Dibenzotetrathiafulvalenes inserted with cycloalkanes and their tricyclic valence isomers: reversible C–C bond making/breaking upon electron transfer

Takanori Suzuki,*[a]† Masahide Kondo,[b] Tatsuo Nakamura,[b] Takanori Fukushima[b] and Tsutomu Miyashi*[b]‡

[a] *Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060, Japan*
[b] *Department of Chemistry, Graudate School of Science, Tohoku University, Sendai 980-77, Japan*

The title TTF derivatives and their tricyclic valence isomers afford the same bicyclic dications upon two-electron oxidation, and the resulting dications regenerate either one or the other of the two isomers selectively upon reduction.

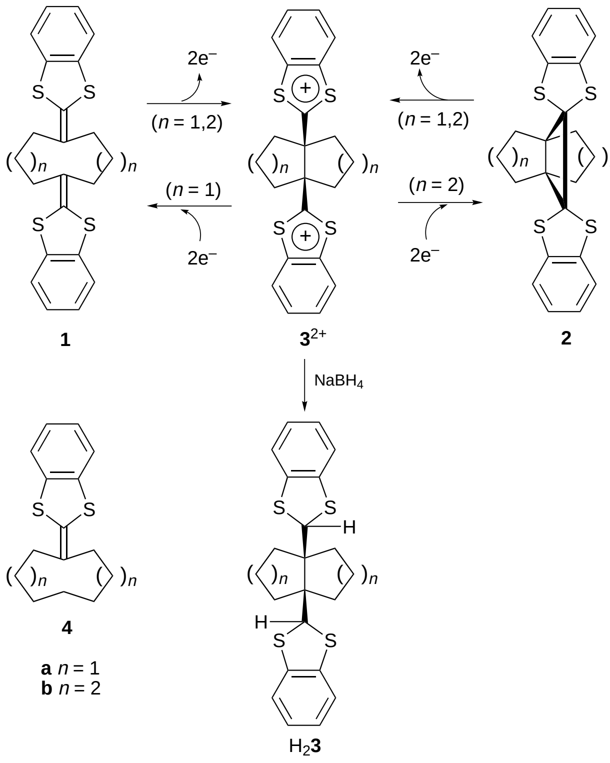
Recently much attention has been focused on molecules whose geometry and properties can be controlled by external signals.[1] From this point of view redox systems that undergo drastic structural changes upon electron transfer (ET) are interesting[2] and might be applicable to the construction of electrochemical switches or molecular devices based on their optical response and bistability. A series of tetraalkylhydrazines[3] was the first group of organic compounds reported to show such a 'dynamic redox' property. Various bicyclic diamines[4] and a variety of dithioethers[5] can also be classified as dynamic redox systems which are further advantageous in regard to the bistability gained by forming a transannular N–N or S–S bond upon ionization. ET-induced transannular C–C bond formation has been well studied in terms of homoconjugation,[6] yet little has been reported on carbocyclic ring systems other than 1,3-dimethylenecyclobutanes. We have designed and prepared the dibenzo-TTF derivatives **1** inserted with cyclooctane or cyclodecane, and their dynamic redox properties are reported herein along with those of their tricyclic valence isomers **2**. It is worth noting that the same bicyclic dications **3**$^{2+}$ were formed upon two-electron oxidation of **1** and **2** by C–C bond formation in the former and breaking in the latter. Furthermore, the resulting dication **3**$^{2+}$ regenerated either **1** or **2** selectively depending on their ring size upon reduction (Scheme 1).

