The Nature of 9-Substituted 9,10-Dihydroanthracene Monoanions Formed by the Monoprotonation of Dianions and the Deprotonation of Dihydroaromatics

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The production of monoanions of the type 9-R-10-metallo-9,10-dihydroanthracene and 9-R-9-metallo-9,10-dihydroanthracene is accomplished by two methods. Method A involves the addition of sodium metal to 9-R-anthracene in anhydrous ammonia/THF. Protonation of the dianion intermediate by ammonia produces a monoanion which persists. In method B, 9-R-9,10-dihydroanthracenes are deprotonated by *n*-butyllithium in THF. By method A, methylation produces a mixture of 9-R-10-methyl-9,10-dihydroanthracene and 9-R-9-methyl-9,10-dihydroanthracene with the latter predominating in all cases (R = Me, Et, *n*-Bu, *i*-Pr, Bz, Ph). By method B, only the 9,10-isomers are produced (except for R = Ph). Mechanistic implications are discussed, and MNDO calculations are presented for both dianions and monoanions.

The alkylation and protonation of anthracene dianions and 9,10-dihydroanthracene monoanions have received considerable attention.[1] Both of these species are intermediates in the metal/ammonia reduction of anthracenes, and in addition, the monoanions have interesting conformational properties.[2] We have been interested in protonation sites in aromatic dianions as well as deprotonation sites in hydroaromatic compounds, and the anthracene/9,10-dihydroanthracene system provides an especially useful case since monoanions can be generated by two standard routes. Method A involves the addition of alkali metals to an anthracene in anhydrous ammonia generating a dianion[3] which is protonated (once) by ammonia furnishing a stable monoanion (i.e., resistant to further protonation by ammonia). The second method (B) involves the deprotonation of 9,10-dihydroanthracenes (DHA's) by base systems such as *n*-butyllithium/THF or amide/ammonia. In the case of 9-substitution, as illustrated in Scheme I, a question arises as to the nature of the monoanions formed by these two different routes (i.e., 1 vs. 2), and this is the subject of our present study.

Reactions were carried out in the following way. With method A, the anthracene (1.0 equiv) in dry THF (1 part) was added to anhydrous ammonia (2 parts) at −78 °C, followed by the addition of sodium metal (1.25 equiv).

Table I. Methylation of 9-R-9,10-Dihydroanthracene Monoanion

R	method[a]	cation	ratio of methylated products[b] 9-R-10-Me-DHA	9-R-9-Me-DHA
Me	A	Na	30	70
Me	A	Li	26	74
Et	A	Na	27	73
n-Bu	A	Na	9	91
Bz	A	Na	43	57
i-Pr	A	Na	10	90
Ph	A	Na	0	100
Me	B	Li	100	0
Me	B[c]	Na[c]	100	0
Et	B	Li	100	0
n-Bu	B	Li	100	0
Bz	B	Li	100	0
i-Pr	B	Li	100	0
Ph	B	Li	67	33

[a] Method A represents reaction of substituted anthracene with sodium (unless otherwise noted) in ammonia/THF (2:1); method B is deprotonation with *n*-butyllithium. In both cases, reaction mixtures were inverse quenched into methyl iodide/THF solution after 30 min at −78 °C. [b] Analysis is by uncorrected gas chromatography. [c] Proton abstraction from 9-Me-DHA with sodium amide in ammonia/THF (2:1).

Table II. MNDO Calculations for 9-R-Anthracene Dianions

R	total electron charge C_9	total electron charge C_{10}	c_1^2 HOMO C_9	c_1^2 HOMO C_{10}
H	−0.382	−0.382	0.192	0.192
Me	−0.444	−0.378	0.196	0.201
Et	−0.436	−0.379	0.197	0.202
i-Pr	−0.426	−0.379	0.198	0.204
Ph	−0.444	−0.377	0.189	0.217

After the metal appeared to be dissolved, a time period was allotted (usually 30 min), and the reaction mixture was pumped into a large excess of methyl iodide in dry THF. This inverse quenching procedure was used to ensure efficient "trapping" of the anion as we have previously demonstrated for these systems.[1o] With method B, *n*-butyllithium (1.1 equiv) was added to the corresponding 9-R-9,10-dihydroanthracene (9-R-DHA) in dry THF at −78 °C, and after 30 min the reaction mixture was similarly inverse quenched into methyl iodide solution. The results are shown in Table I.

