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Syntheses and Properties of 7,9-Diphenyl- and 7,8,9-Triphenylcyclopent[*a*]acenaphthylenide Ions

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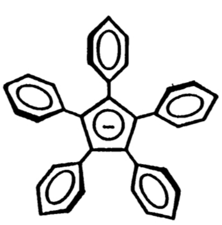
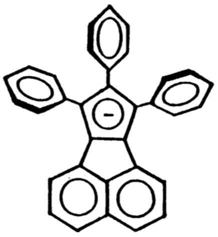
The 7,9-diphenyl- (**3**) and 7,8,9-triphenylcyclopent[*a*]acenaphthylenide ions (**2**) have been prepared and fully characterized in comparison with the pentaphenylcyclopentadienide ion (**1**). The anions **2** and **3** are nearly 1 pK unit more stabilized and about 0.05 V more readily oxidized than the anion **1**. Whereas the one-electron oxidation of **2** affords the persisting radical, the oxidation of **3** gives the dimeric compound quantitatively.

The substituted cyclopentadienide ions are of current interest not only as the typical Hückeloid carbanions, but also as potential ligands in organometallic chemistry.$^{1)}$ As for the pentaphenyl derivative **1**, its properties$^{1a)}$ and the utility as a ligand$^{1b)}$ were disclosed rather recently in contrast to the long history concerning the chemistry of the corresponding radical.$^{2)}$ When two of the neighboring benzene rings in **1** are replaced by a 1,8-naphthylene unit, 7,8,9-triphenylcyclopent[*a*]acenaphthylenide ion (**2**) results, in which charge delocalization into the coplanar naphthalene moiety is expected to alter the intrinsic electronic properties of the anionic five-membered ring. Although the synthesis of the parent anion **4** had already been reported,$^{3)}$ we were interested particularly in the properties of phenyl-substituted derivatives **2** and **3** in comparison with those of the cyclopentadienide ion **1**.



1



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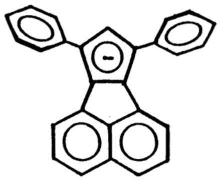

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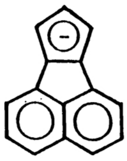

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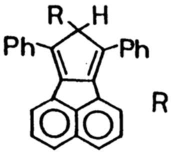
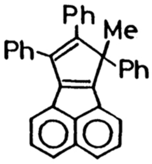
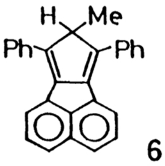
The precursor hydrocarbon **5a**[4)] was synthesized by bromination (AcBr/C_6H_6), followed by reduction (Zn/AcOH), of the corresponding alcohol,[5)] while **5b** was prepared according to the literature.[6)] Treatment of the yellow solutions of **5a,b** in THF with a base (t-BuOK or n-BuLi) under vacuum or the inert gas atmosphere afforded deep red solutions of **2** and **3**, which were quenched with MeI to give **6a**[7)] and **6b**,[7)] respectively in quantitative yields. The anion **2** was isolated as the dark red-brown bis(triphenylphosphoranylidene)ammonium (PPN^+) salt, which was fairly stable under air, by addition of PPN^+Cl^- to K^+**2** in CH_2Cl_2, filtering KCl off, and reprecipitation of the filtrate with ether.


R= Ph, H
5a **5b**


6a


6b

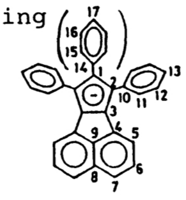
$Ph_3P{=}\overset{+}{N}{=}PPh_3$
(PPN^+)

The spectral data of the anions **2** and **3** are listed in Table 1 together with those of **1** for comparison. Apparently, the visible absorption of **2** and **3** is due to annelation with an acenaphthylene chromophore. The downfield shift observed for the ^1H NMR signals of H-5, H-11, and H-12 in **3** can be ascribed to the mutual ring current effect of the aromatic rings, which can assume more planar

Table 1. Spectral Properties of the Anions **1**, **2**, and **3** Determined under Vacuum

