reaction was quenched with brine, and the product was extracted into ether. Removal of the solvent and chromatography of the residue on silica gel, eluting with 1:10 ethyl acetate-hexane, afforded **3f**: 340 mg (70%); mp 104-105 °C; IR (KBr) 1600, 1363, 1175, 1155 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.30 (3 H, s), 6.36 (1 H, t, J = 3 Hz), 6.70 (1 H, m), 6.77-6.87 (2 H, m), 7.00-7.13 (5 H, m), 7.65 (1 H, m), 7.73 (2 H, d, J = 8 Hz). Anal. Calcd for $C_{17}H_{15}NO_2S_2$: C, 61.98; H, 4.59; N, 4.25; S, 19.47. Found: C, 61.88; H, 4.53; N, 4.56; S, 19.35.

General Procedure for the Isomerization of 3 to 5. A mixture of **3b** (660 mg, 1.95 mmol), 5 mL of 1,2-dichloroethane, and 5 mL of TFA was refluxed for 2.5 h. Removal of the solvent and chromatography of the residue on silica gel, eluting with 1:5 ethyl acetate-hexane, afforded ethyl [(*N*-tosyl-3-pyrrolyl)thio]acetate (**5b**): 576 mg (87%); IR (film) 1735, 1600, 1370, 1170 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20 (3 H, t), 2.45 (3 H, s), 3.40 (2 H, s), 4.15 (2 H, q), 6.35 (1 H, m), 7.17 (1 H, m), 7.30 (1 H, m), 7.35 and 7.80 (4 H, AB q, J = 8 Hz). Anal. Calcd for $C_{15}H_{17}NO_4S_2$: C, 53.07; H, 5.05; N, 4.13; S, 18.89. Found: C, 53.18; H, 5.26; N, 4.37; S, 18.88.

General Procedure for the Hydrolysis of 5. A mixture of **5b** (396 mg, 1.17 mmol), 20 mL of methanol, and 2.9 mL of 2 N NaOH was refluxed for 2 h. The mixture was cooled, diluted with water and acidified (pH 6) with 1 N HCl, and extracted with ethyl acetate. Removal of the solvent afforded (3-pyrrolylthio)acetic acid (**6b**): 173 mg (94%); mp 59-60 °C; IR (KBr) 3380, 3300-2500, 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.35 (2 H, s), 6.27 (1 H, m), 6.73 (1 H, m), 6.92 (1 H, m), 9.6-10.4 (2 H, exchangeable with D$_2$O). Anal. Calcd for $C_6H_7NO_2S$: C, 45.84; H, 4.49; N, 8.91; S, 20.40. Found: C, 45.90; H, 4.52; N, 8.81; S, 20.14.

3-[(3-Methoxypropyl)thio]pyrrole (6a): IR (film) 3500-3100, 2930, 1110 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.85 (2 H, quintet, J = 7 Hz), 2.75 (2 H, t, J = 7 Hz), 3.35 (3 H, s), 3.50 (2 H, t, J = 7 Hz), 6.27 (1 H, m), 6.70-6.90 (2 H, m), 8.20-8.90 (1 H, exchangeable with D$_2$O).

3-[(*p*-Bromobenzyl)thio]pyrrole (6e): mp 59-60 °C; IR (KBr) 3370, 1490, 1070 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.80 (2 H, s), 6.20 (1 H, m), 6.70 (1 H, m), 6.80 (1 H, m), 7.10 and 7.45 (4 H, AB q, J = 8 Hz), 8.0-8.5 (1 H, exchangeable with D$_2$O). Anal. Calcd for $C_{11}H_{10}BrNS$: C, 49.26; H, 3.76; N, 5.22; S, 11.96. Found: C, 49.30; H, 3.68; N, 5.17; S, 11.63.

Isomerization of 3b to 5b in the Presence of 1a. A solution of **1a** (42 mg, 0.20 mmol) and **3b** (34 mg, 0.10 mmol) in 1 mL each of 1,2-dichloroethane and TFA was refluxed for 2 h. The mixture was cooled and concentrated to dryness. Chromatography of the residue on silica gel, eluting with 3:10 ethyl acetate-hexane, afforded 22 mg (65%) of **5b** and 40 mg of **1a**.

Acknowledgment. We thank Drs. J. G. Atkinson and R. N. Young for valuable discussions and Mr. P. Hamel for providing us with quantities of **1b**.

Registry No. 1b, 17639-64-4; **2**, 89597-62-6; **3a**, 89597-63-7; **3b**, 89597-64-8; **3c**, 89597-65-9; **3d**, 89597-66-0; **3e**, 89597-67-1; **3f**, 89597-68-2; **4** (R = CH$_2$CO$_2$H), 89597-78-4; **5a**, 89597-69-3; **5b**, 89597-70-6; **5c**, 89597-71-7; **5d**, 89597-72-8; **5e**, 89597-73-9; **5f**, 89597-74-0; **6a**, 89597-75-1; **6b**, 89597-76-2; **6d**, 82511-51-1; **6e**, 89597-77-3; **6f**, 82511-49-7; 1,3-dibromopropane, 109-64-8.

