

Registry No. 1, 92669-44-8; Ru(TMP)(THF)₂, 97877-73-1; Ru(TMP)(CH₃CN)₂, 97877-74-2; Ru(TMP)CO, 92669-43-7; Ru(TMP)[P(OMe)₃]₂, 92694-64-9; Ru(TMP)(pyr)₂, 97877-75-3; Ru(TT-P)(THF)₂, 97877-76-4; cyclooctene, 931-88-4; cyclooctene oxide, 286-62-4; norbornene oxide, 278-74-0; norbornene, 498-66-8; *cis*- β -methylstyrene, 766-90-5; *trans*- β -methylstyrene, 873-66-5; *cis*- β -methylstyrene oxide, 4541-87-1; *trans*- β -methylstyrene oxide, 23355-97-7.

Tetrakis(1,3-dithiol-2-ylidene)cyclobutane: A Novel and Promising Electron Donor for Organic Metals

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In the past decade much interest has been directed toward development of organic metals.¹ Some organic radical cation salts derived from tetrathiafulvalene (TTF) and tetraselenafulvalene derivatives have been found to show superconductivity albeit at very low temperatures.² In order to stabilize the metallic state of organic metals at higher temperatures and eventually to attain superconductivity at a technologically useful temperature, molecular design and synthesis of new electron donors having a different skeletal structure from that of TTF are needed, in addition to further modification of TTF involving replacement of sulfur with the other chalcogenides and introduction of new substituents. In this paper we wish to report the synthesis, molecular structure, and electrochemical property of a novel and promising electron donor for organic metals, tetrakis(1,3-dithiol-2-ylidene)cyclobutane (**1a**, "1,3-dithiol[4]radialene")³ whose half unit, ethanediyldene-2,2'-bis(1,3-dithiole) (**2**) has already been shown in our laboratory to give an organic metal composed of 1:1 charge-transfer salt with tetracyanoquinodimethane (TCNQ).⁴

The new [4]radialene was synthesized as shown in Scheme I. Thus, ethanediyldene-2,2'-bis(4,5-dicarbomethoxy-1,3-dithiole) (**3**)⁵ was converted quantitatively to the 1,2-dibromo-substituted derivative **4** by the reaction with 2 equiv of bromine in CCl₄ (25 °C, 1 h). Treatment of a THF solution of **4** with 1/2 equiv of Ni(PPh₃)₄ in the presence of an excess of Zn-Cu couple (25 °C, 12 h),⁶ followed by column chromatography of the reaction mixture on silica gel with CH₂Cl₂-CH₃CO₂C₂H₅ (8:1) afforded the octacarbomethoxy-substituted derivative of **1a**, **1b** (purple brown needles; mp 235-238 °C (benzene-hexane)) in 30% yield. The target molecule **1a**⁷ (reddish orange needles; mp 170 °C dec

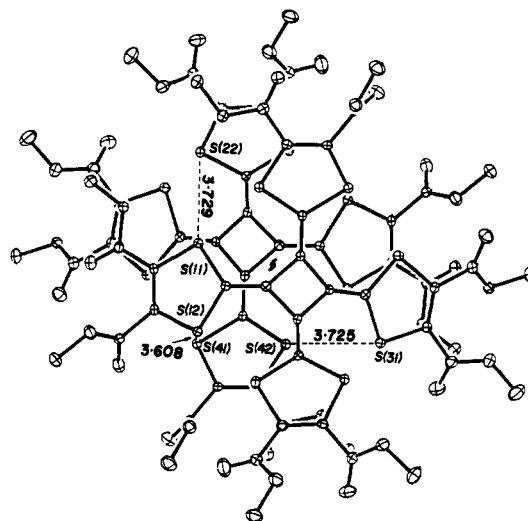
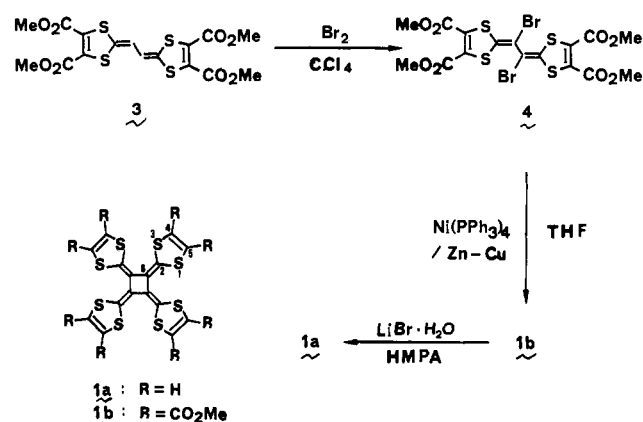


Figure 1. Stacking structure of **1b** molecules projected along the crystallographic 2₁ axis parallel with the *c* axis of the unit cell.

