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# Molecular Actuator: Redox-Controlled Clam-Like Motion in a Bichromophoric Electron Donor

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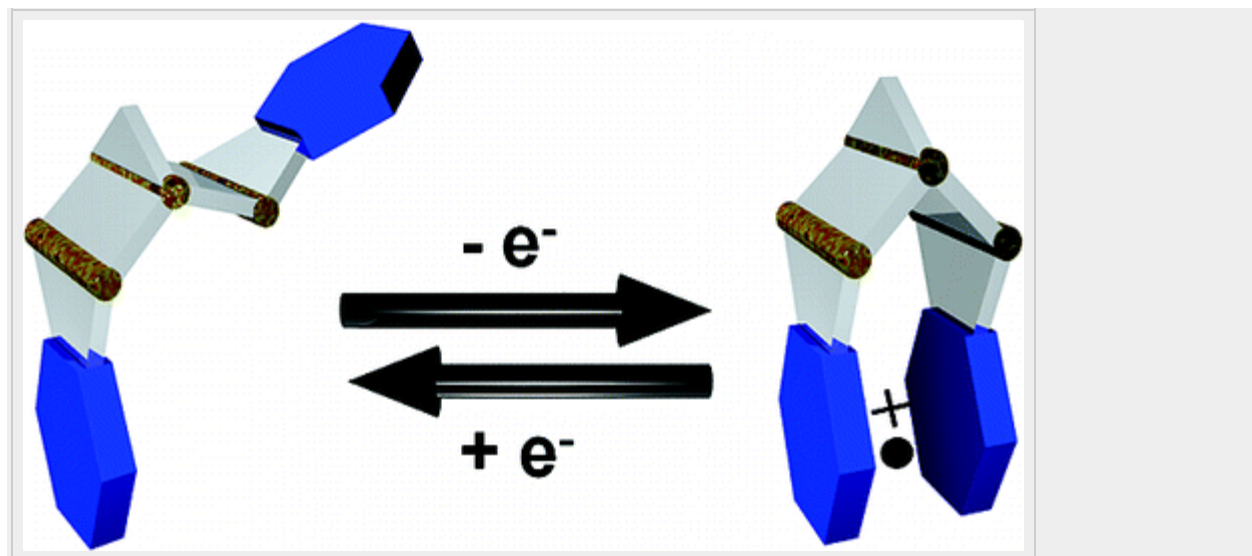Sergey V. Lindeman
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## Abstract

The one-electron oxidation of tetramethoxydibenzobicyclo[4.4.1]undecane (**4**) prompts it to undergo a clam-like electromechanical actuation into a cofacially π-stacked conformer as established by (i) electrochemical analysis, (ii) by the observation of the intense charge-resonance transition in the near IR region in its cation radical spectrum, and (iii) by X-ray crystallographic characterization of the isolated cation radical salt (**4**$^{+\bullet}$ SbCl$_6^-$).

The design and synthesis of functional organic molecules for use as molecular sensors, switches, conductors, ferromagnets, and in nonlinear optics continues to grow with an unabated pace owing to their potential applications in the ever evolving areas of molecular electronics and nanotechnology.[1,2] Among these are a variety of synthetic foldamers,[3] molecular muscles,[4] molecular switches,[5] and functional molecular rotaxanes[6] that exhibit structural (or conformational) changes as well as changes in their physical properties (such as magnetism, conductivity, and optical response) when triggered by external stimuli such as heat, light, pH-changes, metal ion binding, electron transfer, etc. Electro-mechanical molecular actuators[7] are another class of such molecules in which a conformational change (or structural contraction or expansion) is caused by a redox (electrochemical) event, which is tantamount to the conversion of electrical energy into mechanical energy; and such molecules are potentially important as the building blocks for functioning molecular muscles.[4]

In this report, we demonstrate that a readily available[8] bichromophoric dibenzobicyclo[4.4.1]undecane derivative, which exists in rapidly interchanging noncofacial conformations and switching between the mirror image conformations in the neutral state

does not involve the cofacial conformation as an intermediate.[8] Interestingly, however, it undergoes a clam-like molecular actuation upon 1-electron oxidation on an electrochemical time scale, that is, eq 1.



