Polarographic Reduction Potentials of Some Nonbenzenoid Aromatic Hydrocarbons[1,2]

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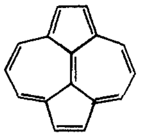
Received August 28, 1973

Maccoll, using the analogy of the behavior of aromatic hydrocarbons with alkali metals as interpreted by Hückel,[4] drew attention to the linear relationship between the Hückel molecular orbital (HMO) energy of the lowest vacant molecular orbitals of aromatic hydrocarbons and their polarographic half-wave reduction potentials,[5,6] and this was rapidly confirmed for a few benzenoid compounds. Subsequently a sizable number of these have been measured and this correlation has been shown to be quite good.[7] At the time the reduction potentials for azulene were first measured in our laboratory,[8] we noted that the point for the first half-wave potential for this nonalternant, nonbenzenoid hydrocarbon fell a significant distance below the line through the point distribution for benzenoid molecules and suggested that this might be due to an error in the calculated values used for the coefficient of the energy of the lowest vacant MO for azulene. The more recent synthesis of dicyclopenta[*ef,kl*]heptalene (azupyrene, 1),[9] 4-methylpentaleno[1,6,5-*def*]heptalene (4-methyl-*as*-azupyrene, 2),[10] cyclopentadieno-[1,5,4:1,11,10]heptalene (aceheptylene, 3),[11] and 3,5,8,10-tetramethylaceheptylene (4)[11] provided the opportunity to test the generality of the deviation found for azulene.



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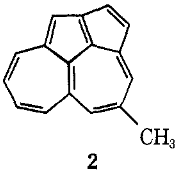

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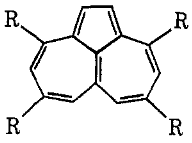


3, R = H
4, R = CH$_3$

The usual solvents for polarographic reductions of organic compounds are aqueous dioxane, DMF, and 2-methoxyethanol, but the insolubility of azupyrene in these media precluded their use and acetonitrile, which is stable up to −2.8 V, was chosen instead.

Experimental Section

Materials. Azulene (Henley & Co., Inc., New York, N. Y.) was used as obtained. Dicyclopenta[*ef,kl*]heptalene (azupyrene)[9] was recrystallized from methanol. 4-Methylpentaleno[1,6,5-*def*]heptalene (4-methyl-*as*-azupyrene), cyclopentadieno-[1,5,4:1,11,10]heptalene (aceheptylene), and 3,5,8,10-tetramethylaceheptylene were provided by Professor K. Hafner. Reagent-grade acetonitrile (Aldrich Chemical Co.) was purified as described by Wong,[12] or Spectrograde was used as obtained. Reagent grade tetraethylammonium perchlorate was dried by heating at 80° (0.1 mm).

Measurements. Polarograms were taken on a Sargent Model 111 polarograph which was calibrated *vs.* a standard resistance (R = 200 kΩ ± 0.1%). The applied potential was measured independently with a Keithley electrometer. The electrolysis cell was a 20-ml Hg anode cell. Contact was made with the Hg pool by a platinum lead into a side arm containing Hg. The potential of the anode *vs.* a saturated calomel electrode (sce) was measured before and after each determination and was found to be stable. The capillary characteristics were m = 1.75 mg/sec and t = 3.0 sec at −1.2 V and h = 40 cm.

Hydrocarbon solutions in acetonitrile of known concentration (Table I) and 2.0 M in tetraethylammonium perchlorate were used. The occasional problem of current maxima was minimized by the addition of a small amount of gelatin. Solutions were deoxygenated by bubbling N$_2$ or Ar through for 15–20 min. The single measurement on 4 was made after the reproducibility of the method had been established.

