From Colorless to Near-Infrared S-Heteroarene Isomers: Unexpected Cycloaromatization of Cyclopenta[b]thiopyran Catalyzed by PtCl₂

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Supporting Information

ABSTRACT: S-heteroarenes containing cyclopenta[b]-thiopyran moieties were synthesized via intramolecular ring-expanding cycloisomerization from 1-acetyl-2-thienyl-substituted precursors catalyzed by PtCl₂. In comparison to the other two S-heteroarene isomers experiencing common 6-endo and 5-exo cyclization processes, the aromatic cyclopenta[b]thiopyran derivative demonstrates intriguing photo-physical and electrochemical properties, such as near-infrared absorption, low oxidation potential, and excellent electrochemical stability. Therefore, this work provides an effective pathway to incorporate cyclopenta[b]thiopyran as building blocks for organic semiconductors with unique properties.

Scheme 1. Different Cyclization Pathways for 1-Acetyl-2-thienyl-Substituted Aromatic Structures

Scheme 2. Synthetic Approach to S-Heteroarene Isomers

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underwent classic 5-exo cyclization and provided isomer 6,12-
unexpectedly, when PtCl2 was used as catalyst, an unusual ring-
ring-expanding cycloaromatization was performed on a
common 6-endo nor 5-exo product was formed in this case as
thiopyran rings in 58% yield. It should be noted that neither
yields of cyclopenta[
f]thiophene derivatives.

The structures of isomeric heteroarenes 6a, 6b, and 6c were
verified by 1H NMR spectroscopies and single-crystal X-ray
diffraction analysis. As shown in Figure S1, a clear singlet peak at
δ = 8.48 ppm can be found in the 1H NMR spectrum of 6a,
which is assigned to the proton signal of H2. Similarly, the 1H
NMR spectrum of 6b displays a triplet peak at δ = 7.20 ppm,
corresponding to the protons H1′ on the vinyl groups. For
isomer 6c, the appearance of the triplet peak at δ = 7.15 ppm is
characteristic of the protons H2′ on the thiopyran rings and
indicates the successful ring enlargement. Moreover, single-
crystal X-ray diffraction analysis (Figure 1) reveals that the π-
conjugated backbones of all the three isomers are coplanar with
dihibited angles between two neighboring aromatic rings less than 3°. Therefore, S-heteroarene isomers 6a, 6b, and 6c
demonstrate offset face-to-face stacking structures with
interplanar distance of 3.40, 3.39, and 3.48 Å, respectively. Isomers 6a and 6b present “fishbone” packing structures, with
the angles between two crossing molecular planes being 83 and
88°, respectively. However, all the π-conjugated backbones of 6c
molecules are parallel to each other. To further investigate the
crystal packing structures, bond length analysis was conducted.
The lengths of S–C bonds in isomers 6a and 6b range from 1.7103 to
1.7405 Å (Tables S3 and S4), which are typical bond lengths for
S–C bonds in the thiophene ring, whereas the lengths of S–C bonds in the thiopyran ring of 6c are 1.7158(18) and
1.7376(17) Å, respectively (Table S5). Similar to those in the
thiopyran rings of isomers 6a and 6b, these values are between
the lengths of well-acknowledged S–C single (1.778–1.882 Å) and
double bonds (1.553–1.611 Å). This suggests that the lone pair electrons of the sulfur atoms are involved in the π-
conjugated backbone of isomer 6c. Furthermore, the lengths of the C–C bonds (Table S5) indicate that the resonance structure
6c is more predominant than the other 6c′ (Figure S5), giving
two specific cyclopla[b]thiopyran moieties in isomer 6c.
Hence, the π-electron numbers of cyclopla[b]thiopyran and those of the skeleton of isomer 6c are calculated to be 10 and 26,
respectively, which perfectly match Hückel’s rule, (4n + 2)π-
electrons. Therefore, it comes to a preliminary conclusion that S-
heteroarene isomer 6c containing cyclopla[b]thiopyran moieties presents aromatic characteristics.

To gain insight into the aromaticity of the resulting S-
heteroarene isomers, nucleus-independent chemical shift (NICS) calculations were performed. As shown in Figure S6, the NICS(1) values of all the rings in isomer 6a are lower than −9.2 ppm, verifying their highly aromatic property. However, the two fulvene rings in isomer 6b display NICS(1) values of −0.7 ppm, which suggest their nonaromaticity.

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Figure 1. ORTEP diagrams with ellipsoid contour probability level of 50% and crystal packings (only carbon and sulfur atoms are shown for clarity) of isomeric S-heteroarenes 6a, 6b, and 6c.
characteristic. Interrestingly, the NICS(1) values for the six rings in isomer 6c are calculated to be \(-6.2, -9.3, -10.7, -10.6, -9.0, \) and \(-6.1\) ppm, respectively. It is notable that the cyclopentadiene rings in isomer 6c present high aromaticity as they are often regarded as antiaromatic.\(^{17}\) Moreover, the NICS(1) values for thiopyran rings in isomer 6c are slightly lower than those for the thiophene rings in isomers 6a and 6b, indicating mediate strong aromaticity of six-membered thiopyran rings.\(^{18}\)

