

Cyclopentathiadiazines, new heterocyclic materials from cyclic enamionitriles†

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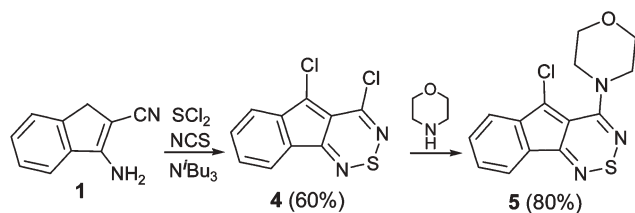
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Indene and cyclopentene enamionitriles were reacted with SCl_2 , tBu_3N and NCS to give the first cyclopenta[1,2,6]thiadiazines that showed unusual characteristics, one as a NIR dye and another as a liquid crystal.

Polycyclic 1,2,6-thiadiazine 2,2-oxides have been studied intensely because of their practical use and economic advantage.¹ Bentazone, a benzothiadiazine 2,2-dioxide, is a well-known herbicide² and pyrazino[2,3-*c*][1,2,6]thiadiazine 2,2-dioxides³ or benzothieno[3,2-*a*]thiadiazine 2,2-dioxides⁴ have shown pharmaceutical properties. In contrast, very few unoxidized polycyclic 1,2,6-thiadiazines are known,¹ probably because of the lack of convenient synthetic approaches. All reported polycyclic 1,2,6-thiadiazines were prepared from preformed 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one or its 4-dicyanomethylene derivative,⁵ with the exception of naphtho- and naphthobis [1,2,6]thiadiazines.⁶ We have developed several new methods for the preparation of cyclopenta[1,2,3]dithiazoles, cyclopenta[1,2]dithioles and cyclopenta[1,2]thiazines by the reactions of simple saturated ketoximes with disulfur dichloride.⁷ We thought that a related procedure could be suitable for the one-pot preparation of 1,2,6-thiadiazines. In this paper, we report the selective preparation of the first cyclopentand benzocyclopentathiadiazines from cyclic enamionitriles. The readily available 3-amino-1*H*-indene-2-carbonitrile⁸ **1**, 2-amino-3*H*-indene-1-carbonitrile⁹ **2** and 2-aminocyclopent-1-enecarbonitrile¹⁰ **3**, containing an enamionitrile moiety, were selected as starting materials and subjected to a reaction with SCl_2 , *N*-chlorosuccinimide (NCS) and triisobutylamine.¹¹ Compound **1** afforded the crystalline orange-red solid **4** (60%) (Scheme 1). Compound **4** showed four aromatic protons in its ¹H NMR spectrum and a molecular formula of $\text{C}_{10}\text{H}_4\text{Cl}_2\text{N}_2\text{S}$ in the HRMS, which is consistent with the formation of a thiadiazine ring accompanied by dehydrogenation and chlorination of the

cyclopentathiadiazine moiety. The structure of **4** was confirmed by single crystal X-ray diffraction¹² and by its chemical properties. Reaction of **4** with morpholine (1 equiv.) gave **5** (80%), which was fully characterized by spectroscopy, microanalysis, and by single crystal X-ray diffraction¹² (Fig. 1), showing that only the 3-chloro was selectively substituted. The UV spectra in CH_2Cl_2 of **4** ($\lambda_{\text{max}} = 453 \text{ nm}$, $\epsilon = 1809$) and **5** ($\lambda_{\text{max}} = 469 \text{ nm}$, $\epsilon = 3917$) had similar bands, probably because steric barriers prevented conjugation.

The reaction of **2** with SCl_2 , NCS and tBu_3N in THF afforded the crystalline green solid **6** (45%) (Scheme 2). Compound **6** showed peaks in its ¹H, ¹³C NMR and HRMS spectra similar to those of its isomer **4**, but its UV spectrum showed a large absorption in the near-infrared region ($\lambda_{\text{max}} = 741 \text{ nm}$, $\epsilon = 879$ and $\lambda_{\text{max}} = 823 \text{ nm}$, $\epsilon = 797$ in CH_2Cl_2) (Fig. 2), that did not appear in the UV spectrum of **4** (Fig. 2). In addition, compound **6** showed a broad signal of low intensity in its EPR spectrum, both in CH_2Cl_2 solution and in the solid state, that could not be resolved (Fig. 2). Under the same conditions, compound **4** did not show any signal in its EPR spectrum (Fig. 2). A cyclic voltammogram of **6** showed two one-electron reductions, the first one reversible at -0.63 V (Fig. 2), the second one irreversible at -1.52 V , and one irreversible oxidation at 1.3 V . No clear oxidation or reduction was seen in the CV of **4**, although the CV of **5** showed a reversible oxidation at 1.15 V probably due to oxidation of the morpholine ring. Structure **6** can be formulated as **6a** \leftrightarrow **6b**, a cyclic sulfurdiumide and an *o*-quinodimethane thiadiazine. Compound **6** did not cycloadd to dimethyl acetylenedicarboxylate (as **6b** should



Scheme 1 Preparation of cyclopenta[1,2,6]thiadiazines **4** and **5**.

