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SYNTHESIS AND ELECTROCHEMICAL CHARACTERISTIC OF 1,2-BIS(PHENALEN-1-YLIDENE)ETHENE. AN AMPHOTERIC FOUR-STAGE REDOX HYDROCARBON[1]

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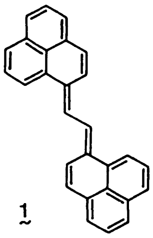
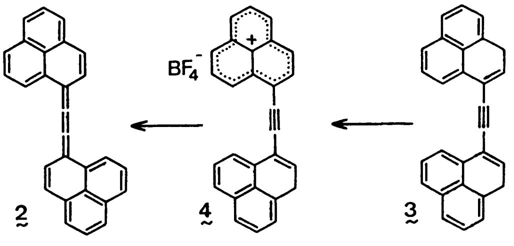
Electrochemical evidence presents that both two-stage oxidation and reduction steps (as an amphoteric four-stage redox system) are possible for 1,2-bis(phenalen-1-ylidene)ethene which has been synthesized starting from an isomeric mixture of diphenalenylacetylene through hydride abstraction and deprotonation procedure.

Extensive investigations on the redox properties of various conjugated systems by Hünig and co-workers2) have led to a resurgence of interest in these molecules. In our own studies3) toward design and synthesis of exotic redox systems we have recently reported the synthesis of 1,2-bis-phenalen-1-ylidene)ethane (**1**)4) as a novel example of multi-stage amphoteric redox hydrocarbon. Indeed, **1** exhibited both two-stage anodic oxidation and cathodic reduction steps with small numerical sum (E^{sum})5) of oxidation (E^{ox}) and reduction potentials (E^{red}). The electrochemical feature of **1** is attributable undoubtedly to the substantial electronic stability of three oxidation states of the two terminal phenalenyl moieties (cation, radical, and anion)6) which are expected to be created in all redox states of **1**. This finding prompted us to extend our idea to the related system, 1,2-bis(phenalen-1-ylidene)ethene (**2**) in which two phenalenyl moieties are connected with two sp-carbon atoms.





Assessing the known instability of both phenafulvene7) and cumulated double bond compared to conjugated double bond having equal number of carbon atoms,8) we envisioned mild conditions for the final conversion of an appropriate precursor into **2**. To this end hydride abstraction - deprotonation sequence has been applied to an isomeric mixture of diphenalenylacetylene (**3**)4) which has already been used for the synthesis of **1**.

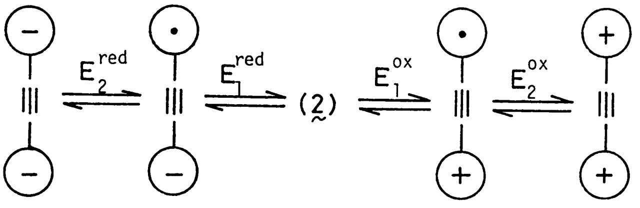
Treatment of **3** with triphenylmethyl tetrafluoroborate in dichloromethane at 0 °C afforded the mono-cation **4** as a greenish black solid. Subsequent deprotonation of **4** with a large excess of triethylamine in dichloromethane gave the desired cumulene **2** as a dark green crystalline solid in 35% yield from **3**. The compound **2** is labile under atmospheric conditions (it can be kept at -78 °C without any detectable decomposition), but purification of **2**9) could be performed by a short column chromatography on Florisil with benzene and then repeated reprecipitation from toluene - cyclohexane; mp 138 °C (dec. in a sealed tube), m/e 352 (M^+), λ_{max} (THF) 720 nm (log ε 3.86), 612 (5.37), 568 (4.42), 528 sh (3.66), 464 (2.81), 384 (3.81), 364 (3.85), 357 sh (3.96), 341 sh (4.06), 320 (4.43), 279 (4.41), and 231 sh (4.60); Raman ν 2017 cm^{-1} (C=C=C=C); δ_H (100 MH_z, CS_2 + C_6D_{12}, Me_4Si) 7.0 - 8.2 (m). Although the spectroscopic data supported the skeletal structure, the geometrical structure (E or Z) of **2** could not be assigned based on the available evidence.

Electrochemical data (E^{ox}, E^{red}, and E^{sum}) of **2** measured by cyclic voltammetry[10] are summarized in the Table together with the corresponding data reported for **1**.[4] The cumulene **2** clearly exhibits an amphoteric four-stage redox behavior in a similar manner as **1** though irreversible in the second oxidation step for both the compounds. The facts that **2** is more easily reduced and less easily oxidized than **1** are presumably attributable to the difference in electronegativity between sp- and sp^2-hybridized carbons. The relatively large difference in reduction potentials than in oxidation potentials between **1** and **2** brings a more decreased E_1^{sum} value to **2**, and hence the value of 1.34 V found for **2** is, at least to our knowledge, the smallest value as a hydrocarbon up to now.

Table. Electrochemical data of **2** and **1**. (V vs. SCE)

Compound	E_2^{ox}	E_1^{ox}	E_1^{red}	E_2^{red}	E_1^{sum}	E_2^{sum}
2	+0.78	+0.51	-0.83	-1.21	1.34	1.99
1[a)]	+0.83	+0.39	-1.12	-1.35	1.51	2.18

a) Ref. 4. For comparison of the data with those of the related compounds, see also ref. 4.



⊕, ⊙, and ⊖ denote phenalenyl cation, radical, and anion moieties, respectively.

References

1) The Chemistry of Phenalenium Systems 34. For part 33, see Y. Sugihara, K. Hashimoto, M. Yoshikawa, and I. Murata, Tetrahedron Lett., 1982, submitted for publication. 2) For reviews, see K. Deuchert and S. Hünig, Angew. Chem., Int. Ed. Engl., 1978, 17, 875., S. Hünig and H. Berneth, Top. Curr. Chem., 1980, 92, 1. 3) K. Nakasuji, K. Takatoh, M. Nakatsuka, and I. Murata, J. Chem. Soc., Chem. Commun., 1981, 717; K. Nakasuji, M. Nakatsuka, and I. Murata, Ibid., 1981, 1143. 4) K. Nakasuji, K. Yoshida, and I. Murata, J. Am. Chem. Soc., 1982, 104, 1432. 5) The numerical sum of E^{ox} and E^{red}, e.g., $E^{sum} = E^{ox} + (-E^{red})$, is independent of the reference potential and hence the E^{sum} values might be used as one of the convenient experimental measures estimating the extent of the amphoteric redox property of a compound being considered. 6) For reviews, see D. H. Reid, Quart. Rev., Chem. Soc., 1965, 19, 274; I. Murata in "Topics in Non-Benzenoid Aromatic Chemistry", T. Nozoe, R. Breslow, K. Hafner, S. Ito, and I. Murata, Eds., Hirokawa : Tokyo, 1976; Vol. 1. p 159. 7) I. Murata, K. Nakasuji, and H. Kume, Tetrahedron Lett., 1973, 3401, 3405. 8) M. Murray in "Methoden der Organischen Chemie (Houben-Weyl)" E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1977, Vol. V/2a, pp. 967. 9) The compound **2** gave satisfactory combustion analysis. 10) The cyclic voltammetry was carried out in N,N-dimethylformamide containing **2** (3×10^{-4} M) and $Et_4N^+ClO_4^-$ (0.1 M) at -60 °C under argon using a standard calomel electrode as a reference electrode and a Pt-electrode as a working electrode in the presence of suspended neutral alumina (O. Hammerich and V. D. Parker, Electrochim. Acta, 1973, 18, 537). Sweep rate is 30 mV sec^{-1}.

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