

Communications to the Editor

**A Contribution to the Design of Molecular Switches:
Novel Acid-Mediated Ring-Closing–Photochemical
Ring-Opening of 2,3-Bis(heteroaryl)quinones
(Heteroaryl = Thienyl, Furanyl, Pyrrolyl)**

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Data storage and molecular device applications have stimulated much interest in organic photochromism.^{1,2} Among the many known photochromic systems, derivatives of 1,2-bis(heteroaryl)ethene (heteroaryl = thienyl, furanyl, indolyl, thiazolyl, among others) have received the most attention because of their remarkable fatigue resistance and thermal and chemical stability.^{3,4} Novel molecular devices based on the 1,2-bis(thienyl)ethene system were also developed.⁵

To date, light is the only trigger that will induce the transformation of 1,2-bis(heteroaryl)ethene systems from the switch-opened to the switch-closed state. This restriction limits the range of possible molecular switches that can be designed, it precludes the efficient preparation of large quantities of the switch-closed form of 1,2-bis(heteroaryl)ethenes, and it renders difficult a thorough study of switch-closed structure–activity relationships. Working from the assumption that a quinone moiety incorporated into the molecular switch could impart novel redox and polar characteristics to the switching process, 2,3-bis(thienyl)-, (furanlyl)-, and (pyrrolyl)quinones were synthesized. These constitute a new class of molecular switch that transforms into the switch-closed state efficiently in the presence of strong protic or Lewis acids such as AlCl₃, FeCl₃, and triflic acid (Figure 1).⁶ Visible light induces reformation of the switch-opened state. A key intermediate was characterized spectroscopically, which helped elucidate the mechanism of the acid-induced ring closure.

The synthesis of 2,3-substituted naphthoquinones **1–10** and benzoquinone **11** was straightforward (see Supporting Information), comprising the Stille cross-coupling^{7,8} of an appropriately substituted 3-(tri-*n*-butylstannyl)heterocycle with either 2,3-dibromobenzo- or naphthoquinone. The halo-substituted 2,3-bis(thienyl)quinones **5–7** were prepared from **1** by bromination with NBS or iodination with I₂/HIO₃.

In a fashion similar to the 1,2-bis(thienyl)- and other 1,2-bis(heteroaryl)ethenes, photolysis of 2,3-bis(heteroaryl)quinones **2–11** through a quartz NMR tube (350 nm) slowly established a photostationary state where only 5–30% conversion to the switch-closed state was achieved. Surprisingly, the 5-unsubstituted compound **1** gave no apparent ring closure on photolysis.

In dramatic contrast to the photochemical switching process, when 2,3-bis(thienyl)quinone **3** was exposed to at least 2 equiv

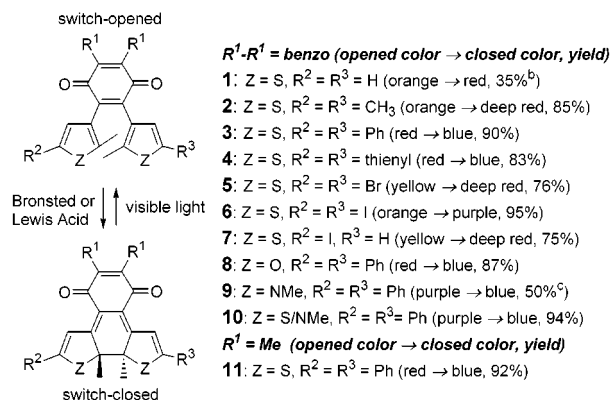


Figure 1. 2,3-Bis(heteroaryl)quinone molecular switch. Yields of the closed form isolated after flash chromatography. ^b45% **1**-opened was recovered. ^c**9**-closed slowly reverted to the opened form at room temperature. After column chromatography, 41% **9**-opened was recovered.

of AlCl₃, FeCl₃, or CF₃SO₃H, a rapid conversion of the red, switch-opened form to a green intermediate ensued. The blue switch-closed form was isolated in high yield after aqueous workup.⁹

To test the generality of this unique acid-promoted molecular switching reaction, compounds **1–11** were exposed to 3 equiv of AlCl₃ in CH₂Cl₂ at room temperature in the dark for 0.5 h followed by an aqueous workup (Figure 1). With the exception of the modest transformations of **1** (35%; 45% opened form recovered) and **9** (50%; 41% opened form recovered), switch-opened compounds **2–8**, **10**, and **11** were transformed into the switch-closed states in very good yields (75–95%). All switch-closed compounds reverted cleanly to the switch-opened state on photolysis with visible light (150 W tungsten lamp). When kept in the dark, all but the 2,3-bis(pyrrolyl)quinone-derived product were readily isolable as stable, pure compounds after chromatography. The reversion of switch-closed 2,3-bis(pyrrolyl)quinone **9** to the opened form on standing in the dark mimics the thermal instability of Irie's related 1,2-bis(indolyl)ethene system.¹⁰ Absorption spectral data for **1–11**, opened and closed, are shown in Table 1. As with other 1,2-bis(heteroaryl)ethene systems, the switched-closed compounds showed strong, substituent-dependent absorptions between 400 and 800 nm.

