Structure of 9-Substituted 9,10-Dihydroanthracene Monoanions. A Semiempirical MO Study

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Received February 12, 1987

The MNDO calculations show that the isolated anions derived from 9-R-9,10-dihydroanthracenes (R = H, Me, Et, *i*-Pr, Ph) may be considered as planar or almost planar structures with hybridization of the anionic center very close to sp^2. Coulombic interactions of the anions with a positive charge do not influence the structures significantly. The planar, sp^2 model of the above anions is therefore proposed for both gas phase and solution. On the other hand, 9-lithio-9,10-dihydroanthracenes are predicted to be substantially more puckered than the anionic species, and such nonplanar structures are expected in the crystal state.

A number of studies have appeared concerning the nature of monoanions derived from 9,10-dihydroanthracene (DHA) and its derivatives.[1] Much of this attention has been directed toward the stereochemical outcome of protonation and/or alkylation which, of course, has necessitated some speculation about the structure of the metallo (usually Li or Na) intermediates. Historically, DHA monoanions were regarded as inverting boating structures with sp^3 hybridization at the anionic center.[1a-t,2] More recently, however, suggestions have been made for sp^2 structures,[1v-x] as well as a greater degree of planarity,[1w,x] based on proton and carbon NMR as well as alkylation studies.

In contrast to numerous theoretical studies on the structure of the parent (neutral) DHA's,[3] there is a lack of such data for the anions. In the present paper we report our results of a semiempirical molecular orbital study on the conformations of some 9-substituted 9,10-dihydroanthracene anions. The aim of this work was (i) to learn how the deprotonation process changes the structure of the whole (isolated) molecule in general, and, in particular, the structure of the region formally bearing the negative charge and (ii) to predict the influence of ion-pairing and salt formation processes on anion conformation.

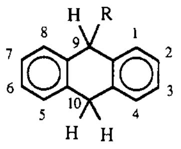
Method

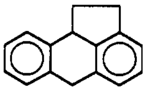
The MNDO method was used throughout this study. The calculations were performed on a CDC Cyber 855 using MNDOC[4] and on an IBM 4381 using MOPAC.[5] All geometries were optimized, some of them with appropriate symmetry constraints. The lithium parameters of Thiel and Clark available in MNDOC were used. It has been shown that these parameters closely reproduce the MNDO results with an unpublished, refined set of parameters used by Schleyer's group.[6]

Results and Discussion

The conformation of 9,10-dihydroanthracene (DHA) itself has been controversial.[3] Recent calculations suggest little difference between slightly puckered (a pseudoboat) and completely planar conformations.[3] On the other hand there is not such ambiguity with 9-substituted DHA's—both experimental and calculated results suggest a boat conformation for the central ring with the substituent occupying a pseudoaxial position.[3]

In the present study, we have carried out calculations on a number of 9-substituted DHA's (2–5), as well as the dihydroaceanthrene 6, which serves as a "fixed" model for boat-shaped DHAs. The optimal MNDO structures have been obtained for each of the neutral hydrocarbons (2–6) and also for two monoanions in each case—one with the proton removed at C-9 and the other at C-10. These will be referred to as the 9-anion and 10-anion throughout.





6

1 R = H
2 R = CH_3
3 R = CH_2CH_3
4 R = $CH(CH_3)_2$
5 R = Ph

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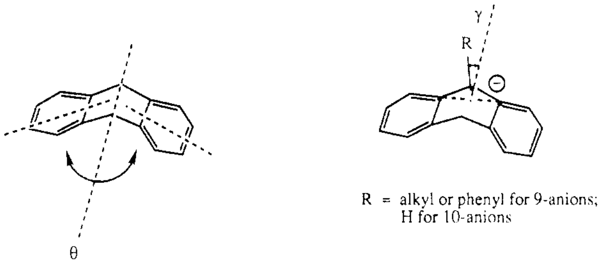
Table I. MNDO Calculated Geometries for 9-R-9,10-Dihydroanthracenes and Corresponding 9-Anions and 10-Anions

	angles (deg)[a]				
	hydrocarbon	9-anion		10-anion	
R	θ	θ	γ	θ	γ
H[b]	159.0	180.0	0.0	180.0	0.0
CH_3	153.2	160.5	1.0	165.1	3.6
CH_2CH_3	151.6	168.6	1.3	164.3	3.7
$CH(CH_3)_2$	137.2	153.6	2.0	148.8	7.0
Ph	158.2	180.0	0.0	169.4	2.2
6	149.6	179.2	0.3	160.5	3.8

[a] θ is the angle between the planes of the two benzene rings. γ is the deviation of C_{anion}–C_R groups (for 9-anions) or C_{anion}–H_{10} (for 10-anions) from an sp^2 plane.

