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Dissolving Metal Reduction of Aceanthrylene and NMR Analysis of a Rigid, Boat-Shaped 9,10-Dihydroanthracene

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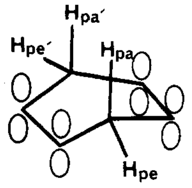
Aceanthrylene is reduced by sodium/ammonia solution to its 2,6-dihydro derivative (4), which indicates a protonation site in the dianion in contrast to the MNDO-calculated position of highest electron density. It is concluded that monoanion stability must be the prevailing feature. Compound 4 is also reduced by sodium/ammonia to provide 1,9-ethano-9,10-dihydroanthracene, which allowed the first proton NMR study of a rigid, boat-shaped dihydroanthracene. Especially interesting are the long range, five-bond homoallylic couplings between the 9- and 10-positions, and the values measured are 4.7 Hz for $^5J_{9,10}$ (dipseudoaxial) and 1.4 Hz for $^5J_{9,10'}$ (pseudoaxial/pseudoequatorial). The protonation and alkylation of (3-phenylindenyl)lithium is also considered so as to better understand the behavior of the intermediates derived from aceanthrylene.

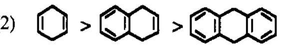
The conformational analysis of 1,4-dihydrobenzenes (DHB), 1,4-dihydronaphthalenes (DHN), and 9,10-dihydroanthracenes (DHA) has attracted considerable attention.[1]

The cyclohexadiene ring in these compounds may adopt a puckered (boat-shaped) conformation or "vibrate" around a planar geometry depending upon the nature and position of substituents. One method for investigating these conformations has involved the use of the homoallylic coupling constants across the six-membered ring.[8,9] This ^5J coupling, which can be quite large (12 Hz), is transmitted through the p orbitals and consequently decreases as the orbital overlap decreases. Hence, the values are largest for a dipseudoaxial (di-pa) relationship in a "fully puckered" boat geometry and smallest in the dipseudoequatorial (di-pe) arrangement. Flattening of the ring will cause di-pa coupling to decrease and di-pe coupling to increase until they become identical (planar ring) and then go on to exchange relationships. As would be expected, pa/pe interactions are intermediate in value and are not as sensitive to geometry changes. However, in contrast to the cis coupling, the trans values are at a maximum with a planar conformation. The magnitude of these couplings for any given geometric relationship also decreases in the order DHB > DHN > DHA. This is presumably a consequence of the decreasing bond order throughout this series.



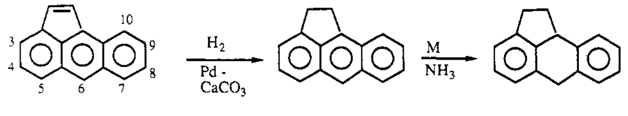
Decreasing ^5J Coupling Constants

(1) $J_{pa/pa'} > J_{pa/pe'} > J_{pe/pe'}$

(2) 

The effective use of these coupling constants to determine preferred geometries depends, of course, on having appropriate reference values. One approach to obtaining such data has involved the preparation and examination of rigid model compounds.[1] Thus, fixed, boat-shaped models for both DHB and DHN have been prepared, and this has allowed measurements of the dipseudoaxial coupling constants, 12.0 and 8.5 Hz, respectively. To date, a corresponding DHA value has not appeared. An early estimate of 2.5 Hz by Brinkman et al.[10] appears to be too low on the basis of subsequent calculations, and a latter "estimate" of 4.8 Hz was made on the basis of the ^{13}C satellite spectrum[8a] of DHA itself (which is not, of course, a rigid model).

For these reasons, we were intrigued by the availability of aceanthrylene (1)[11] since it would seem to be a reasonable precursor for a "locked", boat-shaped DHA. Hydrogenation of 1 to the ethanoanthracene 2 has been reported,[11] and it seemed reasonable that dissolving metal reduction of 2 would produce 3, which would serve as our model compound. The dissolving metal reduction of 1 itself was also of interest, since if the ethylene bridge were to reduce first (producing 2 in situ), 3 could be obtained in one step.