To better understand the mechanism of this unique process, switch-opened **11** was treated with CF₃SO₃H in CD₂Cl₂ and monitored by NMR. Switch-opened **11** and at least 2 equiv of CF₃SO₃H generated a stable intermediate, **12**, which was transformed to switch-closed **11** upon aqueous workup or on treatment with Et₃N. Conversion was complete within 5 min at room temperature. The same stable intermediate, **12**, was generated upon treatment of switch-closed **11** with 2 equiv of CF₃SO₃H.

Scheme 1 shows a plausible mechanism for acid-induced conversion of the switch-opened to the switch-closed 2,3-bis(thienyl)quinone **11**, proceeding by way of the bis-sulfonium salt intermediate **12**. This mechanism, taking place through analogous bis-onium salts, would apply to the acid-induced closure of all

(9) In the photochemical ring closing process, orbital symmetry control leads to a *trans* disposition of the two methyl groups. The Lewis acid-mediated process is stepwise, not concerted, but also leads to the sterically more favorable *trans* methyl relationship, which was verified by an X-ray crystallographic determination of switch-closed **2**.

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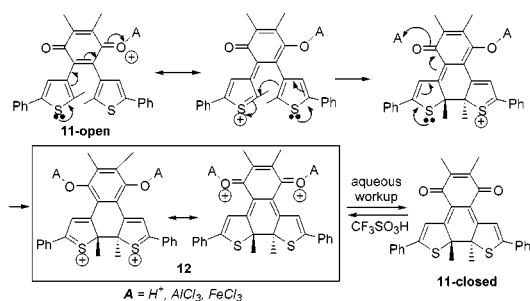
(6) For a related pH-dependent transformation see Shimizu, I.; Kokado, H.; Inoue, E. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1726–1729 and 1730–1734.

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Table 1. UV-Visible Data for 1–11 (Refer to Figure 1 for Structures)

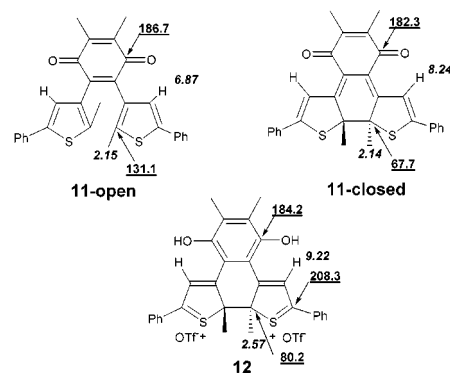
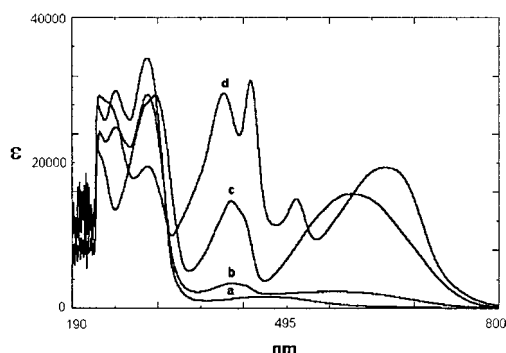
cmpd	λ/nm ($\epsilon \times 10^{-3}/\text{cm}^{-1} \text{M}^{-1}$)
1	opened: 248.5 (30.1), 316.5 (6.55), 419.5 (2.19)
	closed: 231.5 (24.2), 258.0 (22.0), 408.0 (19.9), 496.0 (9.41)
2	opened: 247.5 (32.6), 321.5 (5.98), 449.5 (1.94)
	closed: 233.5 (24.9), 257.0 (22.3), 398.0 (16.7), 507.0 (12.4)
3	opened: 228.5 (26.4), 256.5 (40.2), 292.5 (36.0)
	closed: 227.5 (24.8), 311.0 (35.0), 438.0 (23.7), 580.5 (12.8)
4	opened: 250.5 (36.7), 311.0 (32.9), 452.0 (1.75)
	closed: 240.0 (29.3), 346.0 (26.3), 448.0 (26.1), 645.5 (14.5)
5	opened: 251.0 (32.2), 310.5 (6.39), 424.0 (1.91)
	closed: 260.5 (29.8), 399.0 (17.3), 493.5 (8.86)
6	opened: 251.0 (44.2), 308.5 (8.74), 414.5 (3.14)
	closed: 231.5 (23.5), 267.5 (24.7), 406.0 (16.5), 500.5 (8.39)
7	opened: 250.0 (32.0), 312.0 (6.26), 414.5 (2.20)
	closed: 234.5 (22.7), 259.5 (21.9), 407.5 (17.7), 497.0 (8.38)
8	opened: 227.5 (27.5), 292.5 (47.7), 295.5 (2.72)
	closed: 276.5 (25.4), 301.0 (21.6), 357.5 (27.3), 532.5 (18.4)
9	opened: 253.5 (28.2), 301.5 (30.5), 554.0 (3.08)
	closed: 230.0 (26.1), 280.0 (30.1), 394.5 (19.7), 579.5 (16.5)
10	opened: 254.5 (30.3), 291.0 (30.5), 535.0 (2.51)
	closed: 227.5 (19.6), 281.0 (25.6), 398.5 (14.3), 579.5 (15.4)
11	opened: 227.5 (27.5), 253.5 (30.7), 297.5 (33.6), 463.5 (1.49)
	closed: 227.0 (21.7), 308.5 (29.3), 416.5 (14.7), 587.5 (15.6)

