4,5-Bis(diarylmethylene)-1,3-dithiole: A Novel Helical Electron Donor Exhibiting Electrochromic Behavior

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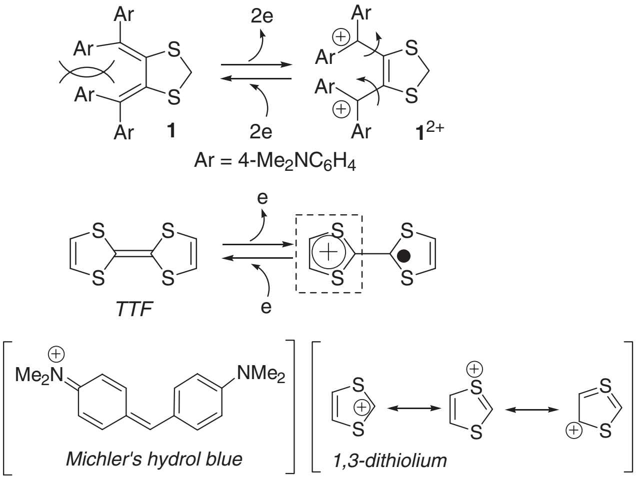
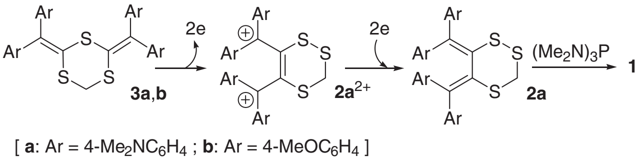
Vivid color change from intense yellow to deep purple was observed upon electrochemcal oxidation of the title donor **1** to bis(Michler's hydrol blue)-type dication $\mathbf{1}^{2+}$. Since the interconversion was also accompanied by drastic geometric changes, configurational stability of the helical π-arrangement is modified upon redox reactions.

Sulfur-heterocycles[1] are important components in designing organic molecules for developing materials science. 1,3-Dithiole and its dehydro dimer (tetrathiafulvalene, TTF[2]) form the most common family. More than a thousand derivatives have been described to date and investigated from the viewpoint of unique solid-state properties[3] (electric conduction/superconducting behavior/magnetism) as well as in the field of supramolecular chemistry.[4] Strong electron-donating properties of TTFs are provided by the stability in cationic states thanks to the aromatic nature of the 1,3-dithiolium unit.

We have designed and prepared here the title molecule **1**, which has very strong electron-donating units on the periphery of the heterocycle. Those diarylmethylene units induce a strained molecular geometry with a helical arrangement of π-electron system. Unlike TTF derivatives, the positive charges formed upon oxidation would be located not on the dithiolium ring but on the exocyclic auxiliaries of Michler's hydrol blue units in $\mathbf{1}^{2+}$ (Scheme 1). Since the latter moieties are known as strong chromophores, the present redox pair ($\mathbf{1}/\mathbf{1}^{2+}$) would exhibit electrochromic behavior. At the same time, one-electron oxidation may cause drastic geometric change to relieve severe steric strain between the adjacent diarylmethylene units in **1**, so that the intermediary ion radical $\mathbf{1}^{+\bullet}$ would be short-lived as in the cases of redox-active 1,2-quinodimethanes.[5] Negligible steady-state concentration of the intermediate reduces the chance of side reactions of the open-shell species, and thus favors the high reversibility of the electrochemical response.[6] Here we report the preparation and X-ray structure of title molecule **1** along with the redox and electrochromic properties.



Scheme 1.



Scheme 2.

