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# CYCLOHEPTA[def]PHENANTHRENYLIUM ION

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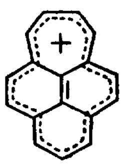
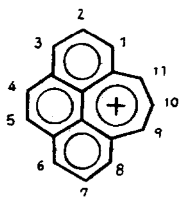
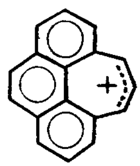
Most of neutral nonalternant isomers of pyrene have been synthesized and their properties were discussed.[1] However, the 14π perimeter ionic species which are isoelectronic with pyrene have received little attention.[2] Among these ionic species cyclohepta[cd]phenalenylium ion (**1**)[3] and cyclohepta[def]-phenanthrenylium ion (**2**) are particularly interesting and have been theoretically predicted to be quite stable by Zahradnik.[4] The first example of the 14π perimeter cationic system, tetrafluoroborate of (**1**), was prepared and demonstrated to be quite stable ($pK_R$+ 8.4)[3] by us. We now report the synthesis and properties of cation (**2**) as a second instance of such cationic species.



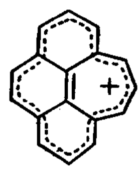
(**1**)




(**2a**)

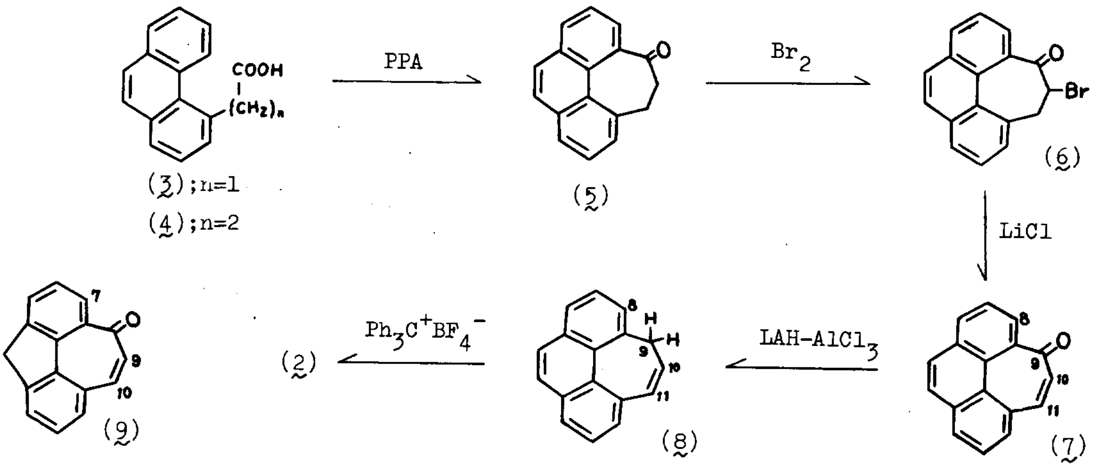


(**2b**)



(**2c**)

Arndt-Eistert reaction of 4-phenanthrylacetic acid (**3**)[5] obtained from 4H-1,2,3,4-tetrahydrophenanthrene-4-one led to 30% yield of 4-phenanthrylpropionic acid (**4**). Ring closure of (**4**) with polyphosphoric acid yielded the tetracyclic ketone (**5**) in 50% yield, mp 81-82° [IR, $\nu_{C=O}$ 1660 $cm^{-1}$]. Conversion of the ketone (**5**) to the corresponding monobromoketone (**6**) followed by an elimination reaction using lithium chloride in HMPA then gave 9H-cyclohepta[def]phenanthrene-9-one (**7**) in 26% yield, mp 150-151°C; IR, 1590, 1610, 1638 $cm^{-1}$; UV $\lambda_{max}$ (in methanol), 222 nm (log ε 3.72), 245(3.44), 273(3.41), 300(3.27) and 345(2.75); $\lambda_{max}$ (in cyclohexane), 222(3.69), 256(3.34), 268(3.39) and 335(2.81); $\lambda_{max}$ (in 98% $H_2SO_4$), 218(3.50), 265(3.71), 330(2.93), 360(2.84), 427(2.69) and 525(2.79); $^1$H-nmr δ (in $CDCl_3$), 6.91(H-10, d, J=12 Hz), 7.68(H-11, d, J=12 Hz), 8.64(H-8, dd, J=6, 1 Hz), 7.7-8.2 (m, 7H); δ (in $CF_3COOH$), 7.58(H-10, d, J=12 Hz), 9.30(H-8, dd, J=6, 1 Hz), 8.1-8.7 (m, 8H).




The chemical shifts of (7) [H-8 and 10] are comparable to those of the corresponding protons of the nonconjugated model compound (9) [H-7, δ 8.33 and H-9, δ 6.79].[6] Furthermore, the longest wavelength band in the uv spectrum of (7) [345 nm, log ε 2.75) is resemble to that of (9) [357 nm, ε 4100].[6] Although this ketone (7) is isomeric with 1H-cyclohepta[cd]phenalene-1-one[7] and 6H-cyclohepta-[cd]phenalene-6-one[8] which are regarded as perturbed [15]annulenone weakly coupled with a localized central vinyl crosslink, above mentioned finding reveals that the electronic structure of (7) is regarded as a phenanthrene coupled with a enone fragment.