$$(1)$$
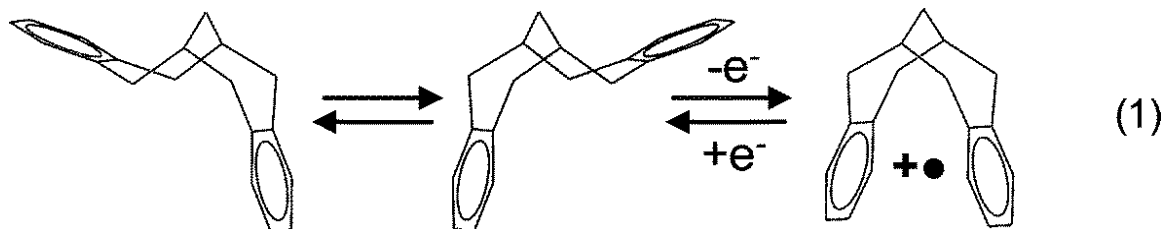
The clam-like functioning of the redox-controlled mechanical motion in a conformationally mobile tetra-methoxydibenzo-bicyclo[4.4.1]undecane, containing two redox-active veratrole (1,2-dimethoxybenzene) moieties, is delineated with the aid of electrochemistry, optical spectroscopy, and by X-ray crystallography of the cofacially locked cationic conformation, as follows.

Tetramethoxydibenzobicyclo[4.4.1]undecane (**4**) was synthesized by adapting the literature procedures[8,9] employed for the preparation of the unsubstituted derivative (see Scheme 1). The noncofacial arrangement of the veratrole moieties in **4** was confirmed by X-ray crystallography (Scheme 1). Interestingly, a ketalization of the ketone **3** using neopentyl glycol afforded a conformationally rigid (model) bichromophoric **5** in which the two veratrole moieties are cofacially juxtaposed at a center to center distance of ~3.03 Å, as confirmed by X-ray crystallography (Scheme 1). A monomeric model donor, that is, 3,4-dimethyl-1,2-dimethoxybenzene (**6**) was easily obtained by a lithium aluminumhydride reduction of the dibromide **1** in refluxing tetrahydrofuran. The structures of **3–5** were established by X-ray crystallography and by $^1H/^{13}C$ NMR spectroscopy (see Supporting Information for the details).
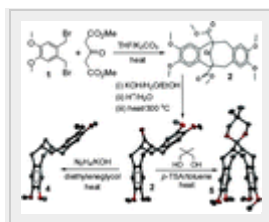


**Scheme 1. Synthetic Scheme for the Preparation of Bichromophoric Actuator and the Molecular Structures of 3–5 Obtained by X-Ray Crystallography**

Variable temperature $^1$H NMR spectroscopy of the conformationally mobile **4** in dichloromethane-$d_2$ over a temperature range of +20 to −80 °C showed that the interchange between mirror image conformations can be frozen at ~−50 °C; and the activation energy for the interchange into two isoenergetic (noncofacial) conformers in eq 1 was estimated[10] to be $E_a$ = 6.5 kcal mol$^{-1}$ K$^{-1}$ by line-shape analysis of the signals in the variable temperature $^1$H NMR spectra in Figure S1 (see Supporting Information).

To establish that **4** exists exclusively in an extended (noncofacial) conformer in solution, we examined the electron donor−acceptor (EDA) complexes of **4** together with the conformationally rigid, π-stacked acetal **5**, in which the veratrole moieties are arranged cofacially, and the model monochromophoric **6** with 1,2,4,5-tetracyanobenzene (TCNB) as an electron acceptor as follows. It is well-known that the redox potentials (or π-basicity) of the cyclophane-like aromatic donors are significantly lower than their extended analogues,[11] and can be readily gauged by formation of the EDA complexes in solution according to the Mulliken theory.[12] Thus, when colorless solutions of **4** and **6** were exposed to a colorless solution of TCNB in dichloromethane, they instantaneously produced red-colored solutions, and they each showed upon UV−vis spectral analyses a broad charge-transfer (CT) absorption band centered at $\lambda_{max}$ = 472 and 468 nm, respectively. The π-stacked cyclophane-like donor **5** is expected to have a lower redox potential than the model electron donor **6** or bichromophoric **4** in an extended conformation. Indeed, when a dichloromethane solution of **5** was exposed to TCNB, it immediately produced a magenta-red solution which upon UV−vis spectral analysis revealed that the charge-transfer absorption band was considerably red-shifted to $\lambda_{max}$ = 540 nm (see Figure 1A). Thus, the identical energies of CT transitions for EDA complexes of **4** and **6** and significantly red-shifted CT transition (~70 nm) for the EDA complex of the rigid cyclophane-like donor **5** clearly implies that there is little or no contribution of the π-stacked (cofacial) conformer of the bichromophoric **4** in solution. As such, this conclusion is further supported by the fact that the UV−vis absorption spectrum of bichromophoric **4** was found to be characteristically similar ($\lambda_{max}$ = 286 ± 1 nm) to that of the model monochromophoric **6**, whereas the cyclophane-like donor **5** showed an additional band at 305 nm (see Figure S3 in the Supporting Information).
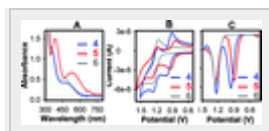
Figure 1. (A) UV–vis absorption spectra of the EDA complexes of **4–6** with TCNB in $CH_2Cl_2$ at 22 °C. B/C. The Cyclic (B) and square-wave (C) voltammograms of **4–6** (1 mM) in $CH_2Cl_2$, containing 0.2 M *n*-Bu₄NPF₆, were measured at a $v$ = 200 mV s⁻¹ at 22 °C. The oxidation potentials were referenced using ferrocene ($E_{ox}$ = 0.45 V vs SCE) as an internal standard.