Scheme I



(benzene)) was obtained in 88% yield by treating **1b** with an excess of LiBr·H₂O in HMPA (95-155 °C, 2 h).

Cyclic voltammetry was performed on the [4]radialenes in CH₂Cl₂ containing (*n*-Bu)₄NClO₄ as supporting electrolyte by use of platinum working and standard silver/silver chloride reference electrodes. The three-step oxidation was found to occur at each potential of +0.19, +0.98, and +1.30 V for **1a**, and of +0.70, +1.29, and +1.79 V for **1b**, respectively. Only the first step showed complete reversibility. From the change of peak current at the first step with respect to sample concentration this step was determined to involve a two-electron transfer,⁸ and according to the Myers-Shain method⁹ the two-electron step was divided into two one-electron steps with oxidation potentials, *E*₁ and *E*₂, that are +0.20 and +0.24 V for **1a** and +0.65 and +0.70 V for **1b**, respectively. In comparing the *E*₁, *E*₂, and (*E*₂ - *E*₁) values of **1a** with those of **2** (+0.20 and +0.36 V)⁵ and TTF (+0.27 and +0.63 V), we note that the *E*₁ values of **1a** and **2** are almost equal¹⁰ and relatively smaller than that of TTF, indicating that the former two compounds have higher electron-donating ability. The *E*₂ values follow in the order TTF > **2** > **1a** and follow the

(7) Satisfactory elemental analyses and spectral data were obtained for **1a** and **1b**. As compared with **1b**, **1a** is less stable and especially sensitive to light.

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(10) The unexpectedly large *E*₁ value of **1a** is due to the nonplanarity of four 1,3-dithiole rings, as seen in the X-ray structure of **1b**. However, such a nonplanar restriction should partly be released in the radical cation state (**1a**⁺), providing the very smaller *E*₂ value. A similar interpretation was made in the redox behavior of 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-[10-(1,1-dicyanomethylidene)anthrylidene-9-ylidene]cyclopropane (Wellman, D. E.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 355).

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(3) The formally similar system to **1a**, tetrakis(1-carboethoxy-4H-pyridin-4-ylidene)cyclobutane was previously synthesized (Horner, M.; Hünig, S. *Angew. Chem.* **1977**, *89*, 424; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 410).

(4) The electrical conductivities in the single-crystal state are 12 and 23 Ω⁻¹ cm⁻¹ at 300 and 200 K, respectively. This result will be reported elsewhere.

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same order in the ($E_2 - E_1$) values, by which the dication state of **1a** is shown to be most stable among them.

X-ray diffraction analysis of **1b**¹¹ indicates that the molecule belongs to the approximate D_{2d} symmetry (excluding eight carbomethoxy groups with flexible conformations) and has the puckered structure of the central four-membered ring. Figure 1 shows a unique stacking structure of molecules of **1b** related by the crystallographic 2_1 symmetry along the c axis resulting in a one-dimensional column in the crystal lattice. Some van der Waals contacts are found between the sulfur atoms of interdonor molecules, the shortest one being 3.608 Å (twice the van der Waals radius of sulfur is 3.70 Å).

These results suggest that the [4]radialenes, in particular **1a**, should be useful electron-donor candidates for organic metals. In fact, **1a** forms a 1:2 charge-transfer salt (black needle crystals, mp > 300 °C) with TCNQ, and the room temperature electrical conductivity on the compressed pellet is fairly high ($0.032 \Omega^{-1} \text{ cm}^{-1}$). Furthermore, the E_a value (0.057 eV) is very small. The preparation and electrical characterization of **1a**-TCNQ single crystals are currently under active investigation.

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Supplementary Material Available: ORTEP drawing and full tables of fractional atomic coordinates and interatomic bond distances and angles in **1b** (5 pages). Ordering information is given on any current masthead page.

(11) Crystal data of **1b**: $\text{C}_{32}\text{H}_{24}\text{O}_{16}\text{S}_8$, FW = 921.1, orthorhombic, space group $P2_12_12_1$, $a = 17.9317$ (1) Å, $b = 25.757$ (2) Å, $c = 8.539$ (1) Å, $U = 3808.7$ (4) Å³, $D_x = 1.606 \text{ g cm}^{-3}$, $Z = 4$. X-Ray diffraction data were measured on a Rigaku four-circle diffractometer using nickel-filtered Cu K α radiation. A total of 3217 reflections were collected up to $2\theta = 120^\circ$ by the θ - 2θ scan technique. The structure was solved by the direct method (MULTAN-78) and refined by the full-matrix least squares (XRAY-76) by using the 3073 observed reflections [$|F_0| \geq 3\sigma(F_0)$] to the R index of 0.052 including non-hydrogen atoms with anisotropic thermal parameters.

