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SYNTHESIS AND PROPERTIES OF BIS(1,3-BENZODITHIOLE)-TYPE REDOX SYSTEMS CONTAINING A XYLYL ROTATOR UNIT: A NEW TYPE OF REDOX-RESPONSIVE MOLECULAR ROTOR

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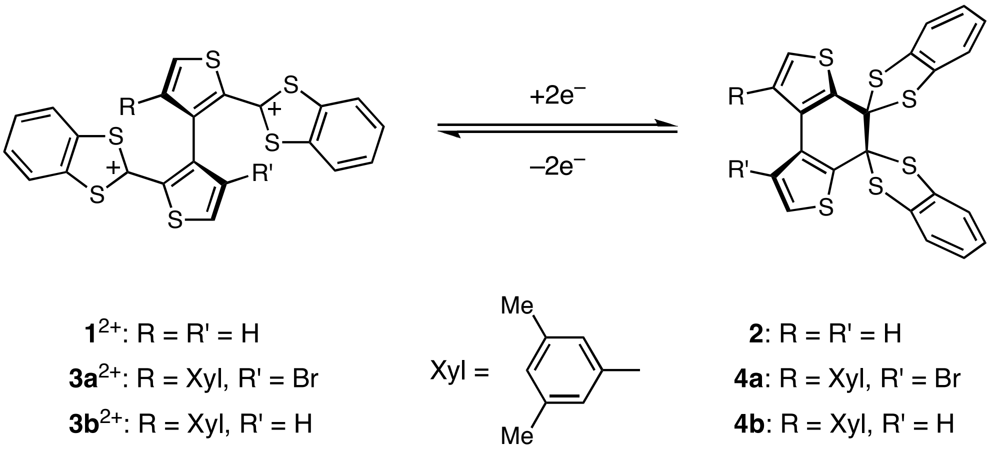
Abstract – A new type of redox-responsive molecular rotors (**3**$^{2+}$/**4**) possessing a xylyl rotator unit have been designed and synthesized. Reduction of **3**$^{2+}$ with zinc gave the corresponding cyclization products (**4**), from which dications (**3**$^{2+}$) were regenerated upon oxidation. Cyclic voltammetry also showed the interconversion between **3**$^{2+}$ and **4**. Variable-temperature ^{1}H NMR measurements revealed that the rotational barriers of the xylyl units in the neutral states (**4**) are higher than those in the dication states (**3**$^{2+}$).

Molecular rotors, molecular systems in which a part (rotator) of a molecule rotates against another part of the molecule, have received considerable attention as artificial molecular machines, and the control of rotary motion in such systems by external stimuli is one of the most important subjects.[1] For this purpose, some stimulus-responsive molecular rotors in which the rate of internal rotation can be regulated by metal ion binding,[2] photochemical isomerization,[3] or redox reaction[4] have been reported. On the other hand, organic redox systems that show reversible structural changes upon electron transfer are of particular interest from the viewpoint of molecular switches and memories.[5,6] Such systems are also attractive as building blocks for construction of molecular machines. In this connection, we recently reported that a redox couple (**1**$^{2+}$/**2**) undergoes intramolecular cyclization and ring-opening reactions upon electron transfer and the dihedral angle of the bithienyl moiety changes largely during the interconversion (Scheme 1).[7] We have now introduced a 3,5-xylyl group as a rotator unit into the redox couple (**1**$^{2+}$/**2**) to construct a novel type of redox-responsive molecular rotors (**3**$^{2+}$/**4**). In this system, the regulation of the rotation of the xylyl unit is based on the structural change of the redox-active unit as shown in Figure 1. In the dication states (**3**$^{2+}$), the molecules are considered to twist around the 3,3'-bithienyl axis[7] and the xylyl rotators can rotate freely apart from the R' group. On the other hand, the rotation in the neutral states (**4**) should be hindered by the R' group. We report here the synthesis, redox properties, and rotational behavior of $\mathbf{3}^{2+}$ and **4**.



