substitution, which is similar to that of the more complex pyrrolizidine alkaloids.[26] Thus the methods described herein may provide an enantioselective entry to this important class of alkaloids. Studies directed toward this end as well as other synthetic ventures using radical carbon–carbon bond forming reactions will be reported in due course.

Acknowledgment. We thank Dr. C. E. Cottrell and Richard Weisenberger for their assistance in obtaining 300-MHz ^{1}H NMR and mass spectra, respectively, at The Ohio State University Chemical Instrument Center. Financial support from donors of The Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 1, 58805-10-0; (±)-**2**, 80664-36-4; (±)-**3**, 80664-37-5; (±)-**4**, 80664-38-6; **5**, 80664-39-7; **6**, 52132-72-6; (±)-**7**, 80664-40-0; (±)-**8**, 80664-41-1; (±)-**9**, 71779-55-0; (±)-**10**, 62279-67-8; (±)-**10** picrate, 62318-95-0; (±)-**11**, 17463-81-9; (±)-**11** picrate, 17463-80-8; (±)-**13a**, 80664-42-2; (±)-**13b**, 80664-43-3; (±)-**13c**, 80664-44-4; **14a**, 80664-45-5; **14b**, 80664-46-6; **14c**, 80664-47-7; (±)-**15**, 80664-48-8; (±)-**16**, 80664-49-9; (±)-**17**, 80664-50-2; (±)-**18**, 80664-51-3; (±)-**19**, 80664-52-4; **21**, 80664-53-5; (±)-**22**, 80664-54-6; (±)-**23**, 78308-08-4; **24**, 80664-55-7; (±)-**25**, 80664-56-8; **26**, 80664-57-9; (±)-**27**, 80664-58-0; (±)-**20**, 80664-59-1; (±)-1-(pent-4-en-1-yl)-5-thiophenoxy-2-pyrrolidinone, 80664-60-4; 1-(pent-4-en-1-yl)-2-pyrrolidinone, 80664-61-5.

Supplementary Material Available: Spectral data (NMR, IR, and mass) on compounds **4**, **6–11**, and **13–27** and schemes for independent syntheses of **9**, **10**, and **26** (10 pages). Ordering information is given on any current masthead page.

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[25] The stereochemical assignments for **27** are based on NOE experiments performed at 300 MHz. For example, irradiation of the C-1 methyl group shows a 15% NOE at H-7.

[26] For an overview see: Robins, D. J. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1979; Vol. 24, p 247.

Design and Synthesis of an Amphoteric Four-Stage Redox Hydrocarbon Bearing Phenalenyl Moieties. 1,2-Bis(phenalen-1-ylidene)ethane[1]

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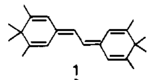
Received October 14, 1981

Recently a rich variety of multi-stage redox-type organic molecules has been synthesized, and their chemical and physical properties, redox potentials in particular, have been correlated with their structural characteristics.[2] One of the unique features of conjugated hydrocarbons is in the amphoteric redox property in which both multi-stage anodic oxidation and cathodic reduction steps are observed. Only a few examples of such redox systems known to date are polycyclic arenes[3] such as anthracene and perylene and cross-conjugated polyenes such as bis(3,4,4,5-tetramethyl-2,5-cyclohexadien-1-ylidene)ethane (**1**) and ethene (**2**).[4,5] However, there are almost no efforts to synthesize molecules designed so as to reduce both oxidation potential (E^{ox}) and reduction potential (E^{red}). To date significant advances have been made on the correlation of E^{ox} and E^{red} with ionization potential and electron affinity of hydrocarbons.[6,7] Furthermore, the numerical sum of E^{ox} and E^{red}, i.e., $E^{sum} = E^{ox} + (-E^{red})$, is independent of the reference potential. Thus, E^{sum} values might be used as one of the convenient *experimental measures* estimating the extent of the amphoteric redox property of a hydrocarbon being considered. In this communication we report the design, synthesis, and some properties of a new class of compound that exhibits the *smallest* E^{sum} *value*.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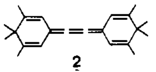
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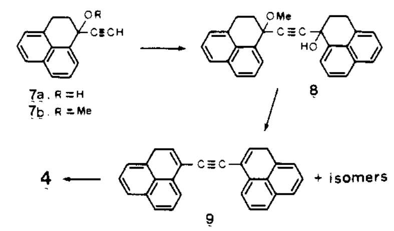
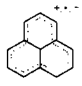
Scheme I