Measurement of the Activation Barrier for Carrier Transport at n-GaAs Semiconductor/Liquid Junctions

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The mechanism of carrier transport at semiconductor/liquid interfaces is an important and controversial topic in photoelectrochemistry. Of particular concern is the transport kinetics for interfaces whose open-circuit voltage, V_{oc} , is constant over some range of solution redox potential.^{1,2} Fermi level pinning has been postulated to apply to n-GaAs, p-GaAs, and p-InP interfaces in both aqueous and nonaqueous solvents.^{2,3} However, direct identification of the various recombination mechanisms has been acknowledged to be difficult,³ and to date, few experimental

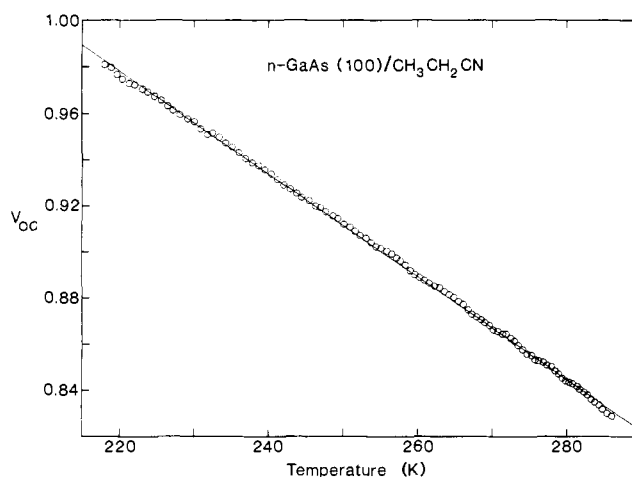


Figure 1. V_{oc} vs. T for the n-GaAs/ $\text{FeCp}_2^{+/0}$ - LiClO_4 - $\text{CH}_3\text{CH}_2\text{CN}$ system. Voltages were measured between an n-GaAs working electrode (0.05–0.2 cm²) and a Pt wire poised at the solution potential. The cell is immersed in an ethanol solution in a strip-silvered Dewar Flask, and the cooling rate is typically 5 K/min.

techniques have been reported which allow correlation of the key photostationary state observable, the open circuit voltage, to the transport mechanism of these interfaces. We report here measurements of the temperature dependence of the open-circuit voltage for the n-GaAs semiconductor/liquid junction system.

For surface barrier systems, activation energies can be obtained from plots of V_{oc} as a function of temperature.⁴ Thermionic emission of majority carriers over a low surface barrier would yield an activation energy equal to the effective barrier height. In contrast, the characteristic activation energies of other transport mechanisms differ from this value and can be predicted by conventional kinetic treatments of semiconductor junction transport.⁴

Figure 1 indicates the temperature dependence of V_{oc} for the n-GaAs/0.05 M FeCp_2 -0.5 mM $\text{FeCp}_2^{+/0}$ -0.2 M LiClO_4 - $\text{CH}_3\text{C}-\text{H}_2\text{CN}$ junction^{1b} (ELH type tungsten-halogen bulb; (100) oriented, $2 \times 10^{17} \text{ cm}^{-3}$ Se doped, n-GaAs; 2-s etch in 4:1:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) at an illumination intensity of 100 mW/cm². We observe a slope for V_{oc} vs. T of $-2.1 \pm 0.2 \text{ mV/K}$ and an extrapolated intercept of $1.45 \pm 0.1 \text{ V}$ at 0 K. The band gap (E_g) of GaAs is 1.42 eV at 300 K and 1.52 eV at 0 K;⁴ thus, the intercept of V_{oc} vs. T , determined over the range of 300–200 K, is very close to E_g . Association of this intercept with the transport activation energy indicates that thermionic emission of majority carriers over a Fermi level pinned barrier is not the dominant transport mechanism at this interface.

Other factors which might complicate the interpretation of V_{oc} vs. T plots for these junctions have been considered in detail. Variation of the bulk semiconductor properties which produce changes in short-circuit photocurrent density (J_{sc}) with temperature, such as the carrier mobilities, the absorption coefficient, and the minority carrier lifetime, will lead to changes in J_{sc} of 2 mA/cm² over the entire temperature range.⁵ This will produce a change of only 3 mV in V_{oc} . Variation in the barrier height as a result of changes in $E(A^+/A)$ with temperature is another possible source of complication. Determination of the temperature dependence of $E^0(\text{FeCp}_2^{+/0})$ in 0.2 M LiClO_4 - $\text{CH}_3\text{CH}_2\text{CN}$ by nonisothermal reference electrode technique yields a temperature coefficient of 0.6 mV/K, in accord with the measurements of Weaver for $E^0(\text{FeCp}_2^{+/0})$ in CH_3CN solvent.⁶ The negative shift in $E(A^+/A)$ with decreasing T might decrease the barrier height; thus, for the n-GaAs/ $\text{FeCp}_2^{+/0}$ - $\text{CH}_3\text{CH}_2\text{CN}$ system, the intercept

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