Redox Properties of Some Novel Cumulene Electron Donors. Electrodimerization and Stability of Heterocumulene Cation Radicals

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Received October 12, 1983

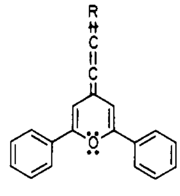
There has been considerable interest recently in organic polymers[1] and crystals[2] that show "metal-like" conductivity. Electronic conductivity in the organic crystals requires the formation of segregated columns of an electron donor, e.g., tetrathiafulvalene (TTF), and an electron acceptor, e.g., 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), as well as partial charge transfer between the donor (D) and the acceptor (A). Novel electron donors and acceptors are being synthesized with the hope of finding the proper combination of D and A or D alone that will produce crystals with superconducting properties at atmospheric pressure and room temperature.[3]

Table I. Electrochemical Behavior of Some Cumulene Derivatives[a]

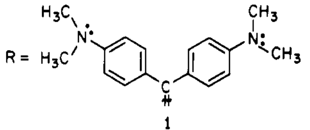
	$E_1^{\circ\prime}$			$E_2^{\circ\prime}$			
compd	$E_p{}^a$	$E_p{}^c$	rev	$E_p{}^a$	$E_p{}^c$	rev	$E_2^{\circ\prime} - E_1^{\circ\prime}$
1	0.14	0.07	rev	0.30	0.24	rev	0.16
2	0.44	0.38	rev	0.76	0.70	rev	0.32
3	0.46	0.40	rev	0.83	0.76	rev	0.37
4	0.27	0.19	rev	0.41	0.33	rev	0.14
5	0.83	0.75	rev				
6	0.69	0.62	rev				
7	0.66[b]		irrev				
8	0.76[b]		irrev				

[a] V vs. SCE, 0.1 N tetrabutylammonium fluoroborate electrolyte in methylene chloride, cyclic voltammetry at -80 °C, $c = 1.0 \times 10^{-4}$ M cumulene, 0.5 V/s scan rate, SCE reference electrode, glassy carbon working electrode. $E_p{}^a$ and $E_p{}^c$ refer to peak potentials for anodic and cathodic waves, respectively. [b] E_p at 200 mV s^{-1} scan rate.

We report the redox behavior of a novel class of electron donors, the cumulenes. The cumulenes **1-8** have a planar structure and low oxidation potentials and form stable cation radicals when properly substituted. The cumulenes are a new class of electron-donor partners that may be used with the appropriate electron acceptors to form charge-transfer salts.[4,5]



General Structure



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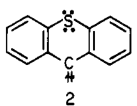

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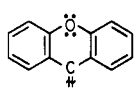

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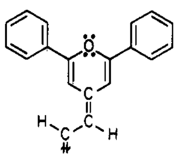

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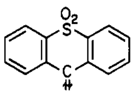

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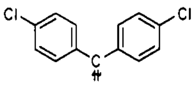

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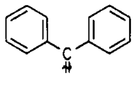

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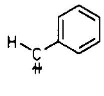

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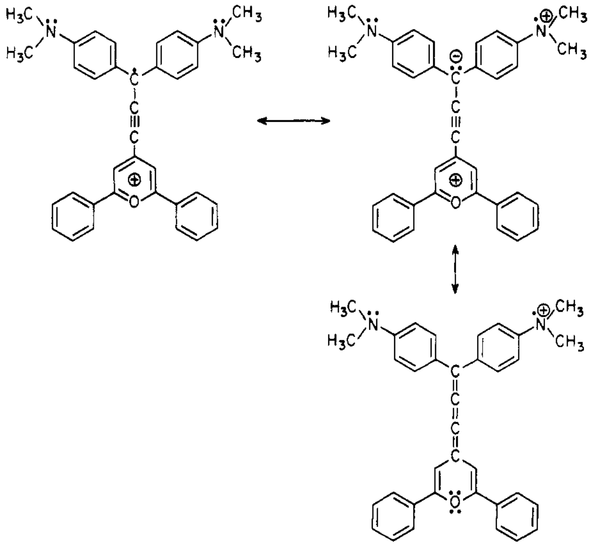
Table II. Redox Behavior of Cumulene Dimers at -80 °C in CH_2Cl_2

compd	$E_1^{\circ\prime}$ (V vs. SCE)^a	
	$E_p^{\,a}$	$E_p^{\,c}$
1		
2	0.35	0.31
3	0.37	0.34
4	0.12	0.06
5	0.68	
6	0.57	
7		
8		

[a] At -80 °C, 1.0×10^{-4} M cumulene concentration in CH_2Cl_2, 200 mV/s scan rate. $E_p^{\,a}$ and $E_p^{\,c}$ refer to peak potentials for anodic and cathodic waves, respectively.