1 2 3

The sodium/ammonia reduction of 1 produced a single product, and GC/MS indicated that two additional hydrogens had been added to 1. Proton NMR showed a single vinyl proton and two upfield singlets of 4.25 and 3.45 ppm. Hence, the assignment as structure 4 is unambigu-

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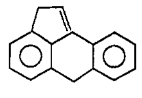
Table I. Methylation of (3-Phenylindenyl)lithium[a]

quenching agent	methox[c]	temp, °C	% composition[b]: 1-methyl-3-phenylindene	3-methyl-3-phenylindene
CH_3I	normal	−78	71	29
CH_3I	normal	25	70	30
CH_3I	inverse	−78	83	17
CH_3I	inverse	25	78	22
$(CH_3)_2SO_4$	normal	25	55	45
$(CH_3)_2SO_4$	inverse	25	72	28
$(CH_3)_2SO_4$	inverse	−78	58	42

[a] Generated by deprotonation by *n*-butyllithium at −78 °C for 30 min. Temperature was then adjusted where indicated. [b] Uncorrected GLPC. [c] Either the methylating agent in THF was added to the reaction mixture (normal) or the reaction mixture was pumped into the methylating agent/THF solution (inverse).

ous. This is not entirely unexpected, however, since the related compound acenaphthylene reduces to **5** when the radical anion is protonated and **6** when a dianion is the intermediate.[12] Herein, we propose that, in ammonia, **1** does indeed form a dianion that is, in all likelihood, promptly protonated by ammonia, affording a monoanion, which persists in solution.[13]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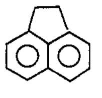
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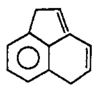
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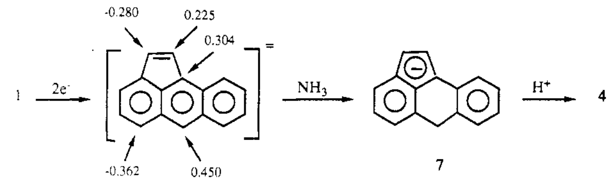
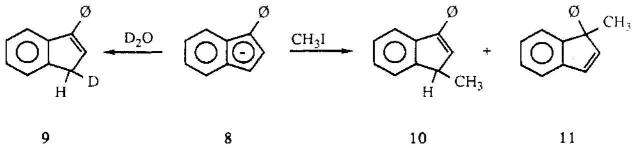
The position of protonation in the dianion can often be predicted by molecular orbital theory and so we carried out MNDO calculations on the dianion of **1**.[13] The HOMO coefficients (illustrated) do indeed suggest protonation at C-6, which would produce the aromatic monoanion **7**.



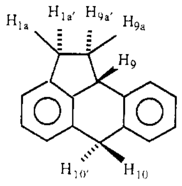
This raised the question about protonation sites in **7**, and we note that this anion is related to the species that would be generated by deprotonation of 1- or 3-phenylindene. Our search of the literature did uncover some p*K* measurements of these compounds, but apparently the protonation product(s) have not been investigated. Hence, we undertook a brief study.

Reaction of 3-phenylindene with a slight excess of *n*-butyllithium in dry THF at −78 °C produced the anion **8** as evidenced by the incorporation of one deuterium upon quenching with D_2O (GC/MS). Furthermore, the NMR spectrum clearly indicated the sole product to be **9**. Inverse quenching the reaction mixture into methyl iodide produced two products, however, **10** and **11** in a 5:1 ratio.



We also noted (Table I) a significant range in product distribution between **10** and **11**. It is tempting to conclude that fast quenching (CH_3I, inverse procedure) under conditions favoring more solvent-separated ion pairing (lower temperature) favors methylation at the unsubstituted position. At any rate, attempted methylation of **7** in ammonia produced an inseparable mixture of products and was not investigated further.