As indicated, these methods can produce different results, and this is especially striking in cases such as *n*-butyl and isopropyl which show almost a total reversal. This

(1) (a) Harvey, R. G.; Arzadon, L.; Grant, J.; Urgerg, K. *J. Am. Chem. Soc.* **1969**, *91*, 4545. (b) Harvey, R. G.; Arzadon, L.; *Tetrahedron* **1969**, *25*, 4887. (c) Harvey, R. G.; Davis, C. C. *J. Org. Chem.* **1969**, *34*, 3607. (d) Harvey, R. G. *Synthesis* **1970**, 161. (e) Zieger, H. E.; Schaeffer, D. J.; Padronnagio, R. M. *Tetrahedron Lett.* **1969**, 5027. (f) Schaeffer, D. J.; Zieger, H. E. *J. Org. Chem.* **1969**, *34*, 3958. (g) Schaeffer, D. J.; Litman, R.; Zieger, H. E. *Chem. Commun.* **1971**, 483. (h) Zieger, H. E.; Gelbaum, L. T. *J. Org. Chem.* **1972**, *37*, 1012. (i) Panek, E. J.; Rodgers, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 6921. See also: Panek, E. J. *Ibid.* **1974**, *96*, 7961. (j) Daney, M.; Lapouyade, R.; Mary, M.; Bouas-Laurent, H. *J. Organomet. Chem.* **1975**, *92*, 267. (k) Fabre, C.; Salem, M. H. A.; Mazaleyrat, J. P.; Tchaplo, A.; Welvart, Z. *Ibid.* **1975**, *87*, 9. (l) Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1145. (m) Bank, S.; Bank, J.; Daney, M.; Labrande, B.; Bouas-Laurent, H. *J. Org. Chem.* **1977**, *42*, 4058. (n) Daney, M.; Lapouyade, R.; Bouas-Laurent, H. *Tetrahedron Lett.* **1978**, 783. (o) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283. (p) Daney, M.; Lapouyade, R. *J. Organomet. Chem.* **1979**, *172*, 385. (q) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1979**, *44*, 2354. (r) Daney, M.; Bouas-Laurent, H.; Calas, B.; Giral, L.; Platzer, N. *J. Organomet. Chem.* **1980**, *188*, 277. (s) Daney, M.; Lapouyade, R.; Bouas-Laurent, H. *J. Org. Chem.* **1983**, *48*, 5055.

(2) Rabideau, P. W.; Wetzel, D. M.; Husted, C. A.; Lawrence, J. R. *Tetrahedron Lett.* **1984**, 31, and references therein.

(3) The addition of one electron produces a radical anion which adds a second electron resulting in a dianion. The dianion is too basic to persist in ammonia. An alternative pathway involving radical anion protonation by ammonia followed by a second electron addition is less likely. See ref 10 for additional discussion.

(4) Mooney, J. L.; Marcinow, Z.; Rabideau, P. W. *J. Org. Chem.* **1986**, *51*, 527.