† Electronic supplementary information (ESI) available: ¹H and ¹³C NMR spectra of **4** and **6**, crystal data and structure refinement for **4**, **5** and **8**, structure of compound **6** and UV spectra and rotational studies. See <http://www.rsc.org/suppdata/cc/b4/b412632g/>
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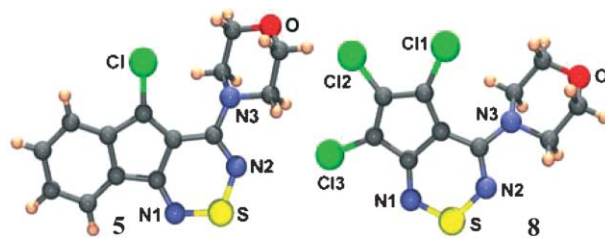
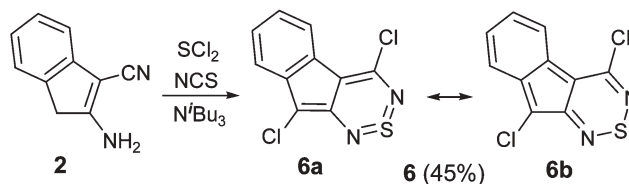


Fig. 1 X-Ray diffraction structures of **5** and **8**.



Scheme 2 Preparation of cyclopenta[1,2,6]thiadiazine **6**.

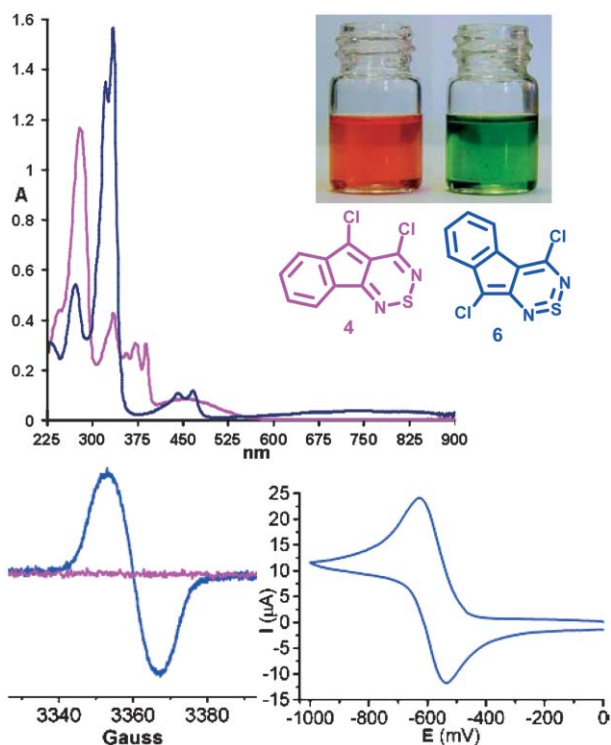
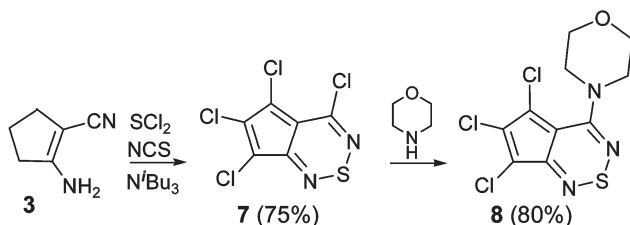


Fig. 2 UV and EPR spectra of **4** (purple) and **6** (blue) and CV of **6**.

do), and reaction with morpholine led to the decomposition of **6**, therefore none of these structures defines compound **6**. The weak near-IR band and the unresolved EPR signal indicates that an intramolecular charge transfer or mixed valence state, that is reversibly reduced, contributes to the structure of **6**. Very few cyclic sulfurdiimides have been described,⁵ and all of them were blue compounds with ambiguous aromatic character.¹³

The reaction of **3** with SCl_2 , NCS and $^i\text{Bu}_3\text{N}$ in THF gave the crystalline red solid **7** (75%), which did not show protons in the ^1H NMR spectrum but showed six signals in the ^{13}C NMR spectrum and a molecular formula of $\text{C}_6\text{Cl}_4\text{N}_2\text{S}$ by MS and microanalysis, consistent with the formation of the cyclopentathiadiazine structure **7** (Scheme 3). Reaction of **7** with morpholine (1 equiv.) gave **8** (80%), which was fully characterized by spectroscopy, microanalysis and single crystal X-ray diffraction¹⁴ (Scheme 3 and Fig. 1). The UV spectra in CH_2Cl_2 of **7** ($\lambda_{\text{max}} = 504 \text{ nm}$, $\epsilon = 573$) and **8** ($\lambda_{\text{max}} = 501 \text{ nm}$, $\epsilon = 3443$) had similar bands. Upon cooling after melting on a hot stage polarizing microscope, compound **7** exhibited strong birefringence indicative of liquid crystallinity (Fig. 3). Differential scanning calorimetry (DSC) showed a mesophase between 111 and 70 °C on cooling. Compound **7** is



Scheme 3 Preparation of cyclopenta[1,2,6]thiadiazines **7** and **8**.