Table I
Polarographic Reduction Data and Lowest Vacant MO Energy Coefficients

Compd	Concn, $M \times 10^{-4}$	$-E_{1/2}$[a]	i_d[b]	$-m_{m+1}$
1	2.475	1.35 1.79[c]	0.80	0.4450[f]
1	1.238	1.387 1.747[c]	0.40	
1	0.619	1.355 1.695[c]	0.20	
1	0.308	1.385 1.795[c]	0.16[d]	
2	10.0	1.48 2.57[c]	2.4	0.3029[e,f]
2	10.0	1.49 2.55[c]	2.4	
3	11.8	1.26	5.50	0.2411[g]
3	11.8	1.30	5.50	
4	10.2	1.42	5.25	0.2411[e]

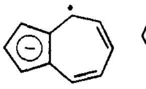
[a] Volts *vs.* sce. [b] Current in microamperes. [c] Second reduction wave. [d] Inaccurate owing to low concentration. [e] Value for parent structure. [f] R. Zahradnik, J. Michl, and J. Paneir, *Tetrahedron*, **22**, 1355 (1966). [g] R. Zahradnik, J. Michl, and J. Koutecky, *Collect. Czech. Chem. Commun.*, **29**, 1932 (1964).

Results and Discussion

Plots of E *vs.* log $(i_d - i)/i$ for azupyrene gave straight lines with slopes of 0.052 (first wave) and 0.074 (second wave), indicating reversible, one-electron processes. Calculation of the electron charge using the Ilkovic equation and a diffusion constant of 0.43 × 10^{-5} cm^2/sec (calculated for naphthalene in 75% aqueous dioxane from the data of Wawzonek and Laitinen[13]) gave a value of 0.98 for the first wave.

The polarographic reduction data and the $-m_{m+1}$ coefficients of the energies of the lowest vacant MOs are given in Table I. The observed half-wave reduction potentials (first wave) were plotted *vs.* $-m_{m+1}$ and compared to the correlations in the literature (Figure 1).[7] For this comparison to be valid, the effect of the solvent difference must be small. It has been found that values measured in 96% aqueous dioxane differ only slightly from those obtained in 75% aqueous dioxane[14] and reductions in dimethylformamide give values very close to those in other solvents.[15] As a further check the value for azulene was redetermined in acetonitrile and found to be −1.64 V as compared to −1.63 V in 75% aqueous dioxane.[16]

The plots for 1, 2, and 3 were, as for azulene, below the line for benzenoid aromatic hydrocarbons. Thus the nonbenzenoid, nonalternant compounds were reduced more easily than was predicted by the MO calculations. We believe these deviations to be larger than the experimental error in the measurements of the reduction potentials. Two reasons may be advanced: "abnormal" solvation energies for the radical anions formed, and the inappropriateness of the calculated values of $-m_{m+1}$ Structures can be written for the radical anions which would result in some localization of the charge and a consequent stabilization of the solvated species (*e.g.*, **5–8**, all of which possess a stable $4n + 2$ π-electron moiety).[17]



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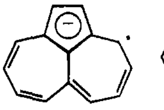

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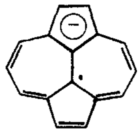

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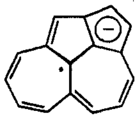

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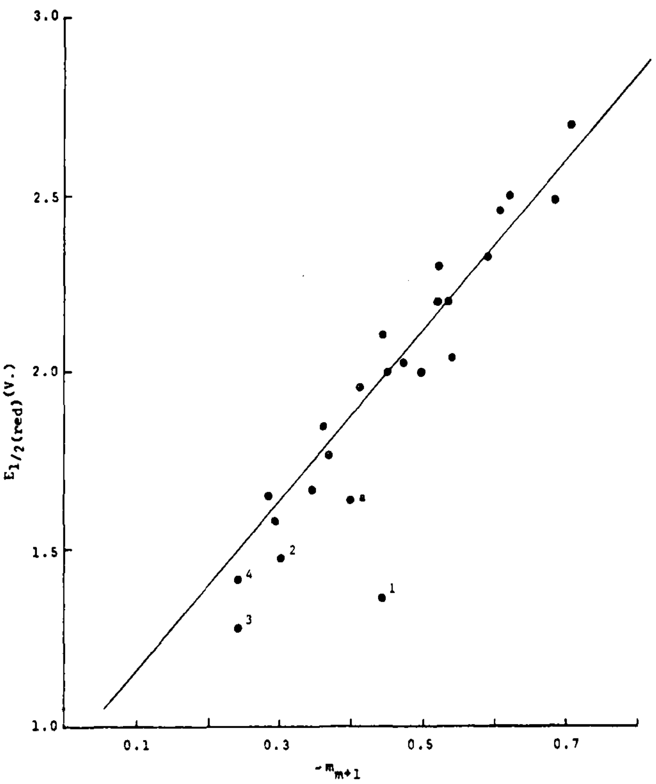