Anion		M^+ **1**	M^+ **2**	M^+ **3**
UV-Vis (DMSO) λ_{max} /nm (log ε) (M=Na)		338 (4.63) 373sh(4.47)	293 (4.42) 358 (4.34) 389 (4.36) 478 (4.04)	367 (4.32) 395sh(4.16) 495 (4.12)
^1H NMR (300 MHz) (THF-d_8) δ /ppm (M=Li)		6.84 (d, *o*-H) 6.80 (t, *m*-H) 6.68 (t, *p*-H)	7.31 (dx2, H-11,15) 7.17 (d, H-5) 7.05 (tx2, H-12,16) 6.98 (d, H-7)[b)] 6.90 (t, H-6)[b)] 6.86 (t, H-13) 6.81 (t, H-17)	7.72 (d, H-11) 7.38 (d, H-5) 7.20 (t, H-12) 7.02 (d, H-7)[b)] 6.93 (t, H-6)[b)] 6.86 (t, H-13) 6.19 (s, H-1)
^{13}C NMR[c)] (25 MHz) (THF-d_8) δ /ppm (M=Li)	cyc-C_5	120.6[d)]	125.8(C-1) 121.4(C-2) 128.1(C-3)	113.4(C-1) 123.7(C-2) 129.7(C-3)
	Ph	143.7(*i*) 125.8(*o*) 132.1(*m*) 120.2(*p*)	143.8(C-10) 127.6(C-11) 130.2(C-12) 122.6(C-13)	143.9(C-10) 125.9(C-11) 128.4(C-12) 122.1(C-13)
	Naph	——	141.7(C-4) 113.3(C-5) 127.4(C-6) 119.5(C-7) 138.9(C-8) 130.9(C-9)	141.6(C-4) 113.8(C-5) 127.7(C-6) 119.6(C-7) 138.5(C-8) 131.1(C-9)
	Ph'	——	143.4(C-14) 127.6(C-15) 132.4(C-16) 122.5(C-17)	——

a) Numbering system:



b) These assignments are tentative due to the severe peak overlapping. c) Assignments are based on peak intensity, peak multiplicity in off-resonance and fully ^1H-coupled spectra, and results of simple HMO calculations. d) Lit. δ (DMSO-d_6) 142.4, 131.0, 125.8, 120.8, 119.8 : Ref. 1a.

arrangements than those in **2**. On the other hand, the ^{13}C NMR signals for the fully substituted carbons in the five-membered ring of both **2** and **3** are in general less upfield shifted than that of **1**, indicating the decreased electron density due to the effective charge delocalization into the naphthalene moiety.

This electronic effect is well reflected on the carbon acidity of the hydrocarbon precursor, $pK_a(RH)$, determined spectrophotometrically in DMSO-EtOH[8] using Bowden's H_- function.[9] The data shown in Table 2 indicate that both of the cyclopent[*a*]acenaphthylenide ions **2** and **3** are about 1 pK unit more stabilized than the pentaphenylcyclopentadienide ion (**1**). This is in good agreement with the extent of stabilization reported for the anion **4** with reference to the unsubstituted cyclopentadienide ion (**7**).[3]

The cyclic voltammetry (CV) data, also given in Table 2, demonstrate that the anions **2** and **3** are somewhat more readily oxidized than **1** but they are reluctant to oxidation by about 0.1 V as compared with the unsubstituted cyclopentadienide ion (**7**). Furthermore, whereas the fully substituted anions **1** and **2** exhibit the well-defined, completely reversible oxidation wave, the unsubstituted anion **7** and also the anion **3** having one unsubstituted ring-carbon are oxidized irreversibly due to the chemical instability of the radical species. In accord with this, while the chemical oxidation ($KMnO_4$, $K_2Cr_2O_7$, or $K_3Fe(CN)_6$/THF) of **2** under vacuum gave a green-colored persistent radical (λ_{max} (THF) 360 nm (log ε 4.10), 710 (3.79)), the oxidation (I_2/THF or $AgNO_3$/MeCN) of **3** resulted in immediate color change to yellow and afforded a dimeric compound in a quantitative yield. The structure of this dimer was assigned as **9**[10] formed by coupling of the radical **8** followed by hydrogen migration.

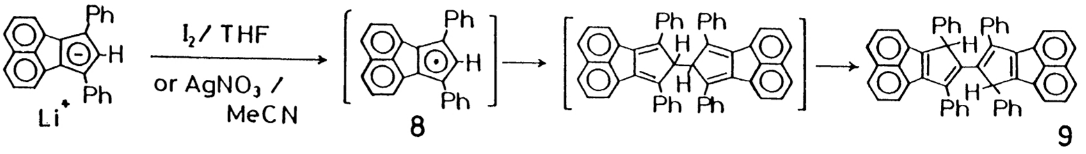


Table 2. The $pK_a(RH)$ and Oxidation Potential for the Anions **1**, **2**, and **3**, and for the Unsubstituted Cyclopentadienide Ion (**7**)