0022-3263/86/1951-3181$01.50/0

Scheme I

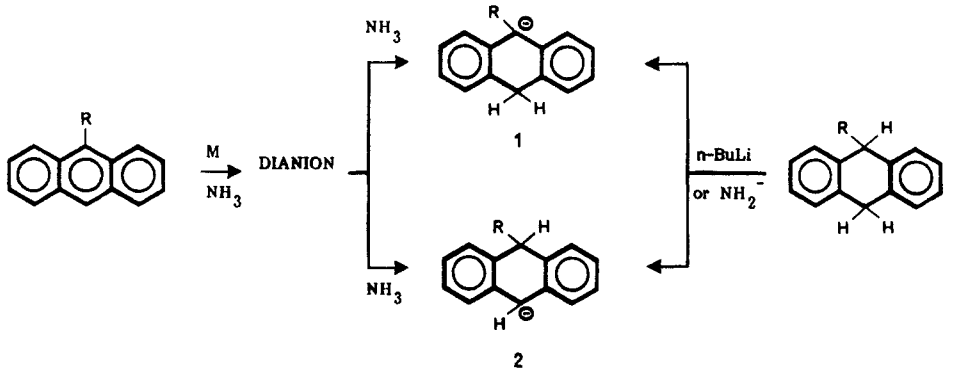


Table III. MNDO Calculations for 9-R-9,10-Dihydroanthracene Monoanions

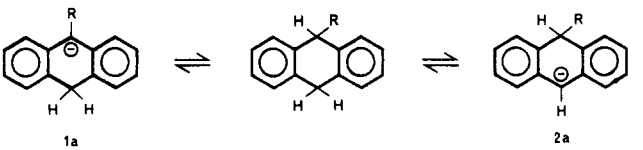
R	heats of formation, kcal/mol	
	9-anion	10-anion
Me	14.16	16.96
Et	11.08	13.67
i-Pr	15.50	18.48
Ph	41.63	49.74

raises important questions concerning the controlling factors in these reactions. Presumably one of these paths may provide a thermodynamic distribution (i.e., equilibration between anions **1** and **2**) but not both since the two methods give different product ratios when done with the same cation and solvent (Table I). Hence at least one of these processes must be controlled by (protonation) kinetics.

Protonation of dianions is generally considered to occur at the position of highest electron density[5] although it has been pointed out by Barton that this process may also be influenced by the stability of the resultant monoanion.[6] Obviously the former approach is based on kinetics whereas the latter is based on thermodynamics. To gain insight, we carried out MNDO calculations[7] on a number of the dianions and monoanions. Total electron charge is calculated to be greatest at C_9 for the dianions in each case. However, the calculated HOMO coefficient is in fact, slightly larger at C_{10}, and it has been suggested that protonations of this type follow the HOMO coefficients.[8] On this basis it is expected that 9-Me, 10-R-DHA products should predominate, and this is consistent with our observations. Interestingly MNDO comparison of the C_9 and C_{10} monoanions (Table III) predicts the C_9 anion to be the more stable, and this would also predict protonation at C_{10} in the dianion if, in fact, monoanion stability had any influence. It should be noted that although alkyl substituents are often thought to be destabilizing in anions, the opposite effect (stabilization) has been observed when the alkyl group is directly attached to a sp^2-hybridized anionic center.[9]

As mentioned above, the possibility of equilibration between **1** and **2** is an important question. We were able to address this issue by examining the reductive methylation (method A) of 9-methylanthracene as a function of temperature. At −33 °C (refluxing ammonia), methylation provides a ratio of 9,10-dimethyl-DHA to 9,9-dimethyl-DHA of 45:55, which is significantly different from the results at −78 °C (30:70). This set up a critical experiment. We added sodium to 9-methylanthracene in NH_3/THF at −78 °C as usual, but after 30 min the temperature was raised to −33 °C, followed by the usual inverse quench into excess methyl iodide. This experiment produced the usual results at −78 °C (30:70) *not* the −33 °C results (45:55). On this basis, we conclude that protonation of the dianion by ammonia is a kinetic (irreversible) process (the absence of dianions in anthracene metal ammonia/THF solutions has also been demonstrated spectroscopically[10]). Moreover, once formed, this anion system appears quite stable since in one reaction at −33 °C, aliquot portions were methylated every 5 min for 40 min and then again after 2 h. The usual ratio of products was observed in each case within a few percent.

Scheme II

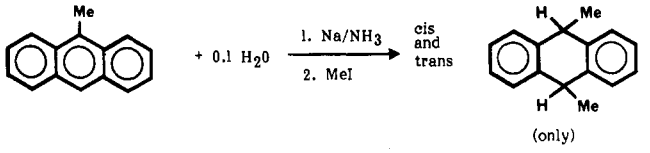


At this point in our study, a report appeared by Müllen and co-workers[10] indicating the reaction of lithium metal with 9-methylanthracene in THF/ammonia (5:1) produces only the 10-anion as evidenced by ^{13}C NMR. Moreover, they suggested that the same 9-methyl-10-metallo-DHA also results from sodium amide or *n*-butyllithium deprotonation of 9-methyl-DHA. These results are in contrast with those reported herein, and so we began to suspect an equilibrium. This would mean that the 10-anion is thermodynamically more stable, which is in opposition with the MNDO calculated results. However, it must be recognized that these calculations are "gas phase" and do not take solvation, counterions, etc. into account.

If, in fact, anion **1a** isomerizes to **2a**, we can rule out an intramolecular hydrogen shift since such a rearrangement would most likely occur under all conditions (solvents, etc.). In any event, a recent report suggests that 1,4-hydrogen shifts are not facile in DHA monoanion systems.[1s] If the anions are not interconverted by an intramolecular process, then a protonation/deprotonation pathway must be considered. We envisioned a mechanism, shown as Scheme II, where the presence of an appropriate acid, AH, could produce neutral 9-R-DHA, which may be deprotonated, provided A is sufficiently basic. The presence of some amount of a neutral 9,10-dihydroanthracene would, of

(5) (a) Streitwieser, A., Jr.; Suzuki, S. *Tetrahedron* **1961**, *16*, 153. (b) Birch, A. J.; Hinde, A. L.; Random, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370 and references therein.
(6) Barton, D. H. R.; Robinson, C. H. *J. Chem. Soc.* **1954**, 3045.
(7) Calculations were performed with *QCPE* Program 455.
(8) See ref 5B and also: Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: Berlin, 1975.
(9) For example, see: Murdoch, J. R.; Bryson, J. A., McMillen, D. F.; Brauman, J. I *J. Am. Chem. Soc.* **1982**, *104*, 600.
(10) Müllen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801.

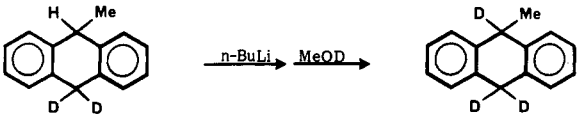
course, serve as AH in Scheme II. In fact, when we carried out the metal/ammonia reduction of 9-methylanthracene in the presence of 9,10-dihydroanthracene, we obtained only the 9,10-dimethyl product. Obviously, the addition



(only)

of a little water would generate a dihydroanthracene in situ, and we were not surprised to learn that reductive methylation of 9-methylanthracene in the presence of 0.1 equiv of water produced 9,10-dimethylation only. Hence only a catalytic amount of a protic impurity could lead to an equilibration, and this may be the reason for the contrast of results with the previous NMR study (also coupled with the usually longer reaction period associated with sample preparation, etc.). Similarly with *n*-butyllithium deprotonation, neutral dihydroanthracene is present as the *n*-butyllithium is added (reverse addition cannot be used due to dianion formation; a second proton is removed almost as easily as the first[11]). Hence if any deprotonation were to occur at C_9, the anion would be reprotonated and ultimately only the 10-anion would persist.

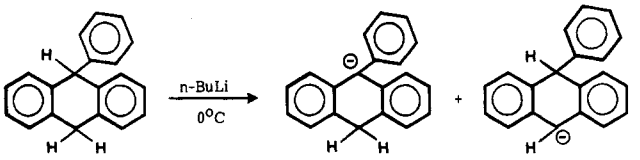
We were also able to demonstrate this intermolecular exchange by reacting 1.0 equiv of 9-*n*-butyl 10-anion with 1.0 equiv of neutral 9-ethyl-DHA. After 30 min at −78 °C, inverse quench into methyl iodide produced products from both *n*-butyl and ethyl-DHA anions in the ratio of 2.5:1 (respectively). However, we were able to demonstrate that deprotonation at C_9 in 9-methyl DHA can indeed occur by repeated reaction with *n*-BuLi/CH_3OD. Once the



10-position is fully deuterated, additional *n*-BuLi/CH_3OD treatments will produce the d_3 derivative. It may be tempting to conclude that deprotonation was always occurring at C_9 and now deuterium is being transferred from the unreacted d_2 derivative. However, it may simply be a reflection of lowered reactivity at C_{10} due to the expected kinetic isotope effect.

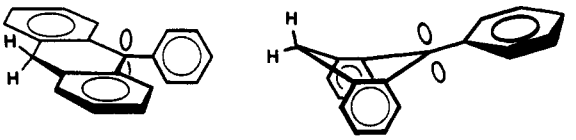
It has been assumed that deprotonation of 9-phenyl-9,10-dihydroanthracene takes place at C_9, producing a flat dihydroanthracenyl anion with a perpendicular phenyl substituent (**3a**), and this system has been used as a model for interaction of a phenyl substituent with an adjacent anionic center by a σ pathway only.[12] Hence we were surprised to find that proton abstraction with *n*-butyllithium produces the 10-anion as the major product (although the 9-anion builds up with time). Evidently, the 9-anion is more stable, but the 10-anion is formed fastest. Even with potassium dimsylate at room temperature for 15 min,[13] the 10-anion prodominates (63:37).

A question may also be raised about the structure of anion **3**. We have recently conducted an NMR study with the analogous 9-carboethoxy anion and found the enolate to be the preferred structure. This is, carbonyl π overlap



10 min.	39	61
30 min.	66	34
60 min.	70	30

predominates, forcing some folding of the central ring. This would translate into **3b** for the present case. Such



3a **3b**

an arrangement, however, is not predicted by MNDO calculations. Carbon chemical shifts for anion **3** have been reported by Müllen et al., but aromatic carbon atom assignments were uncertain. Perhaps further investigation of this point would be warranted, especially with π-stabilizing groups at the para position in the phenyl substituent.

As a final point, we must consider the difference in behavior of the various substituents in the dianion protonations. This is a complex question[14] which may involve steric and electronic effects, as well as solvation and the association of the cation.[15] The rather high level of 10-methylation in the 9-isopropyl case suggests that steric effects could be significant. However, a consideration of the behavior of benzyl and ethyl raises some doubts, and indeed a plot of log (C_9 methylation/C_{10} methylation) vs. E_s[16] shows no correlation. This points to an electronic effect, and in fact a similar plot with σ^* does produce a rough correlation with the alkyl substituents including benzyl (but excluding phenyl). However, the significance of σ^* correlations has been questioned.[14,16] It appears then, that the best approach involves the difference between HOMO coefficients as given in Table II. Although we were not able to obtain results for all of the systems studied, the calculations do predict an increase in protonation at C_{10} (i.e., C_9 methylation) throughout the series Ph > *i*-Pr > Et, Me.

Experimental Section

NMR spectra were obtained on Varian EM-360, EM-390 and CFT-20 spectrometers. Gas chromatographic analyses were performed on a Shimadzu GC-6A employing a 6 ft × 0.25 in., 10% SE Chromosorb W-HD column. Microanalyses were obtained for all new compounds by Galbraith Laboratories, Inc. THF was distilled from benzophenone ketyl immediately before use.

General Procedure for Metal–Ammonia Reductive Methylation of 9-R-Anthracenes (Method A). Excess (1.25 equiv) sodium metal was added to the aromatic substrate dissolved in ammonia/THF (2:1) at −78 °C. After the metal was dissolved and a dark blue color appeared, stirring was continued for 30 min. The mixture was then pumped through a glass tube into an excess of methyl iodide in anhydrous THF. Products were separated

(11) Streitwieser, A., Jr.; Berke, C. M.; Roberts, K. *J. Am. Chem. Soc.* **1978**, *100*, 8271. See also: Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

(12) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; VanDerPuy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321.

(13) Essentially the conditions of ref 12.

(14) Murdoch, J. R.; Bryson, J. A.; McMillen, D. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 600.

(15) We have not fully investigated the effect of the cation, but in one case (9-methylanthracene) we substituted lithium for sodium by method A with little change in results. See Table I.

(16) DeTar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7988; *J. Org. Chem.* **1980**, *45*, 5166.

by ether extraction and analyzed by NMR and GC.

General Procedure for Deprotonation of 9-R-9,10-Dihydroanthracenes (Method B). *n*-Butyllithium (1.1 equiv; standardized before use) was added by syringe to a stirred solution of 9-R-9,10-DHA in dry THF at −78 °C, and stirring was continued for 45 min. The reaction mixture was then pumped through a glass tube into an excess of methyl iodide in dry THF. Products were separated by extraction with ether and analyzed by NMR (and GC, if necessary). 9,9-Dimethyl-DHA,[17] 9,10-dimethyl-DHA's,[1a] 9-ethyl-10-methyl-DHA's,[1a,c,h] 9-methyl-10-isopropyl-DHA's,[1c,h] 9-butyl-10-methyl-DHA's,[1c] and 9-methyl-9-phenyl-DHA[18] were identified by comparison with the literature.

