7 (CH_2), 14.2 (CH_3); IR (KBr) $\tilde{\nu}$ 1724 (C=O), 1480, 1239, 1068, 757 cm^{-1}; EIMS *m/z* 311 ($M^+ + 2$, 18), 309 (M^+, 13), 283 (58), 281 (51), 237 (30), 201 (47), 131 (44), 94 (97), 69 (100); HRMS (EI) calcd for $C_{10}H_6NO_2S^{37}Cl_3$: 314.9096; found 314.9089; calcd for $C_{10}H_6NO_2S^{37}Cl_2Cl$: 312.9126; found 312.9111; calcd for $C_{10}H_6NO_2S^{37}ClCl_2$: 310.9155; found 310.9141; calcd for $C_{10}H_6NO_2SCl_3$: 308.9185; found 308.9180. Anal. Calcd for $C_{10}H_6NO_2SCl_3$: C, 38.67; H, 1.95; N, 4.51. Found: C, 38.85; H, 1.79; N, 4.42. Crystal data for **13**, $C_{10}H_6Cl_3NO_2S$, M = 310.57, triclinic, $P\bar{1}$, a = 5.671(1) Å, b = 8.698(1) Å, c = 12.308(1) Å, α = 96.964(2)°, β = 90.165(3)°, γ = 90.255(3)°; V = 602.6(1) Å^3, Z = 2, D_{calc} = 1.71 g cm^{-1}, μ(Mo Kα) = 0.919 mm^{-1}. Purple−black prism (0.19 × 0.13 × 0.11) mm^3. 2730 measured reflections, 1715 independent (R_{int} = 0.0185), 1501 observed ($I > 2\sigma(I)$). R_1 = 0.0368, wR_2 = 0.1012 (all data). CCDC 277137. Ethyl 3-(5,6-dichlorocyclopenta[1,2,3]dithiazol-4-yl)propionate **12** (117 mg, 15%) was also obtained.

Ethyl 5,6-Dichlorocyclopenta[1,2,3]dithiazole-4-carboxylate 16. S_2Cl_2 (4.67 mL, 58.44 mmol) was added to a mixture of 2-ethoxycarbonylcyclopentanone oxime **14** (1.0 g, 5.84 mmol) and ^{i}Bu$_3$N (14.14 mL, 58.44 mmol) in THF (45 mL) at −20 °C, and then the mixture was allowed to warm to 4 °C and was stirred for 3 days. Workup was as stated previously, and MPLC (hexane to hexane/CH_2Cl_2 70:30) gave **16** as purple crystals (hexane/CH_2Cl_2), mp 197−198 °C (1.07 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (q, J = 7.2 Hz, 2H, CH_2), 1.41 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 160.7, 155.0, 136.6, 111.5, 108.1, 60.8 (CH_2), 14.4 (CH_3); IR (KBr) $\tilde{\nu}$ 1682 (C=O), 1439, 1275, 1207, 766 cm^{-1}; EIMS *m/z* 285 ($M^+ + 4$, 13), 283 ($M^+ + 2$, 53), 281 (M^+, 72), 253 (17), 236 (100), 209 (66), 175 (21), 106 (21); HRMS (EI) calcd for $C_8H_5NO_2S_2{}^{37}Cl_2$: 284.9080; found 284.9103; calcd for $C_8H_5NO_2S_2{}^{37}ClCl$: 282.9109; found 282.9153; calcd for $C_8H_5NO_2S_2Cl_2$: 280.9139; found 280.9178. Anal. Calcd for $C_8H_5NO_2S_2Cl_2$: C, 34.05; H, 1.79; N, 4.96. Found: C, 34.27; H, 1.68; N, 4.73.