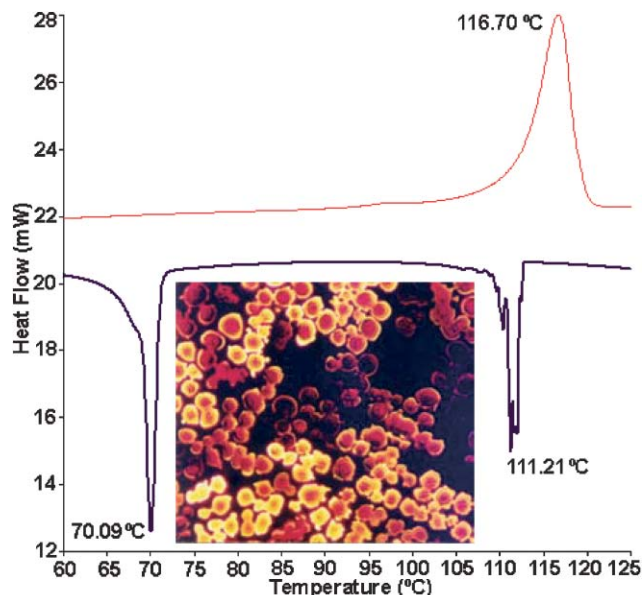


Fig. 3 DSC plot and mesophase at 105 °C of **7**.

therefore a new example of a rare class of liquid crystal pseudoazulenes.¹⁵ The CV of **7** showed a reversible reduction at -0.73 V . Irreversible oxidation or reduction waves were seen in the CV of **8**. In summary, we have described the one-pot synthesis of new cyclopenta[1,2,6]thiadiazines and showed the characteristics of these compounds as new materials. Further examples of this rich chemistry are now being researched.

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- 11 SnCl_2 (20 equiv.) was added at $-20\text{ }^\circ\text{C}$ 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 the residue subjected to flash column chromatography (silica, hexane or hexane- CH_2Cl_2 , 0 \rightarrow 35%) to give, respectively, **4**, mp 166–167 $^\circ\text{C}$ (60%), **6**, mp 155–156 $^\circ\text{C}$ (45%) and **7**, mp 116–117 $^\circ\text{C}$ (75%).
- 12 Single crystal X-ray data were collected on a Bruker SMART 1000 CCD diffractometer at 293 K using Mo-K α ($\lambda = 0.71073\text{ \AA}$) radiation. Crystal data: **4**, $\text{C}_{10}\text{H}_4\text{Cl}_2\text{N}_2\text{S}$, $M = 255.11$, triclinic, $P\bar{1}$, $a = 6.888(4)$, $b = 8.696(5)$, $c = 9.612(5)\text{ \AA}$, $\alpha = 68.241(9)$, $\beta = 83.001(10)$, $\gamma = 70.332(10)^\circ$, $V = 503.5(5)\text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.68\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.812\text{ mm}^{-1}$. 2285 measured reflections, 1452 independent ($R_{\text{int}} = 0.0217$), 1090 observed ($I > 2\sigma(I)$). $R_1 = 0.0489$, $wR_2 = 0.1375$ (all data). CCDC 250853. **5**, $\text{C}_{14}\text{H}_{12}\text{ClN}_3\text{OS}$, $M = 305.78$, monoclinic, $C2/c$, $a = 16.356(6)$, $b = 11.871(4)$, $c = 15.296(5)\text{ \AA}$, $\beta = 114.333(7)^\circ$, $V = 2706.0(17)\text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.50\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.435\text{ mm}^{-1}$. 5954 measured reflections, 1957 independent ($R_{\text{int}} = 0.0582$), 1363 observed ($I > 2\sigma(I)$). $R_1 = 0.0509$, $wR_2 = 0.1368$ (all data). CCDC 247923.‡
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- 14 **8**, $\text{C}_{10}\text{H}_8\text{Cl}_3\text{N}_3\text{OS}$, $M = 324.60$, triclinic, $P\bar{1}$, $a = 7.226(1)$, $b = 8.913(1)$, $c = 10.049(1)\text{ \AA}$, $\alpha = 98.589(3)$, $\beta = 93.045(3)$, $\gamma = 99.426(2)^\circ$, $V = 629.35(15)\text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.71\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.883\text{ mm}^{-1}$. 2820 measured reflections, 1768 independent ($R_{\text{int}} = 0.0145$), 1598 observed ($I > 2\sigma(I)$). $R_1 = 0.0335$, $wR_2 = 0.0988$ (all data). CCDC 247924.‡
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‡ CCDC 247923, 247924 and 250853. See <http://www.rsc.org/suppdata/cc/b4/b412632g/> for crystallographic data in .cif or other electronic format.