Figure 1. Half-wave reduction potentials *vs.* energies of lowest vacant orbitals for azulene (a), azupyrene (1), 4-methyl-*as*-azupyrene (2), aceheptylene (3), and 3,5,8,10-tetramethylaceheptylene (4) in acetonitrile, and benzenoid hydrocarbons[7] in aqueous dioxane.

It has been pointed out[6a] that different values of β, which will change $-m_{m+1}$, may be required when the bond lengths in a conjugated system are not equal. The value of $-m_{m+1}$ used for azulene (0.40) in Figure 1 was obtained by the simple HMO method using a standard length of 1.4 Å. We have checked this and also calculated the corresponding value for $-m_{m+1}$ (0.47) using bond lengths found by the X-ray diffraction analysis of azulene-1,3-dipropionic acid.[18] The use of unequal bond lengths thus causes the point for azulene to be farther from the line for benzenoid aromatics. CNDO/2 calculations for azulene using equal bond lengths and the X-ray data gave $-m_{m+1}$ values of 0.27 and 0.40, respectively, and thus show the same directional trend in magnitude.[19] The values of $-m_{m+1}$ for the benzenoid compounds in Figure 1 were also calculated using equal bond lengths, and the use of alternating, unequal bond lengths might result in comparable corrections. As a check it was determined for naphthalene, and qualitatively for anthracene and phenanthrene, that the corrections would not be significant.[20] The assumption of standard, equal bond lengths for **1**, **2**, and **3** therefore seems not to be responsible for the location of their points on the graph below the line for the benzenoid hydrocarbons.

Compounds **2** and **4** have methyl substituents and the effect of these groups must be considered. Comparison of **3** and **4** shows a difference of 0.14 V due to four methyl groups, and this suffices to put the point for **4** within the distribution for benzenoid compounds. A study[21] on a series of methylazulenes showed that the substituent effects in these compounds amounted to 0.01–0.12 V, which did not agree well with calculated potential changes. These results suggest that the reduction potential of the parent system of **2** would be slightly lower than that of **2**, and thus still farther below the line.

Acknowledgments. The authors wish to express their gratitude to Professor K. Hafner for providing compounds **2**, **3**, and **4**, and also to Professors E. R. Davidson and N. Epiotis and to Mr. W. Cherry for assistance with the calculations.

Registry No.—**1**, 193-85-1; **2**, 781-30-6; **3**, 209-42-7; **4**, 17597-70-5.

References and Notes

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(3) National Institutes of Health Predoctoral Fellow, 1968–1970.
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4-Methylnorcamphor and Its Carbon-13 Nuclear Magnetic Resonance Spectrum

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Received August 29, 1973

Although interest in the chemistry of bicyclo[2.2.1]heptanes has been widespread over a number of years, the 1,3-disubstituted derivatives of this ring system have remained scarce. Indeed, a search of the 8th Decennial Index of Chemical Abstracts revealed 13 entries covering seven different 1,3-disubstituted norbornanes. 4-Substituted norcamphors, which are specific examples of 1,3-disubstituted norbornanes, are unknown. We now report that 4-methylnorcamphor (**8**), the only previously undescribed methylnorcamphor,[1] may be prepared from 3-methylcyclopentenone by a route that should be applicable to the synthesis of a variety of 4-substituted norcamphors.