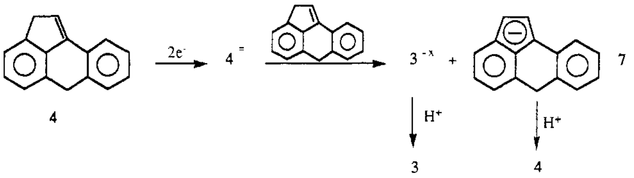
Table II. 500-MHz Proton NMR Results for Compound 3 in Acetone-d_6



position	δ (ppm)[a]	coupling	value, Hz	coupling	value, Hz
H_9	4.03	$J_{9,10}$	4.67	$J_{1a,1a'}$	15.40
H_{10}	3.96	$J_{9,10'}$	1.37	$J_{9,1a}$	0.8[b]
$H_{10'}$	3.88	$J_{9,9a}$	7.15	$J_{9a',1a'}$	8.25
H_{9a}	2.92	$J_{9,9a'}$	10.72	$J_{9a',1a}$	11.55
$H_{9a'}$	1.95	$J_{9a,9a'}$	11.55	$J_{10,10'}$	18.15
H_{1a}	3.13	$J_{9a,1a}$	7.15		
$H_{1a'}$	2.95	$J_{9a,1a'}$	0.82		

[a] Aromatics appeared as a multiplet, 7.05–7.40 ppm. [b] Some uncertainty in this measurement.

We were able to produce the desired compound **3** by the sodium/ammonia reduction of either **2** or **4**. However, reduction of **4** tends not to go to completion and usually results in a 50:50 mixture of **3** and **4**. This may be due to the acidity of neutral **4**. If, in fact, a dianion is formed in the presence of unreacted **4**, protonation should take place rapidly, producing a monoanion (3^-) and the aromatic anion **7** (this could be via NH_3/NH_2^-). The use of large excesses of sodium will eventually increase the production of **3**, and this may result from the more rapid consumption of **4**, which becomes less available for the protonation of 4^{2-}.



A series of homonuclear decoupling experiments allowed assignments to be made in the 500-MHz proton NMR spectrum (acetone-d_6), and these results are presented in Table II. Our main interest was, of course, in the long-range, homoallylic coupling constants and the region involving the benzylic protons H_9, H_{10}, and $H_{10'}$. The resonance due to H_{10} and $H_{10'}$ was easily recognized as an AB quartet with the low-field pair of signals further split into doublets. This additional coupling represents ^5J and as we have pointed out is largest for the dipseudoaxial relationship. Hence, the low-field half of the AB could be assigned to H_{10}. The higher field pair appeared as a single resonance, however, until the upfield portion of the aromatic region was irradiated. This removed weak benzylic coupling with the aromatic protons and resulted in a pair of doublets whereby the second, smaller ^5J coupling could be measured. Hence, this study represents the first example of dipseudoaxial and pseudoaxial/pseudoequatorial coupling in a DHA. The value for $^5J_{9,10}$ (di-pa) is 4.7 Hz, and this agrees well with the estimate mentioned above. As expected, $^5J_{9,10'}$ is much smaller, 1.4 Hz, and the observed value for the rigid model compares favorably with the measurements (around 1.5 Hz) made for a number of 9-R-DHA's where R is large.[1,10] This appears to confirm

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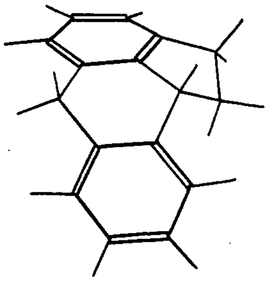
Table III. Calculated Geometries for 1,9-Ethano-9,10-dihydroanthracene

method	central ring pucker,[a] deg	torsion angle H_{9a}-H_{1a}, deg	torsion angle $H_{9a'}$-$H_{1a'}$, deg
MM2	147.4	36.2	40.0
MMP2	143.2	33.8	38.7
MMPMI	149.3	37.1	40.4
MNDO	149.6	16.7	17.7

[a] This represents the mean angle between the two intersecting planes containing the benzene rings.

that large R groups in DHA's do, in fact, force the boat conformation.

As a final point, we note that the validity of 3 as a model must rest on our knowledge of its geometry, and we feel that Dreiding mechanical models may be a little misleading in this case. In fact, depending on the rigidity of the models used, the hydrogens on the ethane bridge may appear to be almost eclipsed. To gain further insight, we performed molecular mechanics as well as MNDO calculations, and the preferred calculated geometries are shown in Table III. The computer models suggest rotation of the ethane bridge, and presumably any accompanying increase in ring strain is more than offset by the decrease in torsional energy. In fact, this deformation is predicted to be greatest by the MMP2 force field, but this is a consequence of the fact that the out-of-plane bending of aromatic rings is "too easy" by MMP2.[14] In any event, we note that the value of the NMR coupling $J_{H9,H9a'}$ is quite large (10.7 Hz), and this is consistent with the computer generated model. Hence, 3 does appear to be a satisfactory model for boat-shaped DHA's.