Scheme 1

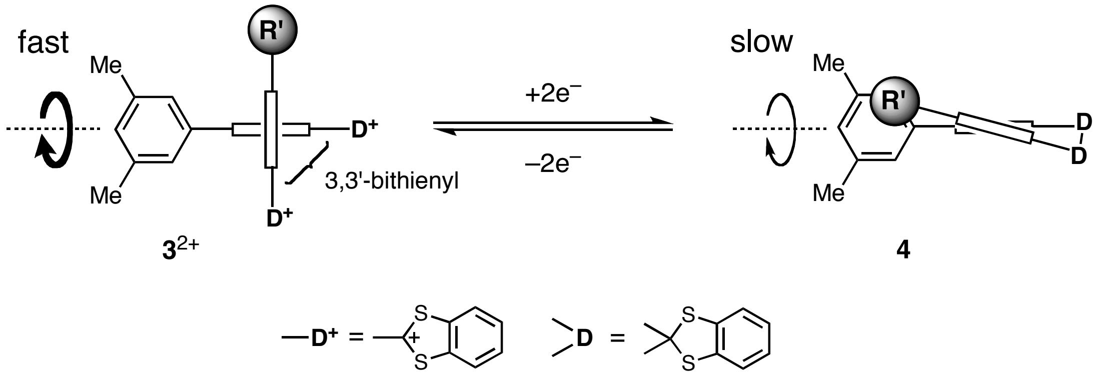
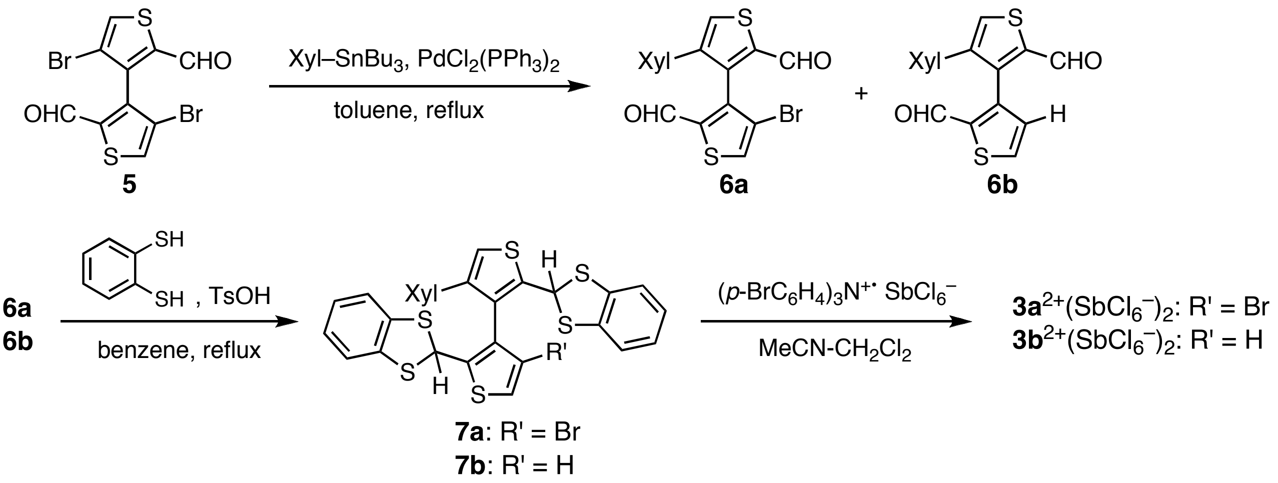


Figure 1. Schematic representation of the molecular rotor ($\mathbf{3}^{2+}$/**4**) viewed along the 3,3'-bithienyl axis.

The dications ($\mathbf{3}^{2+}$) were synthesized as shown in Scheme 2. The Stille coupling reaction of a dibromide (**5**)[8] with xylyltributylstannane gave a monobromide (**6a**) and a reduction product (**6b**) in 31 and 27% yields, respectively. Condensation of **6a,b** with 1,2-benzenedithiol in the presence of *p*-toluenesulfonic acid gave the corresponding bis(1,3-dithiole)s (**7a,b**) in good yields. Treatment of **7a,b** with 4 equiv. of tris(*p*-bromophenyl)aminium hexachloroantimonate [(*p*-$BrC_6H_4)_3N^{+\bullet}SbCl_6^-$] afforded the dications ($\mathbf{3a,b}^{2+}$) as $SbCl_6$ salts in 90 and 88% yields, respectively.[9] The dication salts are air-stable orange solids.



Scheme 2

The interconversion between the dication states ($\mathbf{3}^{2+}$) and the neutral ones (**4**) was confirmed by chemical and electrochemical ways. Reduction of dication salts ($\mathbf{3a,b}^{2+}$)($SbCl_6^-$)$_2$ with zinc in acetonitrile-THF gave the corresponding cyclization products (**4a,b**) as colorless solids in 71 and 69% yields, respectively.[9] The starting dications ($\mathbf{3a,b}^{2+}$) were reproduced by chemical oxidation of **4a,b** with 2 equiv. of (p-BrC_6H_4)$_3N^{+\bullet}SbCl_6^-$ in dichloromethane in 94 and 91% yields, respectively. In the cyclic voltammetry,[10] the neutral states (**4**) exhibited redox waves similar to that of the parent compound (**2**),[7] which are typical for redox systems undergoing reversible C–C bond cleavage and formation upon electron transfer[5,6] (Figure 2). They showed irreversible oxidation peaks at E_{pa} due to the oxidation of **4** to the corresponding dications ($\mathbf{3}^{2+}$). The newly observed irreversible reduction peaks at E_{pc} in the reverse scan can be assigned to reduction of the resulting dications ($\mathbf{3}^{2+}$) to the neutral states (**4**). The redox potentials are as follows: E_{pc}/V: $\mathbf{3a}^{2+}$, +0.15; $\mathbf{3b}^{2+}$, +0.12, E_{pa}/V: **4a**, +1.39; **4b**, +1.34. Any other redox peaks were not observed during the repetition of scans, suggesting that the redox interconversion takes place cleanly. The above results indicate that the substituents on the 4,4'-positions of the bithienyl unit do not interfere the cyclization and ring-opening reactions of the redox core.

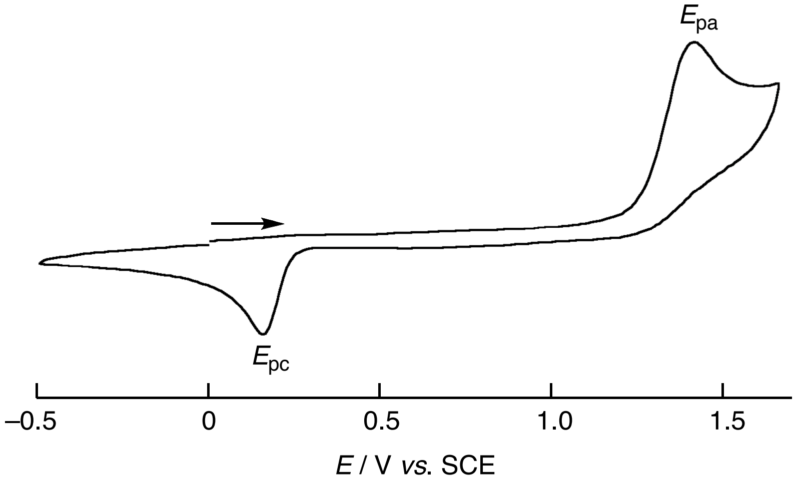


Figure 2. Cyclic voltammogram of **4a** in PhCN.

In order to compare the rotational behavior of the xylyl rotators in the dications ($\mathbf{3}^{2+}$) and neutral molecules (**4**), variable-temperature (VT) ^{1}H NMR measurements (400 MHz) were carried out on the both states. The observed partial spectra of $\mathbf{3a}^{2+}$ and **4a** are shown in Figure 3 as typical examples. The methyl signals of the dications ($\mathbf{3}^{2+}$) in CD_3CN[11] were observed as a singlet at 25 °C and did not show peak separation upon cooling to –40 °C as shown in Figure 3 (a). Similarly, the singlet signals of the 2,6-protons in the xylyl groups remained unchanged at low temperature. These results suggest that the rotational barriers in the dication states ($\mathbf{3}^{2+}$) are quite low and the xylyl rotators rotate freely.[12]

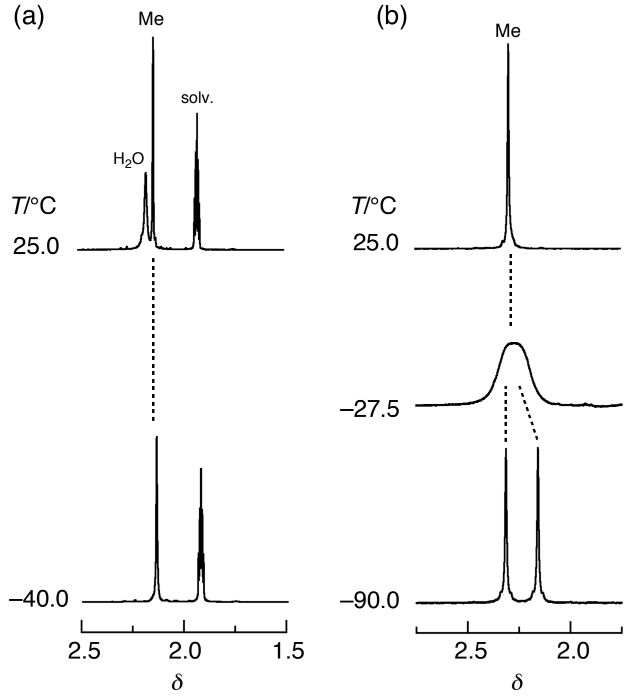


Figure 3. ^{1}H NMR spectra (400 MHz) of the methyl protons of (a) $\mathbf{3a}^{2+}$ in CD_3CN and (b) **4a** in CD_2Cl_2 at various temperatures.

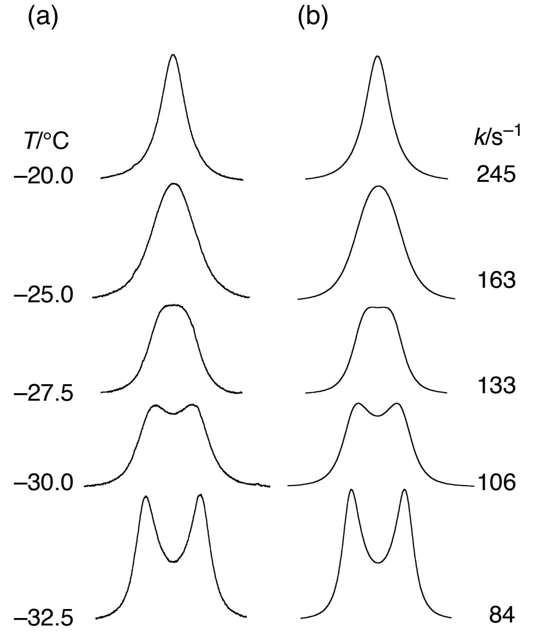
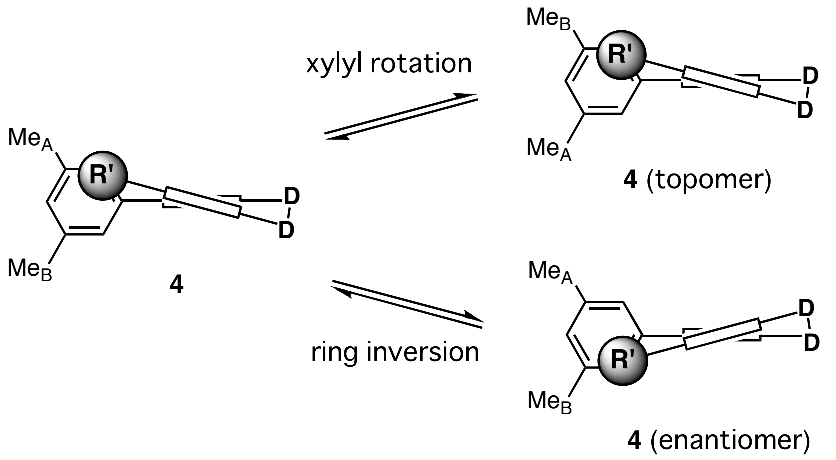


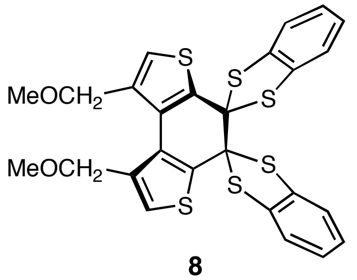
Figure 4. (a) Observed (400 MHz) and (b) simulated ^{1}H NMR spectra of **4a**.

In contrast to the dication states, the methyl signals of the neutral states (**4**) in CD_2Cl_2 resolved into two signals below a decoalescence temperature (**4a**, –27.5 °C; **4b**, –70 °C) [Figure 3 (b)]. The signals of the 2,6-protons also showed the similar lineshape changes. Lineshape analysis[13] on the methyl signals gave rate constants k for the exchange process at various temperatures T (Figure 4). From these data, some activation parameters were calculated as summarized in Table 1. Because of the chiral structure of the neutral molecule (**4**),[7] two dynamic processes causing the exchange of the two methyl groups can be considered as shown in Scheme 3:[14] one is the rotation of the xylyl group (topomerization), the other is the inversion of the central six-membered ring (enantiomerization). Therefore, it is important to determine which process caused the observed lineshape changes. In order to estimate the ring inversion barrier, compound (**8**) possessing diastereotopic methylene protons was prepared[15] and the VT ^{1}H NMR measurements were carried out in DMSO-d_6. The methylene protons were observed as an AB-type quartet (4.46 and 4.62 ppm, J = 12.4 Hz) at room temperature, which coalesced into a singlet at *ca.* 130 °C. The activation free energy for the ring inversion of **8** ($\Delta G^{\ddagger}_{298\,\mathrm{K}}$ = 17.6 kcal mol^{-1}) was obtained by the lineshape analysis. This value is fairly high compared to the $\Delta G^{\ddagger}$ values for **4** (*ca.* 12 kcal mol^{-1}), suggesting that the ring inversion is frozen on the NMR timescale during the VT measurements of **4**. Accordingly, we consider that the decoalescence of the methyl signal upon cooling was caused by deceleration of the xylyl rotation.[16] The higher rotational barrier of **4a** is attributed to the larger atomic radius of bromine atom.

Table 1 Kinetic data of the internal rotation in **4**

	R'	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{298\,\mathrm{K}}$/kcal mol^{-1}
4a	Br	9.9	–8.2	12.3
4b	H	6.3	–17.8	11.6





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Scheme 3

In conclusion, we have synthesized a new type of redox-responsive molecular rotors ($\mathbf{3}^{2+}$/**4**) and succeeded in control of the rotation of the xylyl rotator units. Although the rotational barriers in the dication states ($\mathbf{3}^{2+}$) could not be measured, deceleration of the rotational motion of the xylyl rotators upon reduction of $\mathbf{3}^{2+}$ to **4** could be confirmed by dynamic NMR measurements.

DEDICATION

It is our pleasure to dedicate this paper to Professor Ekkehard Winterfeldt on the occasion of his 75th birthday.

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9. Selected data for **3a**$^{2+}$($SbCl_6^-$)$_2$: mp 232–233 °C (decomp); ^{1}H NMR (400 MHz, CD_3CN, rt) δ 2.14 (6H, s, Me), 6.81 (2H, s, xylyl-2,6-H), 7.03 (1H, s, xylyl-4-H), 7.91–7.95 (4H, m, benzo-H), 8.41–8.45 (4H, m, benzo-H), 8.64 (1H, s, Th-H), 8.67 (1H, s, Th-H); ^{13}C NMR (75 MHz, CD_3CN, rt) δ 21.19, 118.16, 126.75, 127.25, 127.45, 131.88, 132.24, 132.42, 132.69, 133.04, 138.35, 140.01, 140.74, 141.07, 141.64, 142.07, 142.52, 147.71, 186.43, 187.44. For **4a**: mp 152–154 °C; ^{1}H NMR

(400 MHz, $CDCl_3$, rt) δ 2.31 (6H, s, Me), 6.92 (2H, br s, xylyl-2,6-H), 6.95 (1H, br s, xylyl-4-H), 6.97–7.08 (8H, m, benzo-H), 7.25 (1H, s, Th-H), 7.31 (1H, s, Th-H); ^{13}C NMR (100 MHz, $CDCl_3$, rt) δ 21.36, 79.58, 79.98, 109.19, 121.09, 121.21, 121.30, 125.38, 125.66, 125.71, 126.05, 128.22, 128.95, 129.03, 129.51, 131.73, 136.01, 136.29, 137.82, 137.90, 138.12, 142.04, 143.93; MS *m*/*z* (rel. intensity) 652/650 (M^+, 84/79%), 510 (80), 512 (76), 431 (55), 384 (100).

10. The cyclic voltammograms were measured in PhCN with 0.1 M Bu_4NBF_4 using Pt working electrode at a scan rate of 100 mV s^{-1}. Redox potentials were recorded in V *vs*. SCE.
11. Dication salts did not dissolve in CD_2Cl_2. Acetone-d_6 (mp –95 °C) could not be used for the ^1H NMR measurements of the dication salts because of their low solubilities at low temperature and overlapping of the methyl signals and the solvent residual peak.
12. The methyl signals of the compounds (**7a,b**) in CD_2Cl_2 did not show peak separation upon cooling to –90 °C, supporting the low rotational barriers in the ring-open forms ($\mathbf{3}^{2+}$ and **7**).
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15. Compound (**8**) was prepared from the corresponding dialdehyde by a pathway similar to that for the synthesis of **4**.
16. The rotational barriers of **4** are close to those for the aryl rotation in structurally related 1-aryl[4]helicenes ($\Delta G^{\ddagger}$ = *ca*. 13–14 kcal mol^{-1}, Ref. 14a).