Methyl 5,6-Dichlorocyclopenta[1,2,3]dithiazole-4-carboxylate 17. S_2Cl_2 (5.10 mL, 63.69 mmol) was added to a mixture of 2-methoxycarbonylcyclopentanone oxime **15** (1.0 g, 5.84 mmol) and ^{i}Bu$_3$N (15.41 mL, 63.69 mmol) in THF (45 mL) at −20 °C, and then the mixture was allowed to warm to 4 °C and was stirred for 3 days. Workup was as stated previously, and MPLC (hexane to hexane/CH_2Cl_2 70:30 v/v) of the residue gave **17** as purple crystals (hexane/CH_2Cl_2), mp 193−194 °C (1.14 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 167.7, 161.7, 161.1, 155.4, 111.6, 58.8 (CH_3); IR (KBr) $\tilde{\nu}$ 1679 (C=O), 1445, 1270, 1210, 769, 740 cm^{-1}; EIMS *m/z* 269 ($M^+ + 2$, 15), 267 (M^+, 22), 236 (59), 149 (31), 97 (29), 57 (100); HRMS (EI) calcd for $C_7H_3NO_2S_2{}^{37}Cl_2$: 270.8923; found 270.8963; calcd for $C_7H_3NO_2S_2{}^{37}ClCl$: 268.8953; found 268.8984; calcd for $C_7H_3NO_2S_2Cl_2$: 266.8982; found 266.9013. Anal. Calcd for $C_7H_3Cl_2NO_2S_2$: C, 31.35; H, 1.13; N, 5.22. Found: C, 31.32; H, 1.16; N, 5.00.

Ethyl 5,6-Tetrathiinocyclopenta[1,2,3]dithiazole-4-carboxylate 18. S_2Cl_2 (4.0 mL, 50.2 mmol) was added to a mixture of 2-ethoxycarbonylcyclopentanone oxime **14** (0.86 g, 5.02 mmol) and ^{i}Pr$_2$NEt (8.85 mL, 50.2 mmol) in THF (50 mL) at −20 °C, and then the mixture was allowed to warm to 4 °C and was stirred for 3 days. Then, Li_2S (4.60 g, 100 mmol) in THF (25 mL) was added, and the mixture was stirred for 6 h at 4 °C. Then, S_2Cl_2 (8.0 mL, 100 mmol) in THF (20 mL) was added at −20 °C and the mixture was stirred for 10 min at −20 °C and for 45 min at room temperature. Workup was as stated previously, and flash column chromatography (hexane to hexane/CH_2Cl_2 70:30) of the residue gave **18** as a purple solid (hexane/CH_2Cl_2), mp 166−167 °C (546 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (q, J = 7.2 Hz, 2H, CH_2), 1.41 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C RMN (100 MHz, $CDCl_3$) δ 167.7, 164.8, 161.4, 150.9, 119.9, 115.0, 61.3 (CH_2), 14.4 (CH_3); IR (KBr) $\tilde{\nu}$ 2922, 2852, 1738 (C=O), 1463, 1261, 1103, 801 cm^{-1}; EIMS *m/z* 339 (M^+, 10), 307 ($M^+ - S$, 100), 279 (34), 262 (35); HRMS (EI) calcd for $C_8H_5NO_2S_5{}^{34}S$: 340.8603; found 340.8619; calcd for $C_8H_5NO_2S_6$: 338.8645; found 338.8655. Anal. Calcd for $C_8H_5NO_2S_6$: C, 28.30; H, 1.48; N, 4.13. Found: C, 28.58; H, 1.35; N, 3.94. Compound **16** (213 mg, 15%) was also obtained.