MMP2 Calculated Geometry
H Symbols Omitted Throughout

3

Experimental Section

General Methods. The MM2 and MMP2 calculations were performed with the Allinger molecular mechanics program (QCPE no. 395), and the MMPMI results were obtained with the IBM-PC version by Gajewski and Gilbert.[15] MNDO calculations were performed by using QCPE no. 455. NMR spectra were recorded on Varian EM-390 and Bruker AM-500 spectrometers. $CDCl_3$ was used as solvent except for compound 3 where better results were achieved with acetone-d_6. All compounds prepared herein showed satisfactory molecular ions by GC/MS (Hewlett-Packard 5988).

Aceanthrylene (1) was prepared from aceanthrenequinone according to the method of Becker et al.[16] with the exception that 2-aceanthrone was prepared by using pyridine hydrochloride as described by Plummer et al.[17] In this way, 2-aceanthrenol (7.45 g) afforded 1.7 g (25%) of 1, mp 103–104 °C (lit.[16] mp 103–104 °C) after chromatography on neutral alumina (CH_2Cl_2/hexane, 1:9) and recrystallization from CH_2Cl_2 aided by the addition of hexane.

Aceanthrene (2) was obtained by hydrogenation of 1,[17] although this reaction appeared to be quite sensitive to the nature of the catalyst, and we did not obtain reproducible results. However, 2 can also be obtained by the thermal isomerization of 4 (see below).

2,6-Dihydroaceanthrylene (4) was prepared by sodium/ammonia reduction of 1. Sodium (0.57 g, 25 mmol) was added to 1 (1.43 g, 7 mmol) in anhydrous ammonia/THF (75 mL:25 mL) under argon atmosphere. After continued stirring for 30 min at –78 °C, excess aqueous NH_4Cl was added followed by standard ether extraction. Recrystallization from CH_2Cl_2/hexane afforded pale yellow crystals (0.53 g, 37%): mp 111 °C; NMR (CCl_4) δ 7.65 (m, 1 H), 7.1 (m, 6 H), 6.45 (br s, 1 M, vinyl), 4.25 (5, 2 H), 3.45 (br s, 2 H). Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.96; H 5.97.

1,9-Ethano-9,10-dihydroanthracene (3) was prepared by sodium/ammonia reduction of 4.[7] Sodium (0.09 g, 4 mmol) was added to 4 (0.12 g, 0.6 mmol) in anhydrous ammonia/THF (15 mL:5 mL) under argon atmosphere. After continued stirring at reflux (–33 °C) for 45 min, excess aqueous NH_4Cl was added followed by standard ether extraction. Recrystallization from CH_2Cl_2/hexane afforded pale yellow crystals (0.04 g, 33%), mp 82 °C, identical with a sample obtained previously[7] by the sodium/ammonia reduction of 2.

Isomerization of 4 to 2. A few milligrams of 4 was heated to reflux for 60 min in ethanol containing 2 drops of HCl. The recovered material (ether extraction) showed only 2 by GC/MS and NMR.

Methylation of (3-Phenylindenyl)lithium. In a typical procedure, *n*-butyllithium (2.3 mmol) was added to 3-phenylindene[18] (300 mg, 1.56 mmol) in 30 mL of dry THF at –78 °C. An orange-red color developed, and stirring was continued for 30 min. At this point, the quenching agent [CH_3I, $(CH_3)_2SO_4$, or D_2O] was added (normal quench), or the reaction mixture was pumped through a glass tube into the stirred quenching agent (inverse quench). Products were isolated by ether extraction and identified by NMR, GC/MS, and comparison with the previously reported properties[19,20] (see Table I for results). Product ratios were determined by GLPC on an OV-1 column (fid detector).

Acknowledgment. We gratefully acknowledge support from the U.S. Department of Energy, Office of Basic Energy Science, and the Indiana University Computer Network.

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