9-Ethyl-9-methyl-9,10-dihydroanthracene. A solution of 2.8 g (13.4 mmol) of *o*-benzylacetophenone in 30 mL of anhydrous ether was added dropwise to the Grignard reagent (0 °C) prepared from 0.4 g (16 mmol) of magnesium and 1.91 g (17.5 mmol) of ethyl bromide in 30 mL of ether. The solution was then allowed to warm to room temperature, and stirring was continued for 2 h. Saturated NH_4Cl solution was then added, and the solid was removed by filtration and washed well with ether. The combined ether solutions were concentrated in vacuo to provide 3.2 g of a yellowish oil. The oil was added to 30 mL of 85% H_2SO_4 at 0 °C, and the resulting mixture was stirred for 20 min. It was then poured into ice-water and extracted with ether. The washed ether extracts were evaporated, and the resulting oil was chromatographed (aluminum oxide; 1:1 CH_2Cl_2/hexane). The first fraction (1.05 g, 35%) was distilled under reduced pressure (85–87 °C at 2 mm), and a colorless oil was obtained, which solidified under cooling. Recrystallization from methanol gave white needles, mp 51.5–52.5 °C: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.56 (t, 3 H), 1.67 (s, 3 H), 1.91 (q, 2 H), 4.10 (br s, 2 H), 7.26–7.60 (m, 8 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 9.5, 27.2, 35.3, 43.0, 125.5, 125.7, 126.3, 127.9, 135.5, 142.9.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: 91.88, 8.21.

9-Methyl-9-isopropyl-9,10-dihydroanthracene. The mixture of the 9-methyl-9-isopropyl- and 9-methyl-10-isopropylanthracenes obtained by reductive methylation of 9-isopropylanthracene (method A) was distilled (103 °C at 3 mm), giving a colorless oil, which solidified upon standing. The resulting solid was recrystallized (methanol) to provide colorless needles (mp 58.5–59.5 °C) of 9-methyl-9-isopropyl-9,10-dihydroanthracene: ^1H NMR (CCl_4, Me_4Si) δ 0.66 (d, 6 H), 1.70 (s, 3 H), 1.9 (m, 1 H), 4.05 (AB q, 2 H), 7.20 (m, 8 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.8, 18.4, 35.6, 36.5, 46.2, 125.4, 125.6, 126.3, 127.8, 136.2, 143.7.

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: 91.22; 8.43.

9-*n*-Butyl-9-methyl-9,10-dihydroanthracene was obtained in the same way as 9-ethyl-9-methyl-9,10-dihydroanthracene (24% yield) as a colorless oil [bp 106–108 °C (2 mm)]: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.73 (t, 3 H), 1.0 (m, 4 H), 1.64 (s, 3 H), 4.04 (br s, 2 H), 7.1–7.5 (m, 8 H) [the rest of the protons appear as overlapping signals in the aliphatic region]; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 23.0, 27.2, 27.9, 35.4, 42.6, 42.9, 125.5, 125.7, 126.3, 127.9, 135.3, 143.2.

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.00; H, 8.80.

9-Benzyl-9-methyl-9,10-dihydroanthracene was obtained in the same way as 9-ethyl-9-methyl-DHA (30% yield) to furnish white needles from petroleum ether, mp 87.5–88 °C: ^1H NMR (CCl_4, Me_4Si) δ 1.83 (s, 3 H), 2.88 (s, 2 H), 3.63 (AB q, 2 H), 6.2–6.4 (m, 2 H), 6.9–7.5 (m, 11 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.9, 35.4, 44.0, 50.5, 125.7, 125.9, 126.0, 126.2, 127.1, 127.6, 130.4, 136.2, 137.9, 142.4.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: 92.67; 7.06.

9-Benzyl-10-methyl-9,10-dihydroanthracene was obtained from 9-benzyl-DHA with *n*-butyllithium (method B). The crude product was twice recrystallized from methanol to provide white needles, mp 101–101.5 °C. NMR confirmed the presence of only one isomer. The ^{13}C chemcial shift of the methyl group suggested the cis isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.45 (d, 3 H), 3.05 (d, 2 H), 3.95–4.24 (m, 2 H), 6.92–7.33 (m, 13 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 28.3, 40.2, 48.2, 49.1, 125.7, 126.2, 126.4, 128.0, 128.8, 129.9, 138.1, 139.7, 140.9.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.73; H, 7.24.

9-Methyl-10-phenyl-9,10-dihydroanthracene was obtained from 9-methyl-10-phenylanthracene by metal–ammonia reduction followed by inverse quenching into aqueous NH_4Cl. The NMR of the crude product showed a ca. 20:80 ratio of cis and trans isomers. Crystallization from petroleum ether gave white crystals, mp 121–122 °C, and NMR confirmed the presence of only one isomer (the main product). The ^{13}C chemical shift of the methyl group suggested the trans isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.52 (d, 3 H), 4.03 (m, 1 H), 5.20 (br s, 1 H), 7.0–7.5 (m, 8 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.7, 39.2, 50.0, 125.9, 126.1, 126.6, 128.5, 129.9, 139.5, 141.4, 143.1.

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.01; H, 6.76.

No attempt was made to isolate the second isomer, but ^{13}C NMR of the mixture showed the methyl group of the minor product at 26.4 ppm. This confirms the cis isomer.

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Registry No. 1 (R = H), 14314-91-1; 1 (dianion), 103192-12-7; 1 (R = Me), 103192-05-8; 1 (R = Et), 103192-06-9; 1 (R = *i*-Pr), 86853-47-6; 1 (R = Ph), 103192-07-0; 1 (R = Me)·Na, 103192-13-8; 1 (R = Me)·Li, 103192-14-9; 1 (R = Et)·Na, 103192-15-0; 1 (R = *n*-Bu)·Na, 103192-16-1; 1 (R = Bz)·Na, 103192-17-2; 1 (R = *i*-Pr)·Na, 103192-18-3; 1 (R = Ph)·Na, 103192-19-4; 1 (R = Ph)·Li, 94537-56-1; 2 (R = Me), 103192-08-1; 2 (R = Et), 103192-09-2; 2 (R = *i*-Pr), 103192-10-5; 2 (R = Ph), 103192-11-6; 2 (R = Me)·Na, 103192-20-7; 2 (R = Me)·Li, 74783-96-3; 2 (R = Me)·Na, 17239-98-4; 2 (R = *n*-Bu)·Na, 103192-21-8; 2 (R = Bz)·Na, 103192-22-9; 2 (R = *i*-Pr)·Na, 103192-23-0; 2 (R = Ph)·Na, 103192-24-1; 2 (R = Et)·Li, 17228-12-5; 2 (R = *n*-Bu)·Li, 103192-25-2; 2 (R = Bz)·Li, 85193-39-1; 2 (R = *i*-Pr)·Li, 35150-61-9; 2 (R = Ph)·Li, 103192-26-3; 9-Me-DHA, 17239-99-5; 9-Et-DHA, 605-82-3; 9-Bu-DHA, 10394-60-2; 9-BzDHA, 2294-89-5; 9-*i*-Pr-PHA, 17573-50-1; 9-Ph-DHA, 13577-28-1; 9-Me-10-Me-DHA, 22566-43-4; 9-Me-10-Me-DHA, 42332-94-5; 9-Et-10-Me-DHA, 36778-20-8; 9-Et-9-Me-DHA, 54947-85-2; 9-*n*-Bu-10-Me-DHA, 103192-27-4; 9-*n*-Bu-9-Me-DHA, 103192-28-5; 9-Bz-10-Me-DHA, 103192-29-6; 9-Bz-9-Me-DHA, 103192-31-0; 9-*i*-Pr-9-Me-DHA, 103201-05-4; 9-Ph-10-Me-DHA, 103224-47-1; 3-benzylacetophenone, 61608-94-4; 9-methylanthracene, 779-02-2; 9-ethylanthracene, 605-83-4; 9-propylanthracene, 1498-77-7; 9-benzylanthracene, 1498-71-1.

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