Reduction of the ketone (7) by $LiAlH_4$-$AlCl_3$ in ether led to a sole hydrocarbon product which on chromatography on alumina gave 9H-cyclohepta[def]phenanthrene (8) in 75% yield, colorless crystals, mp 60-61°C [m/e 216($M^+$, 100%), 215(M-1, 56%); $^1$H-nmr ($CDCl_3$/TMS) δ, 3.40 (H-9,9', d, $J_{9,10}$=7.0 Hz), 6.28 (H-10, dt, $J_{10,11}$=10.0, $J_{9,10}$=7.0 Hz), 6.75 (H-11, d, $J_{10,11}$=10.0 Hz), 7.35-7.88 (m, 8H)].

Hydride abstraction from this hydrocarbon (8) with trityl tetrafluoroborate gave the desired cyclohepta[def]phenanthrenylium tetrafluoroborate (2) in 40% yield as hygroscopic blue-black crystals, ir(KBr), 1080 $cm^{-1}$ ($BF_4^-$), $\lambda_{max}$($CH_3CN$), 223 nm (log ε 4.54), 265(4.32), 305(4.06), 460(2.51), 618(2.85); $^1$H-nmr ($CF_3COOD$/TMS) δ, 8.42(H-10, dd, $J_{9,10}=J_{10,11}=10.0$ Hz), 9.81(H-9,11, d, J=10.0 Hz), 9.15(H-1, 8, dd, $J_{1,2}=J_{7,8}=7.9$ Hz, $J_{1,3}=J_{6,8}=1.6$ Hz) 8.78(H-2, 7, dd, $J_{2,3}=J_{6,7}=7.6$ Hz, $J_{1,2}=J_{7,8}=7.9$ Hz), 9.31(H-3, 6, dd, $J_{2,3}=J_{6,7}=7.6$ Hz, $J_{1,3}=J_{6,8}=$ 1.6 Hz) 8.62(H-4, 5, s).

The electronic spectrum of (2) in acetonitrile [Fig. 1] agrees reasonably with the values obtained by an PPP-LCI-SCF MO calculation.[9] The spectrum does

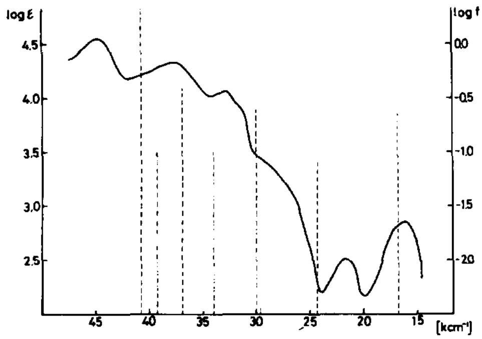



Fig. 1.

Experimental (in $CH_3CN$) and theoretical (dotted line, PPP-LCI-SCF-MO) electronic spectroscopic data for (2).

not resemble that of cyclohepta[cd]phenalenylium tetrafluoroborate (1).[3] This suggests that the π-electron system of (2) differs significantly from that of (1).

The $^1$H-nmr spectrum of (2) [Fig. 2] clearly indicates the presence of $C_2$-symmetry axis in this molecule. Furthermore, the chemical shifts of the benzenoid protons, H-1(9.15), H-2(8.78), H-3(9.31), H-4(8.62), of (2) indicate slight charge delocalization on these positions. However, the wide range of the chemical shifts [~1.4 ppm] compared to that of the compound (1) [~0.7 ppm][3] and the downfield shift of the allylic protons of (2), H-9,11(δ 9.81), seem to be caused

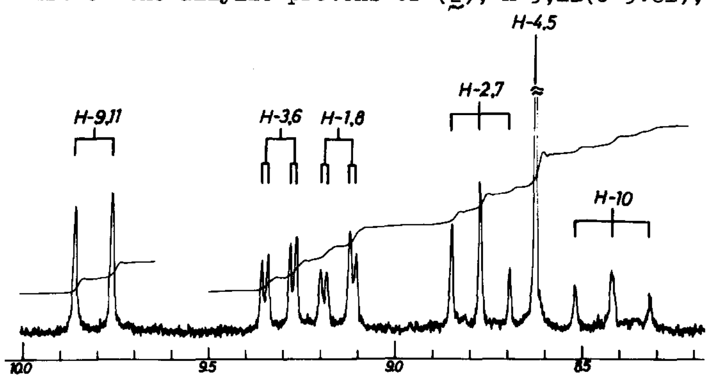



Fig. 2. 100MHz $^1$H-NMR Spectrum of (2) in $CF_3COOD$.

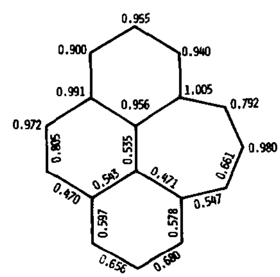



Fig. 3.

Molecular Diagram of (2).

by a localized charge at the allylic moiety of (2). This observation is fully consistent with the calculated electron densities of (2)[9] as shown in Fig. 3.

We prefer to ascribe this phenomenon to the fact that the allyl resonance structure (2b) would make a large contribution to the ground state of this molecule and an induced diamagnetic ring current associated with 14$\pi$ perimeter such as (2c) is of no consequence.[10]

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