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THE CHEMISTRY OF PHENALENIUM SYSTEMS XXI.[1)] CYCLOPENTA[*cd*]PHENALENYL ANION

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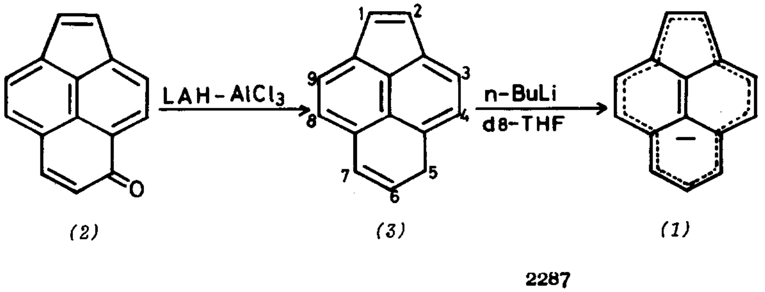
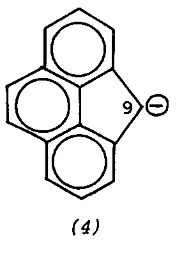
Recently a number of reports[2-5)] have appeared describing the synthesis and properties of 16π-electron ionic species as model systems structurally isoelectronic with pyrene. As part of our investigation into the phenalenyl system, we wished to obtain the cyclopenta[*cd*]phenalenyl anion (*1*) because Hückel molecular orbital calculations[6)] predict that the resonance stabilization of *1* [DE/elect.=0.3914β] should be greater than that of the corresponding cation [0.3646β]. We now report the synthesis of the hitherto elusive anion (*1*).

5*H*-Cyclopenta[*cd*]phenalen-5-one (*2*),[7)] previously prepared by us as a model perturbed [13]-annulenone, is an appropriate starting material for the synthesis of *1*. The ketone (*2*) was reduced with $LiAlH_4$-$AlCl_3$ complex in anhydrous ether at -70°C under a nitrogen atmosphere during 2 hr, and aqueous work-up followed by column chromatography on deactivated alumina containing 10% of water (elution with pet. ether) gave 5*H*-cyclopenta[*cd*]phenalene (*3*) as pale yellow needles.[8,9)] Although the hydrocarbon (*3*) is extremely oxygen- and heat-sensitive, its nmr spectrum convincingly demonstrates the presence of the desired phenalene structure. The vinyl proton resonances consist of a complex multiplet at δ 6.4-7.5 (H-1∼4, H-7∼9), a doublet of triplets at δ 6.17 (H-6, $J_{6,7}$=10.0, $J_{6,5}$=4.0 Hz), and the aliphatic protons absorption appears as a narrow multiplet at δ 3.70 (H-5,5'). Obviously, the possibility of contamination by alternate isomeric forms such as 4*H*-cyclopenta[*cd*]phenalene can be ruled out from the dt-pattern of H-6. The mass spectrum of *3* shows a molecular ion peak at m/e 190 (base peak) and a prominent peak at m/e



(*2*) (*3*) (*1*)



(*4*)

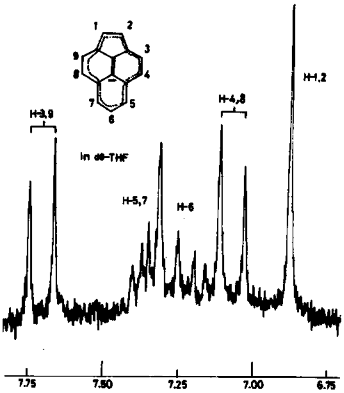


Fig-1 100 MHz nmr spectrum of *1* in d_8-THF.

189 (81%). Treatment of *3* in THF-d_8 with *n*-butyllithium in *n*-hexane at -70°C *in vacuo* yields the anion (*1*), whose nmr spectrum, measured at -50°C and depicted in Figure-1, shows the anticipated absorption pattern. The protons of the cyclopentadiene moiety (H-1,2) give rise to a sharp singlet at δ 6.88 and the phenalenyl protons, H-3,4; 8,9 and H-5,6,7 form an AB-quartet at δ 7.70 and 7.08 with $J_{3,4}=J_{8,9}=8.0$ Hz and A_2B-system at δ 7.33 and 7.20 with $J_{5,6}=J_{6,7}=6.2$ Hz, respectively. These observations, symmetrical spin-systems and a narrow chemical shift range [~0.88 ppm],are fully consistent with the delocalized structure with C_{2v}-symmetry.[11] Despite the fact that in the cyclopenta[*def*]phenanthrenyl anion (*4*),[12] an anion isomeric with *1* , the negative charge resides mainly on the cyclopentadienide moiety [H-9 at δ 6.05; chemical shift range, ca ~1.5 ppm] the findings observed for our anion (*1*) indicate that there is appreciable contribution by the delocalized structure as a perturbed [13]annulenide ion. Our conclusion that species (*1*) and (*4*) may be regarded as delocalized and localized ion, respectively, is in accord with the recent observations on cyclohepta[*cd*]phenalenium[4] and cyclohepta[*def*]phenanthrenium ions.[5]

REFERENCES AND FOOTNOTES

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8) All solvents employed were purified and nitrogen was bubbled through them just before use.
9) A pKa value of 18 for hydrocarbon (*3*) has already been predicted by Streitwieser, Jr.[10] Although experimental verification of the pKa is of interest, attempts to determine the acidity have as yet not met with success due to the instability of *3*.
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11) Our variable-β SCF-MO calculation on *1* (see molecular diagram) clearly shows that an appreciable charge is also found on phenalenyl skeleton.
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