The scope of this Pt-catalyzed ring-expanding cyclization was further investigated by tuning the aryl backbones and the alkyl substituents. As shown in Table S6, a series of mono- and bis-functionalized substrates with benzene, naphthalene, and fluorene as building blocks can be successfully converted to the cyclopenta\([b]\)thiopyran derivatives. Moreover, when the substituent on the acetylene is functionalized by an electron-deficient trifluoromethyl group, this cyclization reaction is deactivated. A probable mechanism of the cycloaromatization has been proposed and is illustrated in Figure 2. The reaction begins with the coordination of PtCl\(_2\) with the alkyne I, activating the alkyne for the following transformation and forms a \(\pi\)-complex II. Then the electron-rich sulfur atom approaches the activated, electron-deficient alkyne to form a new six-membered ring and generates a thienoiou moiety (III). The \(\pi\)-electrons of the alkyne attack the electron-deficient \(\pi\)-carbon on the thienoiou moiety, giving a three-membered ring transition state IV.\(^{19,20}\) Owing to the instability of the sulfur—carbon bond in thienoiou caused by electron deficiency and huge ring tension in the three-membered ring, a ring expansion can easily take place, forming a very thermodynamically stable V. Subsequently, a platinum \(\sigma\)-bond complex VI is generated by [1,2]-alkyl shift from V, followed by the PtCl\(_2\) dissociation to give cyclopenta\([b]\)thiopyran derivative VII. To verify the proposed mechanism, the reaction path and the relative free energies at 383.15 K for all stationary points were calculated using density function theory with LANL2DZ basis set for Pt and 6-31G(d) for other atoms. As shown in Figure S7, all the transition states are confirmed to connect the neighboring intermediates. The model reaction turns out to be exothermic at 27.2 kcal mol\(^{-1}\), and the calculated relative free energies support the instability of transition state IV and the easiness of ring expansion (barrier 7.5 kcal mol\(^{-1}\)). To further support the proposed mechanism, a control experiment was conducted by using 3-methyl-substituted analogue P6 as the precursor (Table S6). The \(^1\)H NMR spectrum of the product indicates that the methyl groups are substituted at the para-positions of the sulfur atoms in the thiopyran rings of T6. Therefore, it proves that the insertion of the carbon atom from the alkylnyl group, which results in the ring expansion of thiophene ring, occurs at the sulfur—carbon bond, while other bonds remain unbroken. Although three isomers contain similar chemical structures, the absorption properties significantly differ from each other. As shown in Figure 3, isomer 6a with six fused aromatic rings only exhibits absorption in the ultraviolet region with the maximum absorption wavelength at 386 nm in dichloromethane (DCM) solution. Under the same conditions, a significant bathochromic shift of 90 nm can be observed for isomer 6b (\(\lambda_{\text{max}} = 476\) nm), which is attributed to the classic nonalternant hydrocarbon absorption.\(^{21}\) Interestingly, isomer 6c demonstrates unusual broad absorption spectra over the whole visible region extending into the NIR range up to 840 nm (\(\lambda_{\text{max}} = 660\) nm). As cyclopenta\([b]\)thiopyran is a \((5\pi + 7\pi)\)-electron system, it is isoelectronic to the familiar azulene, which always displays an absorption band in the NIR region.\(^{22}\) Similar to azulene,\(^{23}\) the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are localized partially in different parts of space in cyclopenta\([b]\)thiopyran (Figure S8). Therefore, the long wavelength absorption of 6c is mainly attributed to the electron transition from HOMO to LUMO, as also revealed by theoretical calculations (Table S12). The absorption edges of isomers 6a, 6b, and 6c locate at 397, 553, and 840 nm, respectively, which indicates that the band gap of the isomers dramatically decreases from 3.12 eV for 6a to 2.24 eV for 6b and further to 1.48 eV for 6c. Correspondingly, isomers 6a and 6b display photoluminescence (PL) maxima at 388 and 547 nm, respectively. However, the emission of 6c is too weak to be detected in the NIR region by the PL spectrometer. Therefore, it can be concluded that the photophysical properties and the energy band gap of S-heteroarene-based organic semiconductors can be easily tuned by varied cyclization reactions from identical starting materials.

\[\text{Figure 2. Proposed mechanism of PtCl}_2\text{-catalyzed ring-expanding cycloaromatization.}\]

\[\text{Figure 3. UV—vis—NIR absorption and PL spectra of S-heteroarene isomers 6a, 6b, and 6c in DCM solutions.}\]
In summary, an unexpected ring-expanding cycloaromatization of cyclopenta[\(b\)]thiopyran from 1-acetyl-2-thienyl derivative catalyzed by PtCl\(_2\) was developed. From an identical precursor, three rigid and planar S-heteroarene isomers were successfully synthesized. Interestingly, the three resulting isomeric S-heteroarenes demonstrated completely different photophysical and electrochemical properties. The NIR absorption, relatively low oxidation potential, and the excellent electrochemical stability will make aromatic cyclopenta[\(b\)]-thiopyran derivatives as promising building blocks for organic semiconductors with unique properties. Our ongoing work is focused on the expansion of the substrate scope and their further applications in optoelectronics.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02546.

Synthesis and characterizations of S-heteroarenes 6a–6c; optimization of the cyclization conditions and scope of the ring-expanding cycloaromatization (PDF)

Accession Codes

CCDC 1579132, 1579137, and 1854147 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Notes**

The authors declare no competing financial interest.