The strained donor **1**[7] with four 4-$Me_2NC_6H_4$ groups was successfully generated upon ring-contracting desurfurization of 1,2,4-trithiane **2a** by hexamethylphosphorous triamide in 72% yield (Scheme 2), which was previously obtained by skeletal rearrangement of 1,3,5-trithiane **3a** upon redox reaction.[8] Orange crystalline **1** can be stored infinitely under ambient conditions despite its very strong donating properties.[5d,9] According to the voltammetric analysis, **1** undergoes reversible two-electron oxidation at +0.12 V vs. SCE in MeCN (Figure S1),[7] which clearly shows that **1** is a stronger electron donor than TTF (E^{ox} +0.31 V under similar conditions). Upon treatment with 3 equivalents of iodine, **1** was cleanly converted to deeply colored dication $\mathbf{1}^{2+}$, which was isolated as stable triiodide salt in quantitative yield. By reduction of $\mathbf{1}^{2+}(I_3^-)_2$ using Zn powder, **1** was regenerated quantitatively. Attempted preparation of less donating 4-$MeOC_6H_4$ derivative following the same scheme was hampered since the skeletal rearrangement into $\mathbf{2b}^{2+}$ does not occur upon oxidation of 2,4-bis[di(*p*-anisyl)methylene]-1,3,5-trithiane (**3b**).

Low-temperature X-ray analysis[10] of **1** has revealed that it adopts a strained helical structure with a torsion angle of 47(1)° for the exocyclic diene unit (Figure 1). Such a large value comes from the repulsive interaction between two inward aryl groups (Ar_{IN}) facing each other in parallel [dihedral angle 6.2(2)°] with the shortest interatomic C···C contact of 3.07(1) Å, which is much smaller than the sum of van der Waals radii (3.40 Å). This also causes a larger twisting angle of the exocyclic double bond (9.9 and 11.4°) than in the case of 1,1,4,4-tetrakis(4-dimethylaminophenyl)-1,3-butadiene (4.8°).[6b]

The ^1H NMR spectrum of **1** can be rationalized by assuming that the geometry in solution resembles the solid-state structure. There are two pairs of resonances for the aryl groups at δ 7.05, 6.63, 6.59, and 6.35 ($CDCl_3$). The former two chemical shifts are similar to those of related compounds with bis(4-dimethyl-

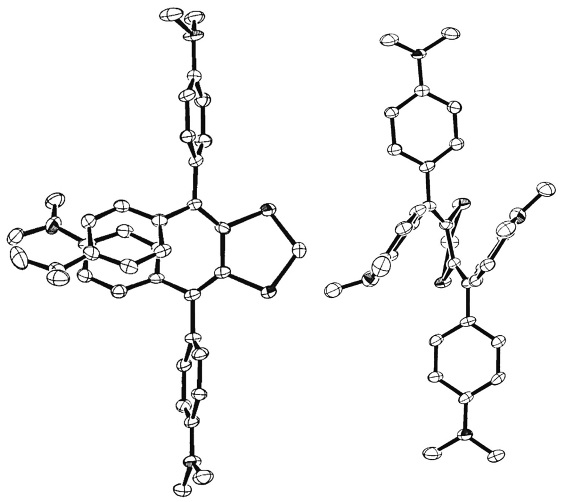


Figure 1. ORTEP drawings of (*P*)-**1** (left: top view; right: side view) obtained by X-ray analysis of *rac*-**1** at 110 K.

amino)ethenyl moieties,[9] thus assigned to those for aryl groups directing outward ($\mathrm{Ar_{OUT}}$). The latter two for $\mathrm{Ar_{IN}}$ are largely upfield-shifted, which can be rationalized by mutual shielding effects through π–π overlap in proximity. There are two singlets at δ 2.96 and 2.84, which are assigned to *N*-Me protons of $\mathrm{Ar_{OUT}}$ and $\mathrm{Ar_{IN}}$, respectively. We found no signs of exchange between $\mathrm{Ar_{IN}}$ and $\mathrm{Ar_{OUT}}$ in the NMR spectra, suggesting that configuration of helicity in **1** is quite stable (vide infra). On the other hand, the spectrum indicates that $\mathbf{1}^{2+}$ adopts a C_{2v}-symmetric structure: only two resonances for Ar groups (δ 7.34 and 6.78) as well as one singlet for *N*-Me protons (3.22) ($\mathrm{CD_3CN}$, Figure S2).[7] Thus, $\mathrm{Ar_{OUT}}$ and $\mathrm{Ar_{IN}}$ in neutral **1** are rapidly interconverting or indistinguishable in $\mathbf{1}^{2+}$, suggesting that two Michler's hydrol blue units are nearly perpendicular to the 1,3-dithiole ring in $\mathbf{1}^{2+}$.