The possibility of nonplanar structures in the 10-anions also raises a question concerning the location of the proton at C-10. Formally two different structures with either pseudo-axial or pseudo-equatorial hydrogen atoms attached to C-10 are possible. We carried out calculations for the 10-anion of **2** in two ways, starting from parent **2**, by first removing the pseudoaxial hydrogen at C-10 and then by removing the pseudoequatorial hydrogen at C-10. Upon optimization, both structures relaxed to a common conformation. Hence only one 10-anion exists as a minimum on the energy surface.

For purposes of this discussion, we shall describe the geometries of the compounds under consideration in terms of two angles. (i) θ is defined as the angle between bisecting planes that contain each of the two benzene rings. (ii) γ is the angle representing the deviation (if any) of the C_{anion}– $C_{R\,group}$ bond (for 9-anions) or the C_{anion}–H_{10} bond (for 10-anions) from the "sp^2 plane." This deviation, of course, is always directed away from the cation (see below).



R = alkyl or phenyl for 9-anions; H for 10-anions

This means that structures with a planar central ring would have $\theta = 180°$, and systems with a trigonal, coplanar anionic center (i.e., completely sp^2 hybridization) would have $\gamma = 0°$. Hence deviations from 180% in θ and 0° in γ indicate a degree of nonplanarity.

Calculated angles for structures **1**–**6** as well as their 9- and 10-anions are shown in Table I. It is apparent that deprotonation of the neutrals at either the 9- or 10-position generally leads to a flattening of the molecule (increase in θ values). The driving force for the flattening is presumably a delocalization of the negative charge formally located on the "benzylic" carbon atom. As the anionic center hybridization becomes closer to sp^2, the overlap of its p orbital with the π orbitals of the benzene rings becomes more important. This effect is strong enough to cause complete planarity in the unsubstituted case (i.e., anion of **1**).[6] The addition of substituents, however, introduces a repulsive interaction between the R group and the peri hydrogen atoms on the aromatic rings.

9-Anions. Although generally the 9-anions of **2**–**6** have been found to be nonplanar (with the exception of the 9-anion of **5**), it is apparent that the anions are flatter than the parent molecules. The increase in θ angles values between the neutrals and the 9-anion varies from 7.3° for **2** to 29.6° for **6**. The tendency toward planarity of the anions is even more apparent when γ angles are considered. For all 9-anions, the γ values are close to 0°, with the largest deviation being 2.0° for **4**. Hence the anionic centers in the 9-anions are essentially sp^2. Moreover, this interpretation is supported by considering the calculated bond lengths at the anionic center of the molecules. For example, in the 9-anion of **2**, the C_9–C_{1a} bond length is 1.435 Å and C_9–CH_3 is 1.495, whereas for neutral **2** the lengths are 1.523 and 1.549 Å, and for 9-methylanthracene 1.430 and 1.512 Å, respectively.[7]

We also repeated the calculations for 9-anions assuming planarity of the DHA system and with optimization of all remaining geometric parameters. We obtained structures with slightly higher energies (0.81, 0.17, 2.16, and 0.05 kcal/mol for 9-anions of **2**, **3**, **4**, and **6**, respectively). Only the isopropyl substituent shows significant (but still small) difference in energy between "planar" and "nonplanar" conformations of the 9-anions. Hence these results indicate that the isolated 9-anions of 9-alkyl(aryl)-9,10-dihydroanthracenes may be regarded as planar or almost planar structures with sp^2 hybridization at the anionic carbon atom.