Anion	1	2	3	7
$pK_a(RH)$ [a]	14.8	13.9	14.0	16.0 [b]
Oxid'n potential [c] / V vs Ag/Ag^+	-0.53_2	-0.57_5	-0.58_2 [d]	-0.68 [d,e]
(Reversibility)	(Rev.)	(Rev.)	(Irrev.)	(Irrev.)

a) pK_a for the corresponding hydrocarbon determined spectrophotometrically in DMSO-EtOH (80:20 to 90:10 by volume); uncertainty limit ±0.1. b) Determined in H_2O : A. Streiwieser, Jr., and L. L. Nebenzahl, J. Am. Chem. Soc., 98, 2188 (1976). c) The half-wave potential ($E_{1/2}$) determined by CV in MeCN with Bu_4NClO_4 as the supporting electrolyte at the scan rate of 0.1 V/s. d) Estimated by taking the potential at 85% of the anodic peak height : R. Breslow and W. Chu, J. Am. Chem. Soc., 95, 411 (1973). e) The peak at the first scan. The peak exhibited a gradual anodic shift at the following scans.

The reaction of **9** with 2 equivalents of n-BuLi in THF under vacuum for 2 days afforded a dark red solution, which exhibited a ^{13}C NMR spectrum indicative of the formation of the corresponding dianion. Further detailed studies on this new dianion and on metal complexation of the anion **2** are currently under way.

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2) The pentaphenylcyclopentadienyl radical has been known for nearly 60 years: K. Ziegler and B. Schnell, Justus Liebigs Ann. Chem., 445, 266 (1925). For the ESR study, see W. Broser, P. Siegle, and H. Kurreck, Chem. Ber., 101, 69 (1968).

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4) Yellow crystals; mp 209-209.5 °C; ^{13}C NMR ($CDCl_3$) δ 144.4(s), 143.7(s), 141.8 (s), 138.5(s), 135.6(s), 132.5(s), 131.8(s), 128.4(d), 128.3(d), 128.2(d), 127.9(d), 127.6(d), 127.1(d), 126.4(d), 125.5(d), 119.0(d), 68.2(d). This compound has been reported as one of the products formed by the pyrolysis of 8-diazo-7,9-diphenylcyclopent[*a*]acenaphthylene: P. Balasubramanian and K. Narasimhan, Tetrahedron Lett., 22, 685 (1981).

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7) **6a**: Red-orange powder; mp 198-204 °C; ^{1}H NMR ($CDCl_3$) δ 7.73-6.80 (m, 21H), 1.64 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.5(s), 149.5(s), 143.5(s), 143.2(s), 143.1(s), 141.0(s), 137.3(s), 135.2(s), 134.8(s), 134.5(s), 131.8(s), 130.0 (d, 2 peaks), 128.1(d), 128.0(d), 127.7(d), 127.6(d), 127.5(d), 127.4(d), 127.2(d), 126.4(d), 123.8(d), 123.4(d), 119.7(d), 115.8(d), 69.5(s), 30.2(q) Analytically pure sample could not be obtained due to the instability and low crystallinity. **6b**: Yellow crystals; mp 195-197 °C; ^{1}H NMR ($CDCl_3$) δ 8.05-7.23 (m, 16H), 4.66 (q, 1H), 1.20 (d, 3H). Found: C, 94.04; H, 5.45%. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66%.

8) R. Kuhn and D. Rewicki, Liebigs Ann. Chem., 704, 9 (1967).

9) K. Bowden and R. Stewart, Tetrahedron, 21, 261 (1965).

10) Yellow Crystals; mp 276-277 °C; UV-Vis (THF) λ_{max} 249 nm (log ε 4.75), 288 (4.66), 399 (4.49); ^{1}H NMR ($CDCl_3$) δ 7.75-6.87 (m, 32H), 5.07 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 144.1(s), 143.9(s), 143.3(s), 139.3(s), 137.1(s), 136.2(s), 135.6(s), 132.2(s), 131.4(s), 129.2(d), 129.0(s), 128.4(d, 2 peaks), 127.3 (d), 127.2(d), 126.9(d, 2 peaks), 126.6(d), 124.9(d), 124.6(d), 118.2(d), 118.0(d), 60.7(d). Found: C, 94.76; H, 4.98%. Calcd for $C_{54}H_{34}$: C, 94.98; H, 5.02%. Molecular weight: found, 653±30 (vapor pressure osmometry); calcd, 682.

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