acid at the same two wavelengths could be determined rather easily, and the value for K_a adjusted for the best fit. The results at the two wavelengths were in good agreement.

pK_a Values of Buffer Acids. pK_a for values for acetic, formic, chloroacetic, and phosphoric acids were determined under reaction conditions of 50 °C in 0.04 M solutions made at a constant 0.5 M ionic strength with sodium chloride. Aliquots of these solutions were titrated with 0.1 M KOH brought to a total ionic strength of 0.5 M with sodium chloride. The titrations were carried out by using an automatic titrator (Sargent-Welch Buret Master and Sargent-Welch Chemical Metering Dispenser) controlled by an Apple IIe computer equipped with a Cyborg Isaac 91a interface. The pH was monitored throughout each titration with an interfaced Orion SA 520 pH meter equipped with a glass electrode and calibrated at each end of the pH range covered. The pK_a was determined from the best fit to the experimental titration curve by software written for that purpose.

Kinetics. The methods used to follow the hydrolysis reactions of 1 and 3 are essentially the same as those described in the previous study,[1] except that spectrophotometric runs were monitored at 324 nm. The pH of each of the buffers was determined at 50 °C and an ionic strength of 0.5 M, which are the same conditions as the kinetic runs.

^{18}O-Label Studies. The reaction samples below were analyzed by GC–MS analysis as previously described.[1]

In order to examine the hydrolysis of 1 in ^{18}O-labeled water, we prepared acetate buffer by dissolving 2.7 mg of sodium acetate (0.033 mmol) and 5.2 μL of acetic acid (0.087 mmol) in 400 μL of labeled water (99% ^{18}O, Stohler Isotopes), giving a solution 0.08 M in acetate. A stock solution of substrate was prepared by adding 0.6 μL of 1 to 120 μL of labeled water (did not dissolve) and then adding 120 μL of the acetate buffer solution (1 dissolved). Aliquots (60 μL) of the resulting solution were placed in tubes, which were sealed with rubber septa and heated at 50 °C overnight. MS analysis of these aliquots indicated an enrichment of 12% when the natural abundance of heavy isotopes (0.8%) was subtracted. A sample of 4-hydroxyquinaldine was treated similarly and was found to incorporate about 2% ^{18}O. Subtraction of this value for exchange within the hydrolysis product gives 10% for the ^{18}O incorporation occurring during hydrolysis of 1. A similar value of 9% was obtained by using 90% ^{18}O-labeled water and dividing the observed enrichment by 0.9 to adjust for the lower level of enrichment in the water.

The hydrolysis of 2 was similarly examined in 90% ^{18}O-labeled water and, after the same corrections noted above, was found to incorporate only about 1–2% ^{18}O during reaction.

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Registry No. 1, 703-62-8; 3, 117498-01-8; 4-aminoquinaldine, 6628-04-2; 4-hydroxyquinaldine, 607-67-0.

^{1}H and ^{13}C Nuclear Magnetic Resonance Reinvestigation of the Dibenzo[*a*,*c*]cyclononatetraenyl Anion and Its 5,9-Diphenyl Derivative. Planarity vs Nonplanarity

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It is found that the dibenzo[*a*,*c*]cyclononatetraenyl anion is readily transformed into the stable 1*H*-cyclopenta[*l*]phenanthren-1-yl anion. Earlier reported NMR data of this compound were incorrectly assigned to a planar structure of the dibenzocyclononatetraenyl anion. The nonplanarity of the initially formed nine-membered ring anion was confirmed both experimentally and theoretically. The ring-closure process does not take place in the anion of the 5,9-diphenyl derivative, which retains a nonplanar conformation of the nine-membered ring.

Introduction

Cyclononatetraenyl anions form a class of compounds that have received considerable attention with respect to the relation between aromaticity and conformation.[1-5] While for instance neutral cyclononatetraene is found to be relatively unstable,[1c,d,6] various cyclononatetraenyl anions which constitute Hückel $4n + 2$ π systems tend to exhibit some degree of extra stability.[1-4] The cyclononatetraenyl (1^-) and the benzocyclononatetraenyl (2^-) anions can exist in an all-cis and a mono-trans form, both having some aromatic character[1,2] (Scheme I). For the monocyclic 1^-, the all-cis structure is found to be the more stable, while the mono-trans form is favored for 2^-. The barrier for isomerization from *mono-trans*-1^- to *all-cis*-1^- is appreciable: 29–34 kcal/mol. The cyclononabiphenylene anion (3^-) seems to prefer exclusively a nonplanar geometry,