4,6,7-Trichlorothieno[3,4-*e*]cyclopenta[1,2,3]dithiazole 22. S_2Cl_2 (1.62 mL, 20.40 mmol) was added to a mixture of 1,3-dichloro-5,6-dihydrocyclopenta[*c*]thiophen-4-one oxime[27] **19** (0.45 g, 2.04 mmol) and $^iBu_3N$ (4.80 mL, 20.40 mmol) in THF (75 mL) at −20 °C, and then the mixture was allowed to warm to 4 °C and was stirred for 3 days. Workup was as stated previously, and flash column chromatography (cyclohexane to hexane/CH_2Cl_2 70:30 v/v) of the residue gave **22** as an orange solid (hexane/CH_2Cl_2), mp 170−171 °C (414 mg, 68%); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.6, 130.9, 128.8, 127.1, 124.5, 113.8; IR (KBr) $\tilde{\nu}$ 1603, 1506, 1290, 750 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 469 (2885); 330 (11129); 253 nm (14545); EIMS *m/z* 305 ($M^+ + 6$, 7), 303 ($M^+ + 4$, 36), 301 ($M^+ + 2$, 89), 299 (M^+, 86), 264 ($M^+ - Cl$, 15), 235 (44), 220 (51), 188 (100), 149 (57), 118 (50), 103 (71), 79 (69); HRMS (EI) calcd for $C_7NS_3{}^{37}Cl_3$: 304.8170; found 304.8179; calcd for $C_7NS_3{}^{37}Cl_2Cl$: 302.8199; found 302.8201; calcd for $C_7NS_3{}^{37}ClCl_2$: 300.8229; found 300.8227; calcd for $C_7NS_3Cl_3$: 298.8258; found 298.8246. Anal. Calcd for $C_7NS_3Cl_3$: C, 27.97; H, 0.00; N, 4.66. Found: C, 28.08; H, not found; N, 4.57.

4,5,7-Trichlorothieno[4,5-*e*]cyclopenta[1,2,3]-dithiazole 23. S_2Cl_2 (2.60 mL, 32.70 mmol) was added to a mixture of 5,6-dihydrocyclopenta[*b*]thiophen-4-one[28] oxime **20** (0.50 g, 3.27 mmol) and $^iBu_3N$ (7.90 mL, 32.70 mmol) in THF (75 mL) at −20 °C, and then the mixture was allowed to warm to 4 °C and was stirred for 3 days. Workup was as stated previously, and flash column chromatography (cyclohexane to hexane/CH_2Cl_2 75:25 v/v) of the residue gave **23** as purple crystals (hexane/CH_2Cl_2), mp 163−164 °C (dec) (716 mg, 73%); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 150.4, 147.8, 134.5, 128.8, 121.8, 108.1; IR (KBr) $\tilde{\nu}$ 1507, 1476, 1298, 1050, 746 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 549 (2204); 359 (11793); 277 nm (10840); EIMS *m/z* 303 ($M^+ + 4$, 19), 301 ($M^+ + 2$, 48), 299 (M^+, 45), 268 (21), 266 (76), 264 (100), 235 (8), 223 (22), 191 (24), 189 (35), 186 (13), 154 (26), 103 (13), 79 (13); HRMS (EI) calcd for $C_7NS_3{}^{37}Cl_3$: 304.8170; found 304.8172; calcd for $C_7NS_3{}^{37}Cl_2$-Cl: 302.8199; found 302.8187; calcd for $C_7NS_3{}^{37}ClCl_2$: 300.8229; found 300.8230; calcd for $C_7NS_3Cl_3$: 298.8258; found 298.8244. Anal. Calcd for $C_7NS_3Cl_3$: C, 27.97; H, 0.00; N, 4.66. Found: C, 28.16; H, not found; N, 4.49.