The Wittig–Horner reactions of the corresponding diketones or ketones with 2-methoxyphosphinyl-1,3-benzodithiole[7] afforded **1**§ and monofunctionalized derivatives **4**,§ respectively. Their oxidation potentials (E^{OX}) measured by cyclic voltammetry in CH_2Cl_2 are summarized in Table 1. The donating ability of **1** is much stronger than that of **4**, and even stronger than the fully conjugated dibenzo-TTF, indicating the presence of considerable interaction between the two chromophores in the cyclooctane skeleton.[8]

Upon oxidation with iodine **1a** afforded the dication salt **3a**$^{2+}(I_3^-)_2$ in 86% yield, the structure of which was deduced from the ^{13}C NMR spectrum in Me_2SO [**1a** δ 22.98, 35.58, 121.47, 122.30, 125.46, 126.37, 135.69; **3a**$^{2+}(I_3^-)_2$ δ 25.03, 37.61, 70.33, 116.95, 121.89, 125.53, 134.60]. Formation of a transannular C–C bond was confirmed by X-ray analyses¶ of the salt [1.63(3) Å] as well as its dihydro derivative H_2**3a** [1.584(6) Å] obtained by the reaction of **3a**$^{2+}$ with $NaBH_4$ in quantitative yield. The two benzodithiolium moieties in **3a**$^{2+}$ are arranged in a face-to-face manner in close proximity (Fig. 1), which causes the very large upfield shift of δ_C for C-2 of benzodithiolium (δ 116.95) in **3a**$^{2+}$ from the normal value (δ 182.4). This salt regenerated **1a** in quantitative yield upon reduction with SmI_2, indicating that **1a** and **3a**$^{2+}$ constitute a reversible redox pair undergoing facile C–C bond formation upon ionization and its breaking in the reverse cycle.

For cyclodecane **1b**, dication salt **3b**$^{2+}(I_5^-)_2$ which has a *cis*-decalin structure was formed in quantitative yield by reaction with iodine.‖ Although this low solubility salt decomposed easily when dissolved in Me_2SO, its stereochemistry and the formation of a transannular bond were confirmed by the X-ray analysis¶ of H_2**3b** obtained by the reaction of this salt with $NaBH_4$ in 90% yield. In contrast to the dication **3a**$^{2+}$, this salt did not regenerate the starting diolefin **1b** upon reduction with SmI_2. The reduction product obtained in 92% yield was proven to be the tricyclic isomer **2b** as determined by X-ray analysis.¶

In order to investigate the involvement of such tricyclic isomers in the whole redox cycle, **2a**§ and **2b**§ were prepared by



Scheme 1

Table 1 Oxidation potentials[a] and synthetic yields of new donors **1**, **2** and **4** (reference compound)

	a (*n* = 1)		**b** (*n* = 2)	
Comp.	E^{OX}/V	Yield (%)	E^{OX}/V	Yield (%)
1	+0.55[b]	37	+0.69[c]	13
2	+1.03[b]	71	+0.95[c]	98
4	+1.03[d]	91	+1.13[d]	61

[a] Anodic peak potentials (E_{pa}) *vs.* standard calomel electrode (SCE), 0.1 mol dm^{-3} $Bu^n{}_4NBF_4$ in CH_2Cl_2, Pt electrode, scan rate 100 mV s^{-1}. Under the same conditions, E_{pa} of dibenzo-TTF is +0.74 V and cathodic peak potential (E_{pc}) of 1,3-benzodithiolium is −0.13 V. [b] E_{pc} = +0.36 V. [c] E_{pc} = +0.14 V. [d] No cathodic peak was observed.

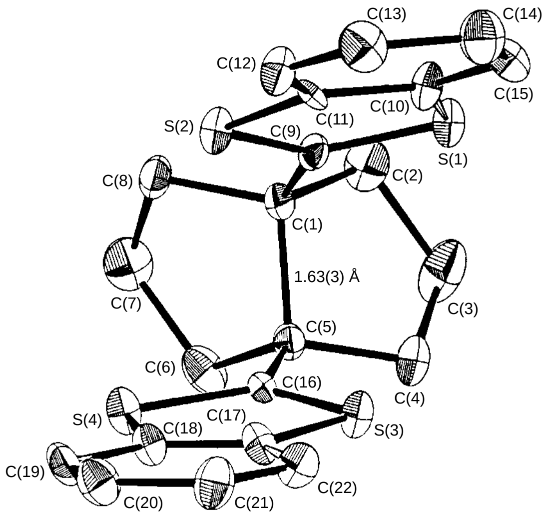


Fig. 1 Molecular structure of the dication $\mathbf{3a}^{2+}$ determined by X-ray analysis on its bis(triiodide) salt. The dihedral angle between 1,3-benzodithiolium moieties is 26°, and the torsion angle for C(9)–C(1)–C(5)–C(16) is 34°. Intramolecular contact between C(9)··C(16) is 2.80 Å.

the solid-state photoreaction of **1a** and p-$MeC_6H_4SO_3H$–catalyzed isomerization of **1b** in CH_2Cl_2, respectively, which are weaker electron donors than **1** (Table 1). Upon oxidation with iodine **2a** and **2b** afforded $\mathbf{3a}^{2+}(I_3^-)_2$ and $\mathbf{3b}^{2+}(I_5^-)_2$, in quantitative and 94% yield, respectively, thus making up the redox cycle shown in Scheme 1. These results indicate that **2b** and $\mathbf{3b}^{2+}$ can be considered as a reversible dynamic redox pair, which is different from the previous case (**1a** and $\mathbf{3a}^{2+}$) in the sense that the C–C bond breaking but not making occurs upon ionization. Although the reason of the divergent pathways for the dications $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$ upon reduction is still unclear,** two different types of dynamic redox systems can be constructed by changing only the number of methylene units of the carbocyclic ring.††

This work was supported by the Ministry of Education, Science and Culture, Japan (No. 06640675 and 08640664).

Footnotes and References

† E-mail: tak@science.hokudai.ac.jp

‡ E-mail: miyashi@org.chem.tohoku.ac.jp

§ All new compounds gave satisfactory analytical data.

¶ *Crystal data* for **2b**: $C_{24}H_{24}S_4$, M 440.70, triclinic $P\bar{1}$, a = 10.966(2), b = 13.137(2), c = 7.987(1) Å, α = 107.56(1), β = 109.07(1), γ = 79.49(1)°, V = 1032.4(6) Å^3, D_c (Z = 2) = 1.418 g cm^{-1}, R = 0.065. For $\mathbf{3a}^{2+}(I_3^-)_2$: $C_{22}H_{20}S_4I_6$, M 1174.07, monoclinic $P2_1$, a = 9.042(7), b = 19.016(7), c = 9.403(7) Å, β = 109.97(5)°, V = 1520(2) Å^3, D_c (Z = 2) = 2.566 g cm^{-1}, R = 0.064. For H_2**3a**: $C_{22}H_{22}S_4$, M 414.64, monoclinic $C2/c$ (molecule on the two-fold axis), a = 22.623(6), b = 7.402(1), c = 12.345(4) Å, β = 109.50(2)°, V = 1948.6(15) Å^3, D_c (Z = 4) = 1.413 g cm^{-1}, R = 0.070. For H_2**3b**: $C_{24}H_{26}S_4$, M 442.69, orthorhombic $Pbca$, a = 12.493(1), b = 15.542(1), c = 21.381(2) Å, V = 4151.6(5) Å^3, D_c (Z = 8) = 1.417 g cm^{-1}, R = 0.042. CCDC 182/642.

‖ Specific formation of the *cis*-decalin skeleton may result from kinetic control because the *trans*-isomer has nearly the same heat of formation as $\mathbf{3b}^{2+}$. It seems that a much larger structural change has to take place to form the *trans*-isomer although no information is available on the conformation of the starting material **1b**. The authors are grateful to one of the referees for pointing out such a possibility.

** One possible explanation is postulating an interaction between the p-orbital of benzodithiolium and the transannular σ bond in $\mathbf{3a}^{2+}$, thus adding the contribution from the σ* orbital to its LUMO. See ref. 9.

†† Unlike **1a** and **1b**, cyclohexane-1,4-diylidenebis[2-(1,3-benzodithiole)] (E_{pa} = +0.96 V) does not form a transannular C–C bond upon oxidation with iodine. The product is the salt of 2-(4′-iodobicyclo[2.2.1]heptan-1′-yl)-1,3-benzodithiolium having a spiro(1,3-benzodithiole) unit at C-7′.

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Received in Cambridge, UK 1st September 1997; 7/06342C