The odd alternant hydrocarbon phenalenyl appears to be a potential candidate to build up this class of redox systems[8] because it is known to exist in three electronically stable oxidation states:[9a,b] the cation (**3**$^+$),[9c] the radical (**3**·),[9d] and the anion (**3**$^-$).[9c] However, the serious disadvantage of the open-shell hydrocarbon **3**· is the lack of its stability, since it is known to dimerize in solution even at low temperature.[9a,10] In order to construct the closed-shell amphoteric four-stage redox hydrocarbons based on the phenalenyl system, two phenalenyl rings as the terminal groups are connected with two sp^2 carbons producing 1,2-bis(phenalen-1-ylidene)ethane (**4**). Although **4** consists of the phenafulvene moiety **5**, which has been shown to be an unstable transient species,[11] fortunately **4** proved to be a stable and isolable compound by our earlier studies.[11,12] However, extremely low yield of its formation prevented us from investigating the detailed properties of **4**. Thus, we synthesized **4** with an unequivocal procedure (Scheme I).[13]



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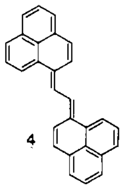
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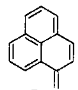
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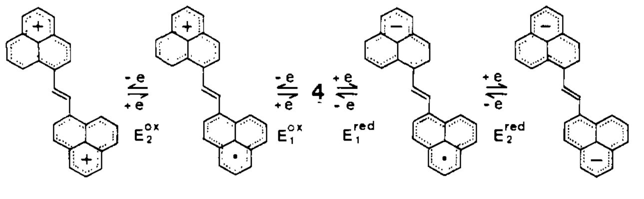
Table I. Cyclic Voltammetric Data for 4 and Some Related Compounds

	E_2^{ox}	E_1^{ox}	E_1^{red}	E_2^{red}	$E_1^{sum\,e}$	$E_2^{sum\,f}$
4[a]	+0.83	+0.39	−1.12	−1.35	1.51	2.18
1[b]	+1.04	+0.68	−2.12	−2.64	2.80	3.68
2[b]	+1.08	+0.68	−2.02	−2.42	2.70	3.50
perylene[c]	+1.59	+1.06	−1.66	−2.19	2.72	3.78
TCVDMA[d]		+0.96	−0.70		1.66	

[a] This work, measured vs. SCE in DMF (8.0×10^{-4} M) with 0.1 M Et_4NClO_4 as supporting electrolyte at −50 °C; sweep rate = 7 mV/s. [b] Reference 4. [c] Reference 7. [d] *p*-(Tricyanovinyl)-*N*,*N*-dimethylaniline, ref 16. [e] $E_1^{sum} = E_1^{ox} + (-E_1^{red})$. [f] $E_2^{sum} = E_2^{ox} + (-E_2^{red})$.

Scheme II



A reasonable key intermediate for the synthesis of **4** is the diphenalenylacetylene **9**, which might be converted to **4** by an appropriate isomerization procedure. The ethynyl alcohol **7a**, prepared in 97% yield by ethynylation of phenalanone (**6**) with lithium acetylide in THF at −78 °C, was converted to its methyl ether **7b** (NaH and then CH_3I in THF, 45–50 °C) in 93% yield as colorless oil. The lithium salt of **7b** (BuLi in THF, −78 °C) was treated with **6** to give the acetylene **8** in 46% yield as a pale yellow solid. Dehydration of **8** with a catalytic amount of β-naphthalenesulfonic acid in benzene at 80 °C for 10 min afforded **9** as an isomeric mixture. Isomerization of the mixture into the final compound **4**, as dark violet needles, mp 243–246 °C (dec),[14] was achieved by treatment with a large excess of triethylamine in dichloromethane (34% yield based on **8**).

The electrochemical behavior of **4** was studied by cyclic voltammetry, and the results are summarized in Table I together with the corresponding data reported for some related compounds. The sums of redox potentials, E_1^{sum} and E_2^{sum}, are also listed in the Table I. The most striking feature is that the span of the second oxidation and reduction potentials of **4** (E_2^{sum} = 2.18 V), not to mention that of the first potentials (E_1^{sum} = 1.51 V), is substantially smaller than the E_1^{sum} of the related hydrocarbons reported so far.[7,15] Furthermore, the E_1^{sum} of **4** can be compared to that of the nonhydrocarbon molecule *p*-(tricyanovinyl)-*N*,*N*-dimethylaniline (TCVDMA), which comprises both the electron donor and acceptor moieties and exhibits the intermolecular π-amphoteric character in solid state.[16]

Such small values of E^{sum} observed for **4** can be attributed to the considerable electronic stability of the three oxidation states of the phenalenyl moiety, which are expected to be created in all of the redox states of **4** as shown in Scheme II.

Further studies are now in progress to design and synthesize novel conjugated hydrocarbons having small E^{sum} values in which intriguing chemical and physical properties might be expected.

Acknowledgment. We thank Professor Shigero Ikeda, Dr. Iwao Watanabe, and Nobuaki Ogawa of our department for their aid in the measurement of cyclic voltammetry, Iwao Miura (Laboratories of Natural Products Chemistry, Otsuka Pharm. Co. Ltd.) for the 400-MHz NMR measurements, and Dr. Robert C. Haddon (Bell Laboratories, Murray Hill, NJ) for his interest and encouragement.

Registry No. 4, 50472-56-5; **6**, 518-85-4; **7a**, 80631-49-8; **7b**, 80631-50-1; **7b** lithium salt, 80631-51-2; **8**, 80631-52-3; **9**, 80631-53-4.

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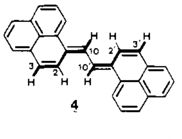
(13) All new compounds afforded proper combustion analyses as well as suitable IR and NMR spectra.

(14) **4**: UV/vis λ_{max} (in THF) 704 sh (log ε 2.94), 583 (5.17), 539 (4.79), 500 (4.30), 470 (3.74), 436 sh (3.15), 408 sh (3.11), 367 (3.46), 334 sh (3.83), 320 sh (3.98), 304 sh (4.22), 280 nm (4.11). The geometrical structure of **4** with C_{2h} symmetry as shown in the text was confirmed unambiguously through its 400-MHz ^1H NMR spectrum δ (CS_2 + CD_3COCD_3) 6.93 (d, *J* = 9.7 Hz, H_3), 7.20 (d, *J* = 7.3 Hz, H_4), 7.29 (dd, *J* = 8.3, 7.3 Hz, H_5), 7.45 (dd, *J* = 8.0, 8.0 Hz, H_8), 7.53 (d, *J* = 8.3 Hz, H_6), 7.58 (d, *J* = 9.7 Hz, H_2), 7.63 (d, *J* = 8.0 Hz, H_7), 7.91 (s, H_{10}), 8.22 (d, *J* = 8.0 Hz, H_9). Furthermore, small long-range coupling through five bonds between H^3 and H^{10} (also $H^{3'}$ and $H^{10'}$) (zigzag path) together with the substantial NOE (20%) between H^2 and $H^{10'}$ (also $H^{2'}$ and H^{10}) could be observed.



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Ruthenium-Catalyzed Oxygenation of Catechols to Muconic Acid Anhydrides and 2*H*-Pyran-2-ones. Intradiol and Extradiol Cleavage of the Carbon–Carbon Bond

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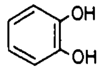
Pyrocatechase and metapyrocatechase are nonheme iron oxygenases capable of oxidatively opening catechol (**1**) by inserting both atoms of molecular oxygen into the substrate.[1] The former causes the intradiol ring cleavage, while the latter sets off the extradiol ring opening. Two types of mechanisms have been proposed for the pyrocatechase reaction: the first includes the formation of the dioxetane intermediate **2** (Hayaishi[2] and Grinstead[3]), and the second is a path through an anhydride **3**, which is more thermodynamically favorable than the dioxetane (Hamilton).[4] Although there have been several nonenzymatic approaches by the use of singlet oxygen,[5] superoxide ion,[6] and a combination of molecular oxygen and copper complexes[7] or iron complexes,[8] none of them have provided a direct evidence of the intermediates **2** or **3**.



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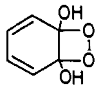

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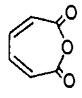

3

We report here a nonenzymatic oxygenation of catechols with molecular oxygen activated by ruthenium, which is just below iron

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