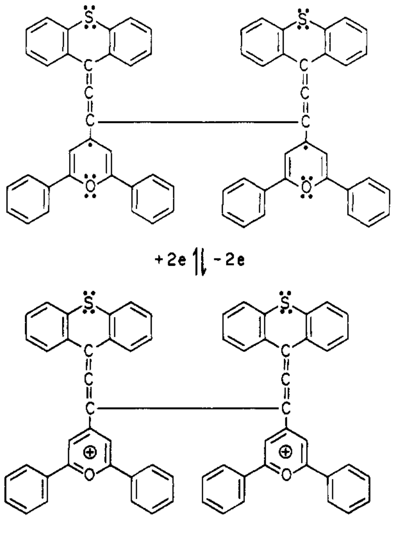
The heterocumulenes **1–8** have been synthesized,[6] and their redox behavior and cation-radical stability have been investigated. Four of the eight cumulenes (**1–4**) show two one-electron reversible oxidation waves at high scan rates (0.5–1.0 V/s) and at low concentrations (1.0×10^{-4} to 1.0×10^{-5} M) in methylene chloride at −80 °C. In compounds **1–5**, oxidation to the cation radical occurs between 0.11 and 0.79 V ($E^{\circ\prime}$ vs. SCE), whereas oxidation to the dication (**1–4**) occurs between 0.27 and 0.80 V (see Table I). The difference in the first and second oxidation potentials varies between 0.14 and 0.37 V.

The cation-radical species of cumulenes **2–8** self-dimerize. Compound **1** is the only cumulene we studied that forms a cation radical that is stable to dimerization even at room temperature. The radical-cation species **1a** is stabilized by captodative[7] (cd) interaction as shown. The dimerization produces species with compounds **2** and **3** that show reversible redox couples, which suggests transfer of more than one electron. The dimer redox couple most likely corresponds to the dimer **2a** (see Table II). The fact that dimerization does occur as a result of one-electron oxidation of the cumulenes was confirmed by mass spectroscopy.



1a

captodative (cd) stabilization of radical



2a

Cation radicals of compounds **2–8** dimerized to the extent of 50 ±2% at −80 °C (at a concentration of 1.0×10^{-4} M in methylene chloride at a scan rate of 200 mV s^{-1}). The extent of dimerization appears to be kinetically controlled.

In summary, five of eight novel cumulene electron donors show reversible redox couples at −80 °C in methylene chloride solution at a glassy carbon electrode surface. The cumulene cation radical dimerizes in every case except compound **1**, which has a high degree of captodative stabilization. The dimers of **2** and **3** show a reversible redox couple, which appears to correspond to a transfer of more than one electron. A structure for the dimers has been proposed.

Experimental Section

Electrochemistry Equipment. For cyclic voltammetry, a Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer were used in the standard three-electrode configuration (glassy carbon working electrode, a platinum auxiliary electrode, and a standard calomel reference electrode). The electrolyte was 0.1 M tetrabutylammonium fluoroborate (TBAF) recrystallized from ethyl acetate/pentane in dry methylene chloride freshly distilled under argon. For coulometry, a Princeton Applied Research Model 179 digital coulometer with a Model 377A coulometry cell system was used. Low-temperature cyclic voltammetry was carried out by immersing the electrochemical cell in an ethyl acetate/liquid nitrogen bath. The temperature of the methylene chloride/electrolyte solution was monitored with an Omega Model 199 digital readout indicator with an iron–constantan thermocouple.

Electrodimerization of 2. A solution of 50 mg of **2** in 50 mL of electrolyte solution was purged with argon and electrolyzed at 0.50 V (vs. SCE) in a coulometry cell system consisting of a platinum-gauze working electrode, a platinum counterelectrode, and a standard calomel reference electrode at room temperature. After the removal of 2 electron equiv, the reaction mixture was flash evaporated, the TBAF was dissolved in cold methanol, and the dark-colored solid was collected by suction filtration and air-dried, giving 41 mg of crude product. Its mass spectrum (FDMS), *m/e* 905, and a weak infrared band at 2020 cm^{-1} (KBr) are consistent with structure **2a**. Cyclic voltammetry of this material was identical with that observed with **2** (see Table II) at −80 °C.

Registry No. **1**, 87031-46-7; **1** radical cation, 89827-56-5; **2**, 87031-49-0; **2** radical cation, 89827-57-6; **2a** (dication), 89827-64-5; **2a** (diradical), 89889-03-2; **3**, 87031-48-9; **3** radical cation, 89827-58-7; **4**, 87031-51-4; **4** radical cation, 89827-59-8; **5**, 87043-71-8; **5** radical cation, 89827-60-1; **6**, 87031-47-8; **6** radical cation, 89827-61-2; **7**, 87031-45-6; **7** radical cation, 89827-62-3; **8**, 87031-50-3; **8** radical cation, 89827-63-4.

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