The cyclic and square-wave voltammograms of **4**, **5**, and **6** recorded in dichloromethane are compiled in Figure 1B/C. The bichromophoric donors **4** and **5** showed two reversible oxidation waves at the potentials of 0.96, 1.22 V and 0.87, 1.22 V vs SCE, respectively, whereas the monochromophoric model donor **6** showed only one reversible oxidation wave at a potential of 1.22 V vs SCE. The observation of two well-separated one-electron oxidation waves ($\Delta E$ = 350 mV) for cyclophane-like **5**, in Figure 1B/C, is consistent with the fact that the removal of the first electron results in a cation radical (**5⁺•**) where the cationic charge is delocalized over both the (preorganized) cofacial veratrole moieties, and thereby rendering the ejection of the second electron difficult by roughly ∼350 mV. Interestingly, however, the observation of two similar well-separated one-electron oxidation waves ($\Delta E$ = 260 mV) in conformationally mobile **4** suggests that upon removal of the first electron, the extended (noncofacial) conformer of **4⁺•** undergoes an instantaneous transformation into the π-stacked conformer on the electrochemical time scale (see Scheme 2) and thereby rendering the second oxidation to occur at a potential ($E_{ox2}$ ≈ 1.22 V) strikingly similar to that of **5**.
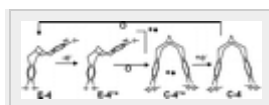


**Scheme 2. Mechanism of Redox-Controlled Electromechanical Actuation**

The observed difference (∼90 mV) in the first oxidation potentials of conformationally mobile **4**when compared to the rigid π-stacked **5** can be attributed to the energy required for the transformation of the extended conformation **E-4** into the cofacially stacked **C-4** conformation (see Scheme 2).

Furthermore, the driving force for the conformational transformation **E-4⁺•→C-4⁺•** is largely due to the stabilization of the cationic charge by the effective electronic coupling between the π-stacked veratrole moieties (vide infra) and thereby significantly lowering its first oxidation potential when compared to the monochromophoric donor **6** ($E_{ox}$ = 1.22 V) by ∼260 mV.[13]

As such, the through-space electronic coupling between the cofacially stacked aryl moieties can also be seen in the electronic spectra of their cation radicals, where characteristic charge-resonance transitions in the near-IR region are observed.[13,14] Accordingly, we generated the cation radicals of **4–6** using stable cation-radical salts [such as **CRET⁺•**, $E_{red}$ = 1.14 V vs SCE and **NAP⁺•**, $E_{red}$ = 1.34 V vs SCE][15,16] as one-electron aromatic oxidants in dichloromethane as follows.