7-Chlorothieno[2,3-*e*]cyclopenta[1,2,3]dithiazole 24. S_2Cl_2 (2.50 mL, 31.37 mmol) was added to a mixture of 4,5-dihydrocyclopenta[*b*]thiophen-6-one[29] oxime **21** (0.48 g, 3.14 mmol) and $^iBu_3N$ (7.60 mL, 31.37 mmol) in THF (75 mL) at −20 °C, and then the mixture was allowed to warm to 4 °C and was stirred for 3 days. Workup was as stated previously, and flash column chromatography (cyclohexane to hexane/CH_2Cl_2 70:30 v/ v) of the residue gave **24** as purple crystals (hexane/CH_2Cl_2), mp 183−184 °C (dec) (305 mg, 42%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 5.0 Hz, 1H, ArH), 7.10 (d, J = 5.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 158.1, 135.1, 133.2 (CH), 119.6, 118.1 (CH), 110.5; IR (KBr) $\tilde{\nu}$ 3084, 1538, 1468, 1125, 760, 705 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 515 (1742); 374 (12409); 267 nm (8804); EIMS *m/z* 233 ($M^+ + 2$, 45), 231 (M^+, 100), 199 (4), 167 (14), 155 (47), 120 (39); HRMS (EI) calcd for $C_7H_2NS_3{}^{37}Cl$: 232,9008; found 232.9001; calcd for $C_7H_2NS_3Cl$: 230.9038; found 230.9035. Anal. Calcd for $C_7H_2NS_3Cl$: C, 36.28; H, 0.87; N, 6.04. Found: C, 36.39; H, 0.76; N, 5.87.

Synthesis of Derivatives 25−32. General Procedure. Compounds **16** (107 mg, 0.38 mmol) or **17** (102 mg, 0.38 mmol) were treated with 1,2-phenylenediamine (41 mg, 0.38 mmol) in THF (20 mL) at room temp for 3 h, with 4,5-dimethyl-1,2-phenylenediamine (52 mg, 0.38 mmol) in THF (20 mL) at reflux for 12 h, with *N*,*N*-dimethyl-1,4-phenylenediamine (52 mg, 0.38 mmol) in THF (20 mL) at room temp for 1 day, and with *N*,*N*-dimethyl-4,4′-azodianiline (91 mg, 0.38 mmol) in THF (20 mL) at reflux for 1 day. Then, the solvent was evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 (20 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (3 × 15 mL), the aqueous layer was extracted with ethyl acetate (2 × 20 mL), and the organic extracts were combined, dried (Na_2SO_4), filtered, and evaporated. Flash column chromatography (hexane/CH_2Cl_2 80:20 v/v to hexane/CH_2Cl_2 40:60 v/v) of the residue gave products **25**−**32**.

Ethyl 5-[*N*-(2-Aminophenyl)amino]-6-chlorocyclopenta-[1,2,3]dithiazole-4-carboxylate 25. Orange crystals (hexane/CH_2Cl_2), mp 173−174 °C (105 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H, NH), 7.14 (m, 2H, ArH), 6.77 (mrH), 4.43 (q, J = 7.0 Hz, 2H, CH_2), 3.90 (s, 2H, NH_2), 1.42 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.4, 146.8, 143.2, 128.9 (CH), 128.1, 127.1 (CH), 123.0, 118.3 (CH), 115.7 (CH), 104.7, 60.0 (CH_2), 14.8 (CH_3); IR (KBr) $\tilde{\nu}$ 3390 and 3227 (NH_2), 1634 (CO), 1424, 1286, 1230, 1065, 720, 690 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 408 (16820); (C_6H_6) 411 (8564); (C_5H_5N) 412 (15236); (cyclohexane) 400 (12654); (DMF) 434 (3766); (MeOH) 399 nm (9315). EIMS *m/z* 355 ($M^+ + 2$, 9), 353 (M^+, 20), 307 (1), 279 (100), 271 (43), 244 (13), 121 (95), 93 (27), 79 (34), 77 (11); HRMS (EI) calcd for $C_{14}H_{12}N_3O_2S_2{}^{37}$-Cl: 355.0030; found 355.0015; calcd for $C_{14}H_{12}N_3O_2S_2Cl$: 353.0059; found 353.0052; Anal. Calcd for $C_{14}H_{12}N_3O_2S_2Cl$: C, 47.52; H, 3.42; N, 11.88. Found: C, 47.49; H, 3.37; N, 11.75. Crystal data for **25**, $C_{14}H_{12}ClN_3O_2S_2$, M = 353.84, monoclinic, *C*2/c, a = 13.913(6) Å, b = 8.713(4) Å, c = 26.063(12) Å, β = 102.622(9)°, V = 3083(2) Å^3, Z = 8, D_{calc} = 1.52 gcm^{-1}, μ(Mo Kα) = 0.528 mm^{-1}. Orange plate, (0.17 × 0.09 × 0.03) mm^3. 6610 measured reflections, 2222 independent (R_{int} = 0.0879), 916 observed ($I > 2\sigma(I)$). R_1 = 0.0598, wR_2 = 0.1200 (all data). CCDC 277138.

Methyl5-[*N*-(2-Aminophenyl)amino]-6-chlorocyclopenta-[1,2,3]dithiazole-4-carboxylate 26. Orange crystals (hexane/CH_2Cl_2), mp 183−184 °C (97 mg, 75%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H, NH), 7.15 (m, 2H, ArH), 6.76 (m, 2H, ArH), 3.94 (s, 3H, CH_3), 3.90 (s, br, 2H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 160.9, 146.9, 143.2, 135.3, 129.0 (CH), 128.4 (CH) 122.8, 118.3 (CH), 115.7 (CH), 104.7, 51.3 (CH_3); IR (KBr) $\tilde{\nu}$ 3390 and 3222 (NH), 1639 (C=O), 1455, 1404, 1235, 774 cm^{-1}; UV−vis (CH_2Cl_2) $\lambda_{máx.}$ (ϵ) 407 (19809); (C_6H_6), 410 (16176); (C_5H_5N) 412 (19436); (cyclohexane) 399 (18091); (DMF) 412 (11094); (MeOH) 404 nm (19014). EIMS *m/z* 341 ($M^+ + 2$, 33), 339 (M^+, 64), 307 (75), 279 (100), 271 (87), 244 (53), 228 (48), 215 (29), 200 (29), 180 (50), 106 (23), 103 (43), 91 (32), 80 (43), 76 (26); HRMS (EI) calcd for $C_{13}H_{10}N_3O_2S_2{}^{37}$-Cl: 340.9873; found 340.9897; calcd for $C_{13}H_{10}N_3O_2S_2Cl$: 338.9903; found 338.9906. Anal. Calcd for $C_{13}H_{10}N_3O_2S_2Cl$: C, 45.95; H, 2.97; N, 12.37. Found: C, 46.04; H, 3.00; N, 12.39.

Ethyl 5-[*N*-(2-Amino-4,5-dimethylphenyl)amino]-6-chlorocyclopenta[1,2,3]dithiazole-4-carboxylate 27. Orange crystals (hexane/CH_2Cl_2), mp 211−212 °C (90 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H, NH), 6.87 (s, 1H, ArH), 6,59 (s, 1H, ArH), 4.42 (q, J = 6.7 Hz, 2H, CH_2), 2.21 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.42 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.0, 146.5, 140.6, 137.4, 130.9, 129.2 (CH), 126.6, 125.0, 120.7, 117.3 (CH), 104.7, 59.9 (CH_2), 19.7, 18.7, and 14.8 (3 × CH_3); IR (KBr) $\tilde{\nu}$ 3350 and 3214 (NH), 1631 (C=O), 1433, 1289, 1227, 1052, 770 cm^{-1}; EIMS *m/z* 383 ($M^+ + 2$, 5), 381 (M^+, 12), 307 (70), 299 (24), 91 (37), 83 (48), 77 (33), 29 (100); HRMS (EI) calcd for $C_{16}H_{16}N_3O_2S_2{}^{37}Cl$: 383.0343; found 383.0311; calcd for $C_{16}H_{16}N_3O_2S_2Cl$: 381.0372; found 381.0360. Anal. Calcd for $C_{16}H_{16}N_3O_2S_2Cl$: C, 50.32; H, 4.22; N, 11.00. Found: C, 50.15; H, 3.98; N, 10.89.

Methyl 5-[*N*-(2-Amino-4,5-dimethylphenyl)amino]-6-chlorocyclopenta[1,2,3]dithiazole-4-carboxylate 28. Orange crystals (hexane/CH_2Cl_2), mp 181−182 °C (71 mg, 51%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, br, 1H, NH), 6.87 (s, 1H, ArH), 6.59 (s, 1H, ArH), 3.94 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.15 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.3, 147.1, 140.6, 137.6, 129.2 (CH), 126.7, 125.5, 120.5, 117.3 (CH), 105.0, 94.4, 51.2, 19.7, and 18.7 (3 × CH_3); IR (KBr) $\tilde{\nu}$ 3227 (NH), 1631 (C=O), 1453, 1262, 1227, 773 cm^{-1}; EIMS *m/z* 369 ($M^+ + 2$, 10), 367 (M^+, 23), 335, (30), 307 (100), 91 (63), 77 (58); HRMS (EI) calcd for $C_{15}H_{14}N_3O_2S_2{}^{37}Cl$: 369.0186; found

369.0169; calcd for $C_{15}H_{14}N_3O_2S_2Cl$: 367.0216; found 367.0189. Anal. Calcd for $C_{15}H_{14}N_3O_2S_2Cl$: C, 48.97; H, 3.83; N, 11.42. Found: C, 49.02; H, 3.68; N, 11.22.

Ethyl 6-Chloro-5-{*N*-[4-(dimethylamino)phenyl]amino}-cyclopenta[1,2,3]dithiazole-4-carboxylate 29. Orange crystals (hexane/CH_2Cl_2), mp 175−176 °C (94 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H, NH), 7.12 (d, J = 8.9 Hz, 2H, ArH), 6.68 (d, J = 8.9 Hz, 2H, ArH), 4.41 (q, J = 7.1 Hz, 2H, CH_2), 2.99 (s, 6H, 2 × CH_3), 1.42 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 160.2, 149.5, 147.5, 127.3 (CH), 125.7, 123.7, 112.0 (CH), 104.7, 94.2, 59.8 (CH_2), 40.5 (CH_3), 14.9 (CH_3); IR (KBr) $\tilde{\nu}$ 3329 (NH), 1617 (C=O), 1525, 1350, 1227, 817; EIMS *m/z* 383 (M^+ + 2, 11), 381 (M^+, 27), 335 (100), 77 (11); HRMS (EI) calcd for $C_{16}H_{16}N_3O_2S_2{}^{37}Cl$: 383.0343; found 383.0353; calcd for $C_{16}H_{16}N_3O_2S_2Cl$: 381.0372; found 381.0377. Anal. Calcd for $C_{16}H_{16}N_3O_2S_2Cl$: C, 50.32; H, 4.22; N, 11.00. Found: C, 50.28; H, 4.18; N, 10.73.

Methyl 6-Chloro-5-{*N*-[4-(dimethylamino)phenyl]-amino}cyclopenta[1,2,3]dithiazole-4-carboxylate 30. Orange crystals (hexane/CH_2Cl_2), mp 227−228 °C (124 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H, NH), 7.13 (s, 2H, ArH), 6.69 (s, 2H, ArH), 3.93 (s, 3H, CH_3), 2.99 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 160.6, 149.6, 147.2, 127.3 (CH), 125.5, 111.9 (CH), 105.2, 94.3, 87.3, 51.1 (CH_3), 40.5 (CH_3); IR (KBr) $\tilde{\nu}$ 3309 (NH), 1621 (C=O), 1525, 1450, 1224, 1075, 773 cm^{-1}; EIMS *m/z* 369 (M^+ + 2, 10), 367 (M^+, 23), 335 (M^+ − S, 100), 292 (13), 167 (21), 119 (11), 58 (80); HRMS (EI) calcd for $C_{15}H_{14}N_3O_2S_2{}^{37}Cl$: 369.0186; found 369.0202; calcd for $C_{15}H_{14}N_3O_2S_2Cl$: 367.0216; found 367.0233. Anal. Calcd for $C_{15}H_{14}N_3O_2S_2Cl$: C, 48.97; H, 3.84; N, 11.42. Found: C, 48.87; H, 3.81; N, 11.36.

Ethyl 6-Chloro-5-{4-[4-(dimethylamino)phenylazo]-phenylamino}cyclopenta[1,2,3]dithiazole-4-carboxylate 31. Orange crystals (hexane/CH_2Cl_2), mp 195−196 °C (88 mg 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H, NH), 7.88 (m, 4H, ArH), 7.35 (d, J = 9.1 Hz, 2H, ArH), 6.77 (d, J = 9.1 Hz, 2H, ArH), 4.43 (q, J = 7.2 Hz, 2H, CH_2), 3.10 (s, 6H, 2 × CH_3), 1.43 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.4, 152.5, 151.4, 143.6, 137.8, 129.9, 126.9, 126.1 (CH), 125.1 (CH), 124.7, 122.7 (CH), 122.0, 111.5 (CH), 53.4 (CH_2), 40.3 (CH_3), 14.1 (CH_3); IR $\tilde{\nu}$ (KBr) 3327 (NH), 1600 (C=O), 1521, 1508, 1450, 1368, 1313, 1060, 814 cm^{-1}; EIMS *m/z* 485 (M^+, 2), 148 (9), 135 (27), 120 (100), 105 (19), 94 (93), 77 (26); HRMS (EI) calcd for $C_{22}H_{20}N_5O_2S_2{}^{37}Cl$: 487.0717; found 487.0695; calcd for $C_{22}H_{20}N_5O_2S_2Cl$: 485.0747; found 485.0697. Anal. Calcd for $C_{22}H_{20}N_5O_2S_2Cl$: C, 54.37; H, 4.15; N, 14.41. Found: C, 54.46; H, 3.99; N, 14.26.

Methyl 6-Chloro-5-{4-[4-(dimethylamino)phenylazo]-phenylamino}cyclopenta[1,2,3]dithiazole-4-carboxylate 32. Orange crystals (hexane/CH_2Cl_2), mp 255−256 °C (dec) (77 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H, NH), 7.88 (s, 4H, ArH), 7.36 (s, 2H, ArH), 6.77 (s, 2H, ArH), 3.96 (s, 3H, CH_3), 3.10 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.6, 152.5, 151.5, 146.5, 143.6, 138.5, 137.7, 135.2, 130.0, 125.9 (CH), 125.1 (CH), 122.7 (CH), 111.5 (CH), 51.3 (CH_3), 40.3 (CH_3); IR (KBr) $\tilde{\nu}$ 3342 (NH), 1634 (C=O), 1591, 1460, 1395, 1371, 1236, 1087, 803 cm^{-1}; EIMS *m/z* 473 (M^+ + 2, 14), 471 (M^+, 31), 263 (26), 219 (21), 120 (100), 77 (39); HRMS (EI) calcd for $C_{21}H_{18}N_5O_2S_2{}^{37}Cl$: 473.0561; found 473.0551; calcd for $C_{21}H_{18}N_5O_2S_2Cl$: 471.0590; found 471.0531. Anal. Calcd for $C_{21}H_{18}N_5O_2S_2Cl$: C, 53.44; H, 3.84; N, 14.84. Found: C, 53.66; H, 3.68; N, 14.59.

Crystal Structure Determination for Compounds 3, 13, and 25. A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Raw frame data were integrated with the SAINT[33] program. The structures were solved by direct methods with SHELXTL.[34] An empirical absorption correction was applied with the program SADABS.[35] In every structure, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. All calculations were made with SHELXTL.

CCDC 277136, 277137, and 277138 contain the crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK; fax: (+44)1223336033 and e-mail: deposit@ccdc.cam.uk).

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Supporting Information Available: Arrangement of molecules of **3**, **13**, and **25** in the crystal packing, and UV−vis spectra of compounds **25**−**26** taken in cyclohexane, benzene, CH_2Cl_2, methanol, pyridine, and dimethylformamide. Crystallographic information file (CIF) of compounds **3**, **16**, and **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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