10-Anions. Deprotonation of the parent hydrocarbons at the C-10 position does not lead to totally planar anions. The isolated 10-anions are slightly puckered with θ angles in the range of 169.4° (for 10-anions of **5**) to 148.8° (for **4**–10 anion). Once again, comparision of the folding angles of the anions with the analogous angles for the parent hydrocarbons shows that deprotonation at the 10 position leads to a flattening of the molecule. The θ angle increases by 10.9–12.7° in every case considered. Inspection of the γ angles collected in Table I shows that the anionic centers of the 10-anions are close to planarity with the biggest deviation being 6.8° for the 10-anions of **4** (but less than 4° for the other anions considered). For comparison, the γ angles are 53.7° and 52.4° for the pseudoaxial and pseudoequatorial hydrogen atoms at C_{10}, respectively, in neutral **2**.

Further, evidence for the sp^2-like anionic center is given by consideration of bond lengths of that portion of the molecules. For example, with the 10-anion of **2**, the C_{10}–C_{4a} distance is calculated to be 1.417 Å and the C_{10}–H_{10} bond length is 1.090 Å. For the parent **2** (sp^3 C_{10}) those distances are 1.513 and 1.116 Å, and for 9-methylanthracene (sp^2 C_{10}) they are 1.409 and 1.093 Å.[7]

In general, the isolated 10-anions of 9-R-9,10-DHAs may be considered as slightly puckered boat structures with the 9-substituent placed in a pseudoaxial position and with the portion of the molecule formally bearing the negative charge close to planarity. However, the 10-anions are slightly more puckered than the 9-anions. The energy required for planarization of the 9,10-dihydroanthracene portion of the molecules is also slightly higher in the case of 10-anions (for example, for the 10-anion of **2**, the energy difference is equal to 1.95 kcal/mol, and for the 9-anion, only 0.81 kcal/mol).

Salt-Formation and Ion-Pairing Effects. Thus far, our discussion has applied, of course, to isolated molecules. That is, to molecules in the gas phase. In order to gain some insight about DHA monoanions in condensed phases, we carried out calculations for the anions of **2** including lithium cations. Actually if no solvent molecules are in-

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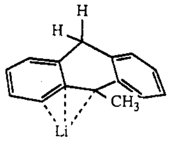
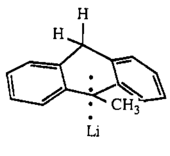
(7) One can expect that comparison of the anion bond lengths with the bond lengths of the neutral molecules may not be valid. However, comparison of the MNDO geometry of 9-methylanthracene with 9-methylanthracene dianion shows only minor differences on bond lengths considered (for the dianion, C_9–C_{1a} = 1.446 Å, C_9-CH_3 = 1.490 Å, C_{10}–C_{4a} = 1.419 Å, and C_{10}-H_{10} = 1.092 Å).

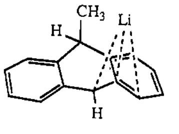
culded in the calculations, such results serve as an approximation to the solid-state structures as pointed out by Schleyer et al.[8] In this way we expected to obtain a second "boundary" structure with very strong interaction of lithium with the organic molecule (the first "boundary" structure is a structure of an isolated anion in which interactions with counterion and solvent are not present at all). In analogy with benzyllithium[8] and lithio-9,10-dihydroanthracene[6] we considered the following structures for 9-litho- and 10-lithio-9-methyl-9,10-dihydroanthracene.



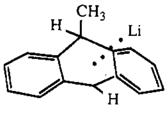
7a



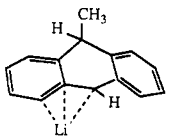
7b



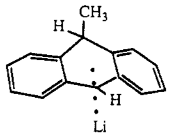
8a



8b

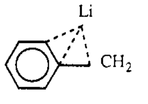


9a

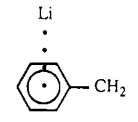


9b

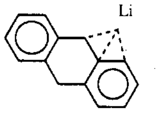
The structures denoted by **a** are the "nonsymmetrical" structures with lithium in bonding distance to three carbon atoms. In the case of structures **b**, lithium is located over or under the central six-membered ring. The question arises as to which arrangement, **a** or **b**, represents the minimum energy structure. With benzyllithium, for example, MNDO predicts structures **10b** to be more stable than **10a** by 2.2 kcal/mol (see also ref 8), whereas X-ray crystal structure determination showed **10a** to represent solid-state benzyllithium (with TMEDA).[9] It is known that MNDO overestimates the energy of the C–Li bond,[10] so one can expect that the relative stabilities for structures of type **b** (with six formal C–Li bonds) may be also overestimated when compared to structures **a** (with three formal bonds). For lithio-9,10-dihydroanthracene, **11b** has also been found to be more stable than **11a** by 6.2 kcal/mol,[6] but the crystal structure is not known. The MNDO heats of formation, along with θ and γ angles for **7a–9b**, are presented in Table II. It is apparent that the anion structures are changed substantially when a lithium cation is included. Generally the organic moiety becomes more puckered—only **7b** and **9b** have θ angles close to 180°, whereas the other structures considered have θ values in the range 149.8–162.9°. Also the values of γ indicate significant nonplanarity of the anionic center with the nonplanarity being greater for the edge-lithiated (**a** type) alternatives. This means that 9-Li-9-R-9,10-DHAs should not be considered as essentially planar structures and preferred conformations of these molecules should be very sensitive to the location of the lithium.



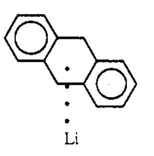
10a



10b



11a

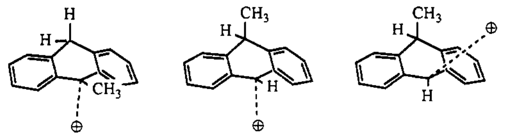


11b

Table II. MNDO Calculated Heats of Formation and Geometries for 9- and 10-Lithio-9-methyl-9,10-dihydroanthracene

structure	ΔH°_f (kcal/mol)	θ (deg)[a]	γ (deg)[a]
7a	26.9	155.5	26.8
7b	25.6	176.5	11.4
8a	32.8	162.9	41.8
8b	23.9	149.8	30.3
9a	31.7	155.4	40.5
9b	26.9	178.2	13.2

[a] θ is the angle between the planes of the two benzene rings. γ is the deviation of C_{anion}–$C_{R\ groups}$ (for 9-anions) or C_{anion}–H_{10} (for 10-anions) from an sp^2 plane.



	12	13	14
ΔH°_f (kcal/mol)	-55.9	-52.9	-52.3
θ (deg)	160.1	164.3	163.8
γ (deg)	6.4	2.4	16.0

Figure 1. Heats of formation and geometries of sparkle complexes.

It should be emphasized at this point that according to MNDO, the C–Li bond is substantially covalent. The covalency of the C–Li bond has been a subject of controversy for some time, and most recently the opinion that such bonds are mostly ionic seems to have gained wide acceptance.[8,10–12] On the other hand a very good correlation between MNDO and X-ray structure data for monolithio and dilithio organic compounds[8,13] suggests that covalency may play an important role, at least in the solid state. Our results for lithio-**2** therefore appear to be valid for the prediction of the structure of related compounds in that state of matter. In solution where solvation is important (mainly solvation of the cation in ether solutions), the counterion (cation) is located further away from the anionic center. In such cases, the overlap between the orbitals of lithium and the anionic center decreases, and only coulombic interactions are important. We were able to model such purely ionic interactions with MNDO calculations performed on **2** anions using "sparkle" (a + 1 point charge with an effective radius 0.7 Å).[5] The resulting structures of the pairs 2^-/⊕ along with their heats of formation and θ and γ values are given in Figure 1.

In contrast with the lithio derivatives **7a–9b**, we were able to find only one energy minimum for each isomer (**12–14**). The structures calculated with the "sparkle" are quite different from either η^6-type (**b**) lithio-**2** or edge-type (**a**) lithio-**2**. The counterion in **12–14** is located over (or under) the carbon atom formally bearing the negative

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charge (not over the center of the central six-membered ring). Also, the optimal position of the positive charge is symmetrical (that means the structures **12**, **13**, and **14** have C_s symmetry with a plane of symmetry defined by $\oplus$-C_9-C_{10}; this differs from **7a**, **8a**, and **9a**).