Thanks to the very strong absorptions in the visible–NIR region of $\mathbf{1}^{2+}$ [UV–vis (MeCN): $\lambda_{\max}$ 703 nm (log ε 4.75), 600 (4.69), 544 (4.74)], electrochemical interconversion of the present pair is accompanied by vivid color change from intense yellow to deep purple. The presence of isosbestic points in the spectroelectrogram indicates clean interconversion as well as negligible steady-state concentration of intermediary cation radical species (Figure 2). This is the successful demonstration of electrochromic behavior of a novel 1,3-dithiole electron donor **1**.

Another interesting feature is the configurationally stable helical geometry of **1**, whereas dication $\mathbf{1}^{2+}$ is achiral due to (time-averaged) C_{2v}-symmetry. After many efforts, we succeeded in partial optical resolution (55% ee) of helical diene **1** by using chiral HPLC (CHIRALPAK-IA, EtOAc:hexane = 1:3 with 0.5% w/w $\mathrm{Et_3N}$). Thanks to the helical π-system, resolved diene **1** shows very strong Cotton effects [λ_{ext}346 nm ($\Delta\varepsilon$ −4.8), 335 (+25.9), 304 (−96.6), 273 (−80.6), 239 (+14.5) in MeCN; major in the first fraction component of HPLC] (Figure S3).[7] The CD spectrum remained unchanged after several days at room temperature, thus confirming configurational stability of helical diene **1**. In this way, it is suggested that the present pair can serve as a chiral unit whose racemization barrier can be changed upon redox reactions.[11] Studies in this vein as well as making new materials by using **1** as a synthon are now in progress.

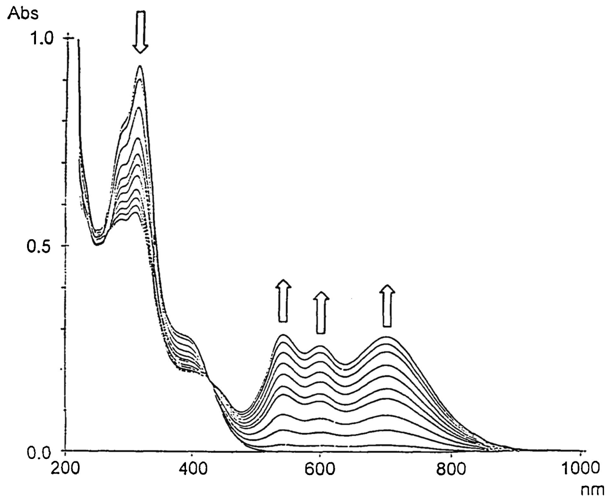


Figure 2. Continuous changes in the UV–vis spectra of **1** upon constant-current electrochemical oxidation (29 µA) at 2 min intervals in MeCN.

References and Notes

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10 Crystal data of **1**: $\mathrm{C_{37}H_{42}S_2N_4}$, $M_\mathrm{r} = 606.89$, triclinic, $P\bar{1}$, $a = 10.253(3)$, $b = 11.225(6)$, $c = 16.472(7)$ Å, $\alpha = 66.38(2)$, $\beta = 70.378(7)$, $\gamma = 75.929(10)°$, $V = 1623(1)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.242\ \mathrm{g\,cm^{-3}}$, independent reflection 6706 (all), 2723 (3σ), $R = 6.3\%$.

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