Scheme 1. Proposed Mechanism of Acid-Induced Ring Closure of 2,3-Bis(thienyl)quinone **11**

2,3-bis(heteroaryl)quinone compounds studied herein. The mechanistic requirement of at least 2 equiv of protic or Lewis acid is borne out in the stoichiometric details of the reaction. Catalytic quantities of acid were ineffective, and less than 2 equiv led to incomplete conversion.

Support for the proposed mechanism comes from analysis of the ^1H and ^{13}C NMR spectra of switch-opened and switch-closed **11**, and the $\text{CF}_3\text{SO}_3\text{H}$ -generated intermediate **12**, which are consistent with assignment of a symmetric structure to **12** (Figure 2). The prominent difference in the ^1H NMR spectra of switch-opened and switch-closed **11** is the downfield shift of the sole thiophene proton from 6.87 to 8.24 ppm. Intermediate **12** shows a similar downfield absorption at 9.22 ppm, which suggests that the structure of **12** resembles switch-closed **11**. In the ^{13}C NMR spectra, both switch-closed **11** and intermediate **12** share a similar sp^3 -carbon peak (67.7 and 80.2 ppm). Finally, UV spectra of **11**-opened, **11**-closed, and intermediate **12** (Figure 3) are also consistent with structural similarities between **11**-closed and intermediate **12**.

In contrast to all other 2,3-bis(thienyl)quinone systems studied, the modest yield of acid-induced closure of the 5-unsubstituted

**Figure 2.** ^1H and ^{13}C NMR data of **11**-opened, **11**-closed, and intermediate **12**. ^1H NMR data in italics; ^{13}C NMR data underlined.**Figure 3.** UV spectra of **11**-opened and closed, intermediate **12**, and photostationary state of **11**. (a) **11**-opened; (b) photostationary state of **11**; (c) **11**-closed; (d) intermediate **12**.

2,3-bis(thienyl)quinone **1** left questions concerning the reversibility of the switch-opened–switch closed transformation in the presence of acid. The complicated ^1H NMR spectrum obtained upon treatment of switch-opened **1** with triflic acid in CD_2Cl_2 at room temperature was not informative. In contrast, a pure sample of switch-closed **1** treated with triflic acid in CD_2Cl_2 for 5 min generated a clean ^1H NMR spectrum assigned to a bis-sulfonium salt intermediate. Upon addition of D_2O , the intermediate was transformed back to switch-closed **1** in >95% yield. Of mechanistic significance, this experiment suggests that the switch closing transformation is irreversible under the reaction conditions, that is, once the bis-sulfonium intermediate is formed, it transforms exclusively to the switch-closed form upon aqueous workup.

In conclusion, a novel molecular switch system based upon the 2,3-bis(heteroaryl)quinone core was developed. Strong protic and Lewis acids have a unique effect on this system; they catalyze a ring-closing reaction to generate a switch-closed state in good yield. Reversion to the switch-opened state occurs with visible light.

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Supporting Information Available: A complete description of experimental details, product characterization, and X-ray crystallographic studies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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