For example, a treatment of the orange-red solution of **CRET⁺•** ($\lambda_{max}$ = 518 nm, $\epsilon_{518}$ = 7300 $M^{-1}cm^{-1}$)[15] with substoichiometric increments of **4** led to the disappearance of the absorption bands due to **CRET⁺•**, and a concomitant growth of a new band at 466 nm together with a broad featureless absorption band centered at ~1224 nm (Figure 2A). Addition of donor **4** beyond one equivalent showed no additional spectral changes (Figure 2B). Also, Figure 2C shows that the electronic spectra of **4⁺•** ($\lambda_{max}$ = 466, 1224 nm; $\epsilon_{1220}$ = 6,990 $M^{-1} cm^{-1}$) is indistinguishable with that of the rigid cyclophane-like **5⁺•** ($\lambda_{max}$ = 464, 1218 nm; $\epsilon_{1220}$ = 7,170 $M^{-1} cm^{-1}$). Moreover, the observation of a highly characteristic charge-resonance transition at ~1220 nm in both **4⁺•** and **5⁺•**, and its singular absence in the monochromophoric **6⁺•** (Figure 2C), further suggests that **4⁺•**adapts a cofacial conformation similar to that of rigid **5⁺•**.
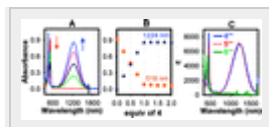


Figure 2. (A) Spectra obtained upon the reduction of 1.5 × 10⁻⁴ M **CRET⁺•** (red) in CH₂Cl₂ by an incremental addition of 5.4 × 10⁻³ M **4**. (B) Plot of increase of absorbance of **4⁺•** (at 1224 nm) and decrease of absorbance **CRET⁺•** (at 518 nm) against the equivalent of added **4** in A. (C) Overlay of the absorption spectra of the **4⁺•**, **5⁺•**, and model **6⁺•** ($\lambda_{max}$ = 442 nm; $\epsilon_{442}$ = 5,400 $M^{-1} cm^{-1}$) in CH₂Cl₂ at 22 °C.

To obtain definitive X-ray crystallographic evidence for the transformation of the extended cation radical **E-4⁺•** into the cofacially stacked **C-4⁺•** in Scheme 2, the single crystals of the highly robust **4⁺•** SbCl₆⁻ were obtained by a slow diffusion of toluene into its dichloromethane solution during a period of 2 days at 22 °C (see Supporting Information for experimental details). The molecular structure of **4⁺•** SbCl₆⁻, obtained by X-ray crystallography, establishes the cofacial arrangement of the veratrole moieties as shown in Figure 3.
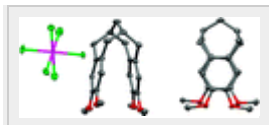
Figure 3. Crystal structure of $4^{+\bullet}$ $SbCl_6^-$ cation radical showing the cofacial arrangement of veratrole moieties (left), and a slight twist of ~8° around the local 2-fold symmetry axis of the $4^{+\bullet}$ (right).

The crystal structure of $4^{+\bullet}$ $SbCl_6^-$ also revealed that it contained two symmetrically independent molecules of $4^{+\bullet}$ that have essentially the same geometry. Unlike, the neutral **4**, both of the 7-membered rings of the bicyclododecane framework in the $4^{+\bullet}$ adopt a chairlike conformation[17] which allows a close cofacial arrangement of the veratrole rings (with dihedral angles of 15.2 and 15.6° for the two independent molecules) with an interplanar separation between the veratrole rings as close as 2.73 Å—which is much less than the equilibrium van-der-Waals separation of 3.4 Å and is indicative of efficient electronic coupling between them.

A closer look at the structural parameters of the veratrole groups in $4^{+\bullet}$ suggests that they are identical (within the experimental precision of ~0.004 Å for various C–C bond lengths) and the cationic charge is evenly distributed over both the veratrole moieties (see Table 1). Furthermore, the bond length changes in the cation radical $4^{+\bullet}$, together with a comparison with its neutral form, the structure of which was established by X-ray crystallography, correspond to the predominant contributions from *para*-quinoidal resonance structures **A/B**, as judged by the significant shortening of bonds labeled **a** and elongation of bonds labeled **d** and **e**, along with only marginal shortening of the bonds labeled **b** and **c**, (see Scheme 3 and Table 1). It is also noted that the alternate resonance structures **C–E** do not seem to contribute to the stabilization of the cationic charge in any significant way.

**Table 1. Experimental and Theoretical Bond Lengths of the Neutral and Cation Radical of 4 Presented in Picometers (pm)**
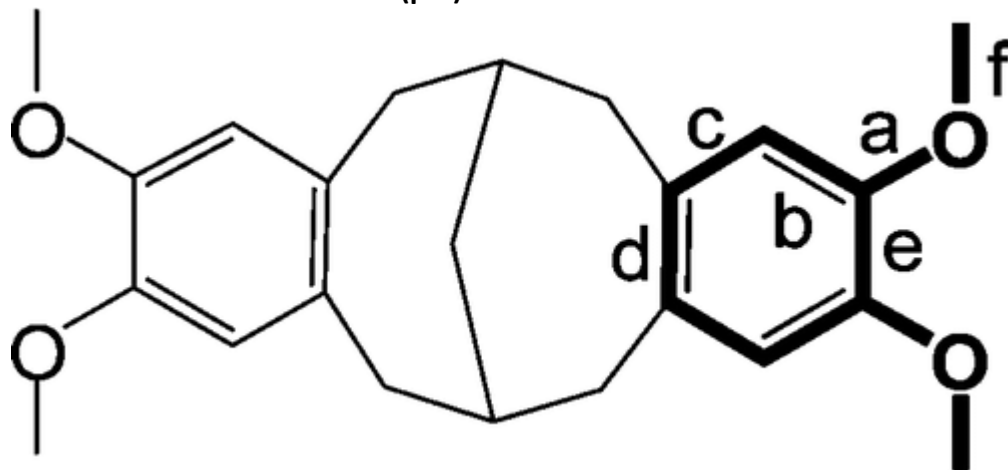


| bond[a] | B3LYP/6-31G* | | | X-ray crystallography | | |
|---|---|---|---|---|---|---|
| | 4 | 4$^{+•}$ | Δ (4$^{+•}$−4) | 4 | 4$^{+•}$ | Δ (4$^{+•}$−4) |
| a | 136.5 | 134.5 | −2.0 | 137.1 | 135.4 | −1.7 |
| b | 139.3 | 139.7 | +0.4 | 138.3 | 138.2 | −0.1 |
| c | 140.6 | 139.6 | −1.0 | 140.1 | 139.3 | −0.8 |
| d | 140.4 | 143.1 | +2.7 | 139.9 | 142.1 | +2.2 |

| | B3LYP/6-31G* | | | X-ray crystallography | | |
|---|---|---|---|---|---|---|
| bond[a] | 4 | 4[+•] | Δ (4[+•]−4) | 4 | 4[+•] | Δ (4[+•]−4) |
| e | 141.3 | 143.5 | +2.2 | 140.5 | 142.7 | +2.2 |
| f | 141.6 | 143.7 | +2.1 | 142.5 | 144.1 | +1.6 |
| σ | – | – | – | 0.2 | 0.4 | – |

[a] Average of equivalent bonds and/or independent molecules.
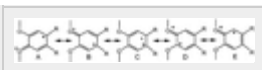


**Scheme 3. Resonance Stabilization of the Cationic Charge in 4[+•]**

The experimental observations of the bond length changes in **4[+•]** were found to be in reasonable agreement with the calculated values using DFT calculations at B3LYP/6-31G* level (see Table 1).[18]

In summary, we have demonstrated that conformationally mobile **4** exists exclusively in the extended conformation in the neutral state as judged by the spectral analysis of the electron donor−acceptor complexes of **4** in comparison with the cofacially stacked model compound **5** and a monochromophoric donor **6** with tetracyanobenzene as an electron acceptor. The one-electron oxidation readily transforms the extended **4** into a clam-like folded π-stacked conformer as confirmed by the electrochemical analyses and by the observation of the intense charge-resonance transitions in the near IR region in its cation radical spectrum. Moreover, definitive evidence for the clam-like electromechanical actuation of the extended cation radical **E-4[+•]** into the cofacially stacked **C-4[+•]** was obtained by its isolation and

characterization by X-ray crystallography. We are actively engaged in exploiting the usefulness of such a redox-controlled molecular motion in readily available **4** as well as the design and synthesis of higher homologues of these electro-active materials.

## Acknowledgment

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[13] Compare:  Rathore, R.; Chebny, V. J.; Kopatz, E. J.; Guzei, I. A. *Angew. Chem., Int. Ed.* **2005**, 44,2771

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[17] The cofacial arrangement of the veratrole moieties in **4⁺•** induces a slight distortion in the chairlike conformations of the 7-membered rings in bicyclododecane framework from the ideal chair conformations.

[18] Compare:  Banerjee, M.; Vyas, V. S.; Lindeman, S. V.; Rathore, R. *Chem. Commun.* **2008**, 1889