Comparison of θ and γ angles found for **12**–**14** with the data for the isolated anions of **2** (Table I) shows only minor differences. The only significant change is observed for the γ angle in **14**. In this case the well-known effect of bending a proximal hydrogen atom away from a positive charge forces the H_{10} hydrogen atom to occupy a pseudoequational position and increases the γ angle from 3.6° (for the isolated 10-anion of **2**) to 16.0° for **14**. However, in the alternative structure **13**, which is slightly more stable (by 0.65 kcal/mol), that angle is again very close to 0°. We therefore conclude that according to MNDO calculations, interaction of a purely coulombic nature with the cation does not cause significant changes in the structure of the anions considered herein. This means that calculated structures of the isolated anions of 9-R-9,10-dihydroanthracenes may well serve as models for not only gas-phase studies but also condensed phases (solution, various state of ion-pairing) provided that MNDO correctly reproduces structures of the isolated anions. This model of slightly puckered 9-R-9,10-DHA anions with the "anionic center" hybridization close to sp^2 agrees well with the recent alkylation and NMR studies.[1w]

Acknowledgment. We gratefully acknowledge the U.S. Department of Energy, Office of Basic Energy Sciences, for support of this work. We also appreciate the assistance of Dr. Ken Lipkowitz.

Chemistry of Organolanthanoids. Lanthanoid-Mediated C–C Bond Formation and Cleavage and C–C Double Bond Reduction

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Received May 1, 1987

Reactions of the organolanthanoid σ-complexes RLnI with α,β-unsaturated carbonyl compounds and allylic alcohols under various conditions are described. An equivalent of RYbI reacts with α,β-unsaturated carbonyl compounds to give 1,2-addition products **1** regioselectively. On the other hand, the reaction of an excess of RYbI with chalcone gives C–C bond cleavage products **2** and **4** and deoxygenation product **3** instead of **1**. In the reactions of PhYbI with benzalacetone or cinnamyl alcohol, compounds **5**, derived from addition of RYbI to the C–C double bonds of the substrates, are obtained as main products. An excess of PhEuI reacts with α,β-unsaturated carbonyl compounds to give **2**–**4**. C–C double bonds conjugated with phenyl group are hydrogenated by PhYbI/MeOH. Reduction of *trans*-stilbene with Yb/MeOD gives the deuteriated product **6a**.

Although numerous compounds of lanthanoid metals (Ln) have been prepared and characterized,[1] much less is known about their applications in organic reactions. Recently, considerable efforts have been made on the utilization of these elements, especially their salts, in organic reactions, and some interesting synthetic procedures have been developed.[2,3] However, relatively few reports may be found on organolanthanoids in organic reactions.[4]

The first divalent organolanthanoid σ-complexes of type RLnI were prepared from lanthanoid metals and organic iodides (RI) in tetrahydrofuran(THF) by Evans et al.[5] We are interested in the reactions of lanthanoids for the aim of exploring new synthetic reactions and investigated some reactions of organolanthanoids RLnI with ketones, aldehydes, esters, nitriles, and acid chlorides.[6] We have showed that although the complexes RLnI are similar to the Grignard reagent (RMgX) in formula, they have rather different reactivities: the reaction of RLnI (Ln = Yb, Eu) with esters giving ketones as main products rather than tertiary alcohols[6a] and the reaction with aldehydes resulting in formation of Tishchenko condensation products (Ln = Sm, Pr, Nd, Dy).[6f] In this paper we report on the reactions of RLnI with α,β-unsaturated carbonyl compounds and allyl alcohols in which formation and/or cleavage of C–C bonds takes place depending upon reaction conditions. The PhYbI/MeOH-mediated hydrogenation of C–C double bonds conjugated with a phenyl group is also described.

Table I. Reactions of RYbI with α,β-Unsaturated Carbonyl Compounds[a]

run	RYbI	carbonyl compd	1,2-addition product (yield, %[b])
1	PhYbI	chalcone[c]	**1a** (62)
2	PhYbI	acrolein	**1b** (66)
3	PhYbI	methyl vinyl ketone	**1c** (37)
4	PhYbI	benzalacetone	**1d** (43)
5	MeYbI	2-cyclohexen-1-one	**1e** (39)

[a] Yb/RI/carbonyl compound = 0.5:0.75:0.5 (mmol); room temperature; 18 h. [b] GC yields based on the substrate. [c] Yb/PhI/chalcone = 1.25:1.0:1.0; −30 °C, 1 h, and then room temperature, 18 h.

Preliminary accounts of a portion of this work have appeared.[7]

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