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(1) (a) Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1963**, *85*, 2852. (b) LaLancette, E. A.; Benson, R. E. *Ibid.* **1963**, *85*, 2853. (c) Katz, T. J.; Garratt, P. J. *Ibid.* **1964**, *86*, 5194. (d) LaLancette, E. A.; Benson, R. E. *Ibid.* **1965**, *87*, 1941. (e) Boche, G.; Martens, D.; Danzer, W. *Angew. Chem.* **1969**, *81*, 1003. (f) Boche, G.; Weber, H.; Martens, D.; Bieberbach, A. *Chem. Ber.* 1978, 2480.

(2) (a) Anastassiou, A. G.; Griffith, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 611. (b) Anastassiou, A. G.; Reichmanis, E. *Angew. Chem.* **1974**, *86*, 784.

(3) (a) Garratt, P. J.; Knapp, K. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1215. (b) Rabinovitz, M.; Gazit, A.; Bergmann, E. D. *Ibid.* **1970**, 1430. (c) Rabinovitz, M.; Willner, I.; Gamliel, A.; Gazit, A. *Tetrahedron* **1979**, *35*, 667.

(4) Wilcox, C. F., Jr.; Blain, D. A. *Tetrahedron* **1986**, *42*, 6389.

(5) (a) Simmons, H. E.; Chesnut, D. B.; LaLancette, E. A. *J. Am. Chem. Soc.* **1965**, *87*, 982. (b) Anastassiou, A. G.; Kasmai, H. S.; Hasan, M. *Tetrahedron Lett.* **1985**, *26*, 1695.

(6) (a) Boche, G.; Böhme, H.; Martens, D. *Angew. Chem.* **1969**, *81*, 565. (b) Radlick, P.; Alford, G. *J. Am. Chem. Soc.* **1969**, *91*, 6529. (c) Masamune, S.; Baker, P. M.; Hojo, K. *Chem. Commun.* **1969**, 1203. (d) Anastassiou, A. G.; Orfanos, V.; Gebrian, J. H. *Tetrahedron Lett.* **1969**, 4491.

0022-3263/89/1954-0171$01.50/0

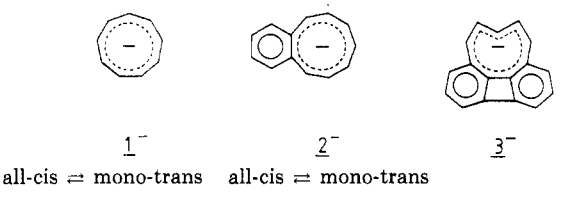
Table I. ^1H and ^{13}C NMR Chemical Shifts of the Lithium Salts of 4^-, 5^-, and 6^-[a,b]

positions:		1,13	2,12	3,11	4,10	5,9	6,8	7	4a,9a	13a,13b	1′,1″	2′,2″	3′,3″	4′,4″	average
4^-, THF-d_8	^1H	−6.96 (m, 4 H) and 6.68 (m, 4 H)−				4.29	5.49	2.96							
						($J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 8.3 Hz)									
	^{13}C	−134.8, 129.8, 127.7, 126.6−				97.6	120.9	77.7	−142.3, 142.2−						
6^-, THF-d_8	^1H	7.12	6.80	7.09	6.67		6.36	4.11				6.33	6.56	6.17	6.48
		($J_{1,2}$ = $J_{2,3}$ = $J_{3,4}$ = 7 Hz)					($J_{6,7}$ = 8 Hz)								
	^{13}C	127.6	124.3	128.4	131.9	114.9	130.6	94.6	146.5	148.7	146.5	120.3	127.3	116.3	128.15
6^-, Et_2O-d_{10}	^1H	7.17	6.99	7.24	6.87		6.52	3.64				6.62	6.78	6.52	6.66
							($J_{6,7}$ = 8 Hz)								
		+0.05[c]	+0.19	+0.15	+0.20		+0.16	−0.47				+0.29	+0.22	+0.35	
	^{13}C	129.0	126.3	129.3	130.4	115.9	129.7	78.9	145.5	147.3	144.2	122.1	128.0	120.7	128.13
		+1.4[c]	+2.0	+0.9	−1.5	+1.0	−0.9	−15.7	−1.0	−1.4	−2.3	+1.8	+0.7	+4.4	

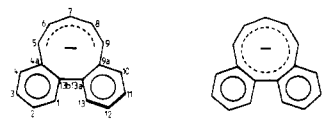
positions:		1,3	2	4,11	5,10	6,9	7,8	3a,11b	3b,11a	7a,7b
5^-, THF-d_8	^1H	6.52	6.31	7.97	7.17	6.98	8.31			
		($J_{1,2}$ = 3.3 Hz)		($J_{4,5}$ = 8 Hz, $J_{5,6}$ = 7 Hz, $J_{6,7}$ = 8.2 Hz)						
	^{13}C	96.5	111.6	122.6	125.5	119.9	123.5	120.4	133.6	126.4

[a] Cyclohexane was used as internal reference, with the chemical shifts 1.43 and 27.70 ppm on the TMS scale for ^1H and ^{13}C, respectively. [b] H–H coupling constants are given within parentheses. [c] Chemical shift difference between the Et_2O and the THF system.

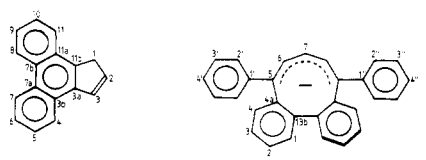
Scheme I



1^- all-cis ⇄ mono-trans 2^- all-cis ⇄ mono-trans 3^-

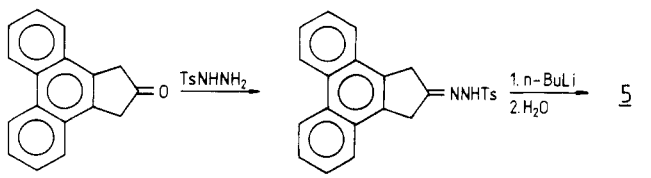


4^- nonplanar $4a^-$ planar



5 6^-

Scheme II



8 9

corresponding to a mono-trans structure.[4] For 2^- and 3^-, the nonplanar shapes appear to be favored relative to the more planar all-cis forms due to lower bond angle strains and van der Waals interactions.[4,9] Nine-membered ring anions thus constitute interesting borderline compounds, since annulenes of 10 or more ring carbons avoid all-cis conformations.

In an early ^1H NMR investigation of the dibenzo[*a*,*c*]-cyclononatetraenyl anion, a rearrangement from a nonplanar, nonaromatic anion (4^-) to a planar, aromatic species ($4a^-$) was suggested to occur slowly at room temperature.[3a] The gain in delocalization energy was indicated to be an important driving force for this transformation. However, this is unexpected on the basis of the isomerization of 2^-. For this system, benzannelation causes an all-cis to mono-trans isomerization, which is attributed to the removal of the H–H peri repulsions when going to the mono-trans structure.[2] It is therefore difficult to explain why additional benzannelation should change this condition. In the case of 4^-, substantial amounts of 1*H*-cyclopenta[*l*]phenanthrene (**5**) was obtained after quenching with water.[3a] Also 1^- undergoes a ring-closure process on quenching with water, where indene and 8,9-dihydroindene are formed.[1a,c,d] Ring closure of neutral cyclononatetraenes to form dihydroindene derivatives has been amply demonstrated in other studies.[2a,6,7] Nevertheless, none of the reports reveal that this process can occur directly from cyclononatetraenyl anions. However, similar ring-closure reactions have been reported in other cyclic conjugated anions. The anion obtained by deprotonation of 1,3- or 1,5-cyclooctadiene was found to rearrange to a cyclopentenyl system at 35 °C with a half-life of 1.5 h.[8a,b]

In view of the remarks in the foregoing paragraph and a recent report on calculated energies of different conformations of 4^-, where the planar symmetric $4a^-$ was found to have a relatively high energy,[9] we have undertaken an NMR reinvestigation of the transformation of the anion 4^-. The NMR spectra are compared with the spectra of the anion obtained from deprotonation of **5** at C_1, i.e., 5^-. Furthermore, we also communicate our results from a similar study of the anion 6^-, where the ^1H NMR spectrum earlier was found to undergo changes that indicated a process similar to the one suggested for 4^-.[3c]

Synthesis and Carbanion NMR Assignments

The parent hydrocarbon **4** (7*H*-dibenzo[*a*,*c*]cyclononatetraene) was prepared according to the earlier described method,[3] i.e., by a Wittig reaction between biphenyl-2,2′-dicarbaldehyde and the bis ylide from 1,3-bis(triphenylphosphonio)propane dibromide. The diphenyl derivative **6** (5,9-diphenyl-7*H*-dibenzo[*a*,*c*]cyclononatetraene) was obtained via the nine-membered ring diketone.[3c] Reaction with phenyllithium followed by dehydration of the diol formed gave **6**.[3c] Compound **5** was synthesized by the route indicated in Scheme II. The anions 4^-–6^- were prepared by deprotonation of the hy-

(7) (a) Radlick, P.; Fenical, W. *J. Am. Chem. Soc.* **1969**, *91*, 1560. (b) Waali, E. E.; Allison, N. T. *J. Org. Chem.* **1979**, *44*, 3266. (c) Waali, E. E.; Wright, C. W. *Ibid.* **1981**, *46*, 2201.

(8) (a) Bates, R. B.; McCombs, D. A. *Tetrahedron Lett.* **1969**, 977. (b) Slaugh, L. H. *J. Org. Chem.* **1967**, *32*, 108. (c) Bates, R. B.; Ogle, C. A. *Carbanion Chemistry*; Springer-Verlag: Berlin, 1983; Chapters 6 and 8.

(9) Sygula, A.; Edlund, U.; Rabideau, P. W. *J. Chem. Res., Synop.* **1987**, 312.

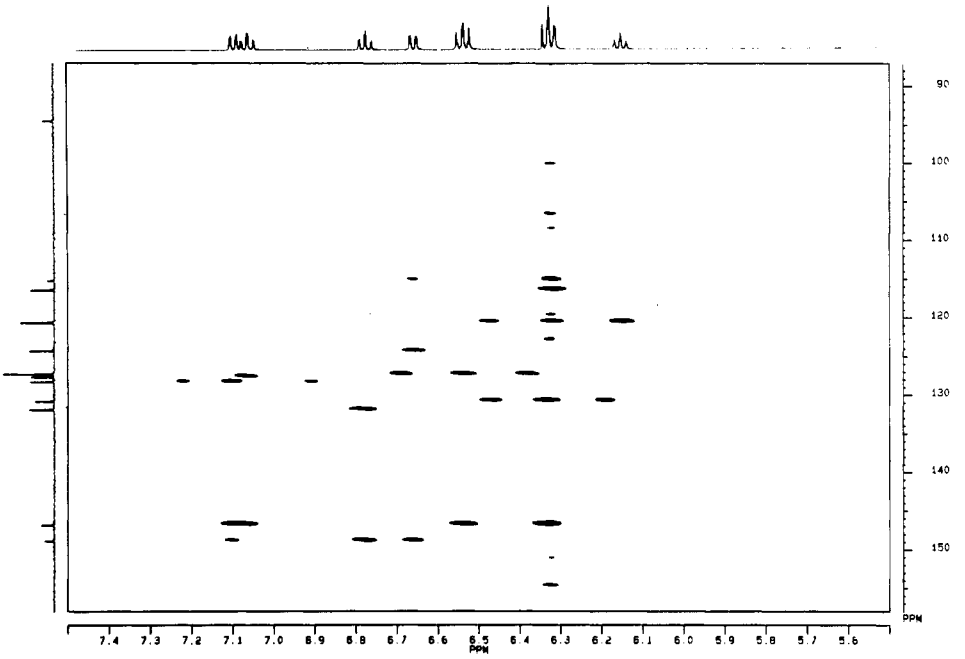


Figure 1. Inverse 2D NMR long-range ^1H–^{13}C shift correlated spectrum of 6^- in THF-d_8.

drocarbons **4**–**6** by using *n*-butyllithium (*n*-BuLi) as described in the Experimental Section.

The ^1H and ^{13}C NMR chemical shifts of 4^-–6^- are given in Table I. The ^1H NMR signals of 5^- were assigned with the use of the COSY and NOESY 2D NMR spectra. The ^{13}C signals of the proton-bearing carbons were assigned from C–H shift-correlated 2D experiments, while long-range shift correlation (COLOC) was utilized for the quaternary carbons.[10] In the COLOC analysis, the three-bond trans C–H couplings (C_{3a}–H_2, C_{3b}–H_5, C_{7a}–H_6) served to establish the assignment. Also Hückel MO charge densities and the ^1H NMR coupling pattern and signal intensities were in agreement with the ^1H and ^{13}C assignments. For 6^- in deuteriated tetrahydrofuran (THF-d_8), the assignment of the ^1H signals and the ^{13}C signals of the proton-bearing carbons was achieved by 2D inverse C–H shift-correlated and relayed coherence transfer techniques,[11] in combination with the 1D NMR spectra. Inverse long-range shift-correlated 2D experiments were used in order to assign the signals of the quaternary carbons (Figure 1). The inverse experiments were necessitated by low sample concentrations. The 1D NMR spectra of 6^- in deuteriated diethyl ether (Et_2O-d_{10}) were similar to those of the THF-d_8 samples. The assignment was thus possible with the help of some complementary selective ^1H-decoupled ^{13}C experiments.

Results and Discussion

The ^1H NMR chemical shifts of the species formed upon deprotonation of **4** agree well with those reported for 4^- [3a] (Table I). In accordance with the observation in that study, the original peaks gradually disappeared and a new set of signals developed. The ^1H chemical shifts and the coupling constants in the new spectrum also agree with those earlier reported, except for the integral in the 6.9–7.2 ppm region, which we find to correspond to four instead of six hydrogens. Since both the ^1H and ^{13}C NMR spectra could be explained by a structure similar to 5^-, we prepared

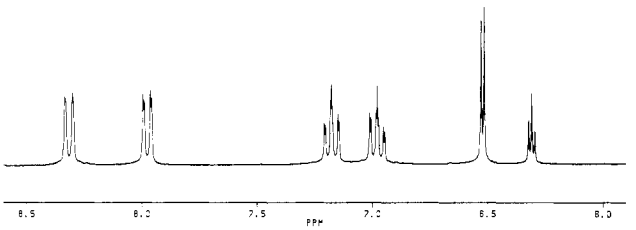


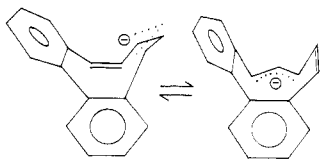
Figure 2. ^1H NMR spectrum of 5^- in THF-d_8.

this anion from **5** (Table I, Figure 2). The NMR data of 5^- were found to be identical with those of the final compound in our samples of 4^-. Moreover, the ^1H coupling constants of 5^- have values similar to those earlier reported for the suggested fully delocalized *all-cis*-**4a**$^-$. Hence, the NMR data are consistent with a ring closure in 4^-, followed by an elimination which produces the anion 5^-. Clearly, 5^- has a pronounced aromatic character as displayed by the ^1H chemical shifts. With orbital symmetry rules in mind, one may assume that the ring closure takes place in a disrotatory fashion which involves six π-electrons in the C_5–C_9 subunit. Several examples exist in the literature where reduction/elimination of this type might occur.[8]

The conformational energy surface of 4^- should also be considered when the formation of the new ring system is discussed. In a recent study, the preferred conformation of 4^- was calculated by MNDO and AM1 methods.[9] The most stable form was found to comply with a nonplanar structure having an angle of approximately 80° between the two benzene-ring planes. Further, the energy of this conformation was calculated to be considerably lower than that of the fully planar structure; the difference was determined to be around 65–70 kcal/mol with neglect of the C–Li interactions. The energy of the dihydro derivative of 5^-, which is likely to be formed initially from 4^-, was found to be roughly the same as for the nonplanar 4^-. We find support for the skewness of the benzene rings in 4^- from both the ^1H and ^{13}C NMR data. The chemical shifts of the proton-bearing carbons in the six-membered ring (126.6–134.8 ppm) indicate no net charge delocalization into the benzene rings. Further, the signals of $H_{1,13}$ and $H_{4,10}$ appear at higher field than expected if steric interactions between H_1 and H_{13} and between $H_{4,10}$ and $H_{5,9}$

(10) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.
(11) Kessler, H.; Bermel, W.; Griesinger, C. *J. Magn. Reson.* **1985**, *62*, 573.

Scheme III



would be present. Most of the charge in 4^- is located to the C_7 and $C_{5,9}$ positions as probed by both ^1H and ^{13}C chemical shifts. In addition, the ^{13}C data are consistent with regular sp^2-hybridized carbons. On the basis of the NMR data and the structural calculations, it appears that 4^- exists in an equilibrium between two identical allyl-anion conformations (Scheme III). According to these calculations, the nine-membered ring has a boat shape, where the double bond and the six-membered rings lack appreciable conjugation with the allylic part due to the different orientations of the π-orbitals. This complies with the sparse delocalization of charge into the benzene rings. The barrier for interconversion between the two states is most likely small since no major adjustments of bond angles or bond lengths seem to be required in a reasonable transition state.

The anion 6^- in Et_2O-d_{10} solution was earlier found to exhibit changes in the ^1H NMR spectrum in a situation resembling that of 4^-.[3c] In order to resolve this ambiguous case, we examined both THF-d_8 and Et_2O-d_{10} solutions of 6^-. In the THF samples, the anion was found to be stable without noticeable decomposition at room temperature for prolonged periods of time. Hence, no ring-closure reaction could be observed. Both the ^1H and ^{13}C chemical shifts of the biphenyl component of 6^- agree reasonably well with those of 4^- (Table I). Again, this implies that the biphenyl rings are not coplanar and that there is no significant charge residing in the biphenyl subunit. Instead, the chemical shifts display clearly that some charge is delocalized into the phenyl rings attached to carbons C_5 and C_9. In the same context, less charge is found in the positions 5–7 in 6^- compared with 4^-, as deduced from the corresponding ^1H and ^{13}C data. It may also be noticed that this analysis is in agreement with the suggested allyl-anion equilibrium since a phenyl ring readily can be coplanar with the allyl carbons in the boat-type structure. Moreover, it seems likely that the delocalization of charge is an important reason for the stability of 6^-.

A comparison of the chemical shifts of 6^- in THF-d_8 and Et_2O-d_{10} reveals that the ^1H signals appear at slightly lower field (0.05–0.35 ppm) in the Et_2O system, except for the H_7 resonance, which is shifted 0.47 ppm upfield (Table I). The ^{13}C NMR spectrum also shows some interesting features. First, δ C_7 is shifted 15.7 ppm upfield in the Et_2O sample. Secondly, the $C_{1-3,5,9,11-13}$ and $C_{2'-6',2''-6''}$ signals exhibit downfield shifts in the range 0.9–4.4 ppm, while the remaining carbons show 0.9–2.3 ppm upfield shifts. This is consistent with a charge concentration toward the nine-membered ring system, and to the C_7 position in particular. The sum of the induced shifts (THF → Et_2O) of the biphenyl-unit ^{13}C signals is close to 0, which supports the proposed nonplanarity and biphenyl twisting. The individual shifts of these ^{13}C resonances are most likely caused by an increased cation-induced π-polarization.[12] On the contrary, the phenyl carbons seem to be affected both by π-polarization and by charge withdrawal from the phenyl rings. For a delocalized carbanion, a solvent change from THF to Et_2O generally results in a more tight ion pair due to the lower cation-solvating ability of Et_2O.[13] However, the average δ ^{13}C is usually found to be fairly constant when the ion-pair structure is changed, at least for diatropic carbanions.[12,14] In our case, the average chemical shift is unchanged, which can be taken as firm support for a cation-induced charge redistribution caused by the solvent change. The effects on the ^1H chemical shifts can be well explained from the factors that influence the ^{13}C shieldings and a C–H bond-polarization model, where a cation that is located close to a proton-bearing carbon can withdraw electron density from the proton.[12b,c] Thus, although the charge density at C_7 increases on the change to Et_2O, the C_7–H_7 bond becomes more polarized because of the increased cation coordination to C_7. The H_6–H_7 coupling constant is the same in Et_2O-d_{10} and in THF-d_8 (8 Hz) as expected if no rehybridization at C_7 occurs due to the altered ion-pair situation. This further strengthens the notion of charge redistribution. It should also be mentioned that 6^- in the Et_2O-d_{10} solution is less stable than in THF-d_8. The samples are slowly degraded with a half-lifetime of about 2 weeks at room temperature. A possible explanation for the lower stability of 6^- in Et_2O-d_{10} as compared with THF-d_8 is the less pronounced charge delocalization in the former solvent.

In summary, we have shown that the dibenzo[*a*,*c*]-cyclononatetraenyl anion and its 5,9-diphenyl derivative prefer nonplanar conformations. The unsubstituted anion undergoes a ring-closure process followed by dehydrogenation to form the stable cyclopenta[*l*]phenanthrenyl anion. This transformation is prevented if the 5,9-positions are phenyl-substituted.

Experimental Section

Preparation of 4. 1,3-Bis(triphenylphosphonio)propane dibromide (3.17 g, 4.4 mmol) was suspended in 720 mL of dry benzene under argon and stirred for 1 h. Freshly sublimed *t*-BuOK (2.25 g, 20 mmol) was added in one portion, and the mixture was stirred until a bright orange solution was obtained. Biphenyl-2,2′-dicarbaldehyde[15] (0.92 g, 4.4 mmol) in 180 mL of dry benzene was then added during 45 min. After being stirred overnight under argon, the black solution was washed twice with water and with brine. The combined aqueous layers were back-extracted with benzene, and the benzene extract was dried with $MgSO_4$. After filtering and evaporation of the solvent, the residue was flash chromatographed on silica gel with a combination of CH_2Cl_2 (25%) and CCl_4 (75%). The fast band was collected and passed through a silica gel column with CCl_4. The resulting oily product was identified by NMR as **4** (40 mg), which crystallized slowly:[3] ^1H NMR ($CDCl_3$) δ 7.0–7.3 (m, 8 H), 6.32 (br d, 2 H, J = 12 Hz), 5.55 (d, t, 2 H, J = 6, 12 Hz), 2.70 (t, t, 2 H, J = 1.7, 6 Hz); ^{13}C NMR (THF-d_8) δ 142.8, 138.1, 132.0, 129.1, 128.6, 128.3, 127.5, 127.0, 30.6.

Compound 6 was synthesized according to the earlier described method:[3c] ^1H NMR (THF-d_8) δ 7.0–7.2 (m, 18 H), 5.93 (t, 2 H, J = 6.0 Hz), 2.96 (t, 2 H, J = 6.0 Hz).

Preparation of Methyl and Ethyl 3,3a-Dihydro-3a-hydroxy-2-oxo-2*H*-cyclopenta[*l*]phenanthrene-1-carboxylates (7a and 7b, Respectively). A Knoevenagel condensation reaction between phenanthrenequinone and methyl or ethyl acetoacetate was performed according to a method for **7b**.[16] Crude **7a** was obtained in 91% yield, mp 204–206 °C after one

(12) (a) Eliasson, B.; Johnels, D.; Wold, S.; Edlund, U. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 155. (b) Eliasson, B.; Edlund, U. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1837. (c) Eliasson, B.; Edlund, U. *Org. Magn. Reson.* **1983**, *21*, 322.

(13) (a) *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. 1. (b) Hogen-Esch, T. E. *Adv. Phys. Org. Chem.* **1977**, *15*, 153.

(14) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937.

(15) Hall, D. M.; Prakobsantisukh, B. *J. Chem. Soc.* **1965**, 6311.

(16) Cope, A. C.; Field, L.; MacDowell, D. W. H.; Wright, M. E. *J. Am. Chem. Soc.* **1956**, *78*, 2547.

recrystallization from acetonitrile: ^{1}H NMR ($CDCl_3$) δ 7.35–8.0 (m, 8 H), 3.87 (s, 3 H), 3.29 and 3.15 (q, AB, 2 H, J = 18.2 Hz), 2.49 (br s, 1 H). ^{1}H NMR of **7b** ($CDCl_3$): δ 7.35–8.0 (m, 8 H), 4.33 (q, 2 H), 3.32 and 3.19 (q, AB, 2 H, J = 18.2 Hz), 2.71 (br s, 1 H), 1.29 (t, 3 H).

Preparation of 2,3-Dihydro-2-oxo-1*H*-cyclopenta[*l*]phenanthrene (8). Compound 8 was obtained from treatment of **7a** or **7b** with hydroiodic acid followed by sodium bisulfite solution.[16] From several attempts to synthesize 8 in this way, we found it necessary to modify the published workup procedure in order to get an acceptable purity of the compound. The dark greenish material was air-dried, ground in a mortar, and mixed with Celite (0.4 g per gram of crude product). The mixture was then Soxhlet extracted with absolute ethanol. Care was taken to avoid overheating and charring of precipitated material. After the first 20–25 extraction cycles, the brown solution was replaced with pure solvent, and the extraction was continued for 24 h. The light green material so obtained melted around 206 °C. After recrystallization from dioxane, the material melted at about 217 °C (lit.[16] mp 223–223.6 °C): ^{1}H NMR ($CDCl_3$) δ 8.65–8.71 (m, 2 H), 7.50–7.72 (m, 6 H), 3.63 (s, 4 H).

Preparation of the Tosylhydrazone 9 of Ketone 8. To a gently boiling stirred solution of 8 (0.70 g, 3.0 mmol) in a mixture of 70 mL of absolute ethanol and 30 mL of dioxane was added a lukewarm solution of (*p*-tolylsulfonyl)hydrazine (0.59 g, 3.4 mmol) in 30 mL of absolute ethanol, followed by 1 mL of glacial acetic acid. The product rapidly precipitated from the boiling solution. The mixture was allowed to cool while still being stirred. The precipitate was filtered, washed with ethanol, and air-dried. The off-white **9** weighed 1.02 g (85%) and melted with rapid decomposition at about 208 °C: ^{1}H NMR (DMSO-d_6) δ 10.49 (s, 1 H), 8.77–8.92 (m, 2 H), 7.43–8.00 (m, 10 H), 4.08 (s, 2 H), 4.02 (s, 2 H), 2.45 (s, 3 H).

Preparation of 5. This synthesis (a Shapiro reaction)[17] is an alternative to an earlier described method for the preparation of **5**.[16] To a stirred suspension of **9** (1.0 g, 2.5 mmol) in 40 mL of dry THF was added under argon 5 mL (ca. 7.5 mmol) of *n*-BuLi (ca. 1.5 M in hexane) at room temperature during 0.5 h. After an additional hour, the brown-red reaction mixture was carefully quenched with water. After ether extraction, the organic phase was washed with water and dried with $MgSO_4$. The solid material obtained on evaporation was column chromatographed on silica gel 60 with CCl_4. The white crystalline material obtained after removal of the CCl_4 was dissolved in a small amount of CH_2Cl_2 and passed through a small pad of silica gel supported on glass wool in a Pasteur pipet. The solvent was evaporated with a stream of argon, giving 140 mg (26%) of white crystals of **5**. The yield for this synthesis represents nonoptimal conditions: ^{1}H NMR ($CDCl_3$) δ 8.7–8.8 (m, 2 H), 8.0–8.3 (m, 2 H), 7.5–7.8 (m, 5 H), 6.7–6.8 (m, 1 H), 3.86 (t, 2 H, J = 1.7 Hz).

Preparation of Carbanions. The ether solutions of the different compounds in NMR tubes were initially degassed and subsequently disconnected from the vacuum line in an argon atmosphere. Typically, 2–4 equiv of concentrated *n*-BuLi (8–10 M) was added to cooled samples. The NMR tubes were then again evacuated and finally sealed off from the vacuum line. The NMR spectra of the carbanions were obtained on a Bruker WM-250 spectrometer, except for the 2D inverse relayed coherence transfer and inverse long-range shift-correlated assignment experiments which were performed on a Bruker AM-500 instrument. The chemical shifts were measured relative to internal cyclohexane and adapted to the TMS scale with δ ^{1}H (cyclohexane) = 1.43 ppm and δ^{13}C (cyclohexane) = 27.70 ppm. The reported NMR data refer to room temperature measurements with sample concentrations of 0.05–0.2 M.

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Registry No. **4**, 29045-70-3; **4**$^-$, 117775-62-9; **5**, 235-92-7; **5**$^-$, 117775-63-0; **6**$^-$, 117775-64-1; **7a**, 117775-59-4; **7b**, 117775-60-7; **8**, 37913-11-4; **9**, 117775-61-8; 1,3-bis(triphenylphosphonio)propane dibromide, 7333-67-7; biphenyl-2,2′-dicarbaldehyde, 1210-05-5; (*p*-tolylsulfonyl)hydrazine, 1576-35-8.

(17) For reviews on the Shapiro reaction, see: (a) Shapiro, R. H. *Org. React. (N.Y.)* **1976**, *23*, 405. (b) Adlington, R. M.; Barrett, A. G. M. *Acc. Chem. Res.* **1983**, *16*, 55.

Chiral Dipole-Stabilized Anions: Experiment and Theory in Nonbenzylic Systems. 100% Stereoselective Deprotonation and Two-Electron vs Single-Electron Transfer in the Chemistry of Lithium and Copper Piperidinooxazolines

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A chiral oxazoline derived from valine mediates the 100% stereoselective deprotonation of the 2-position of piperidine, forming a single diastereomer organolithium, which is dipole-stabilized. The organolithium species undergoes either two electron or single electron transfer processes, but the latter predominate for most electrophiles. The corresponding cuprates undergo only single electron transfer processes. MNDO calculations indicate little difference in energy between most of the conformational and stereoisomers of the organolithium, suggesting that the single organolithium diastereomer is formed under kinetic control. Mechanistic rationales for the unprecedented deprotonation, as well as the single electron transfer processes, are presented.

Dipole-stabilized anion mediated alkylation of carbons bearing heteroatoms is a useful process for the elaboration of a number of systems.[1] One such application is the α-alkylation of a nitrogen heterocycle. Among the more versatile functional groups for mediation of this process via dipole stabilization of the intermediate carbanion are aliphatic or aromatic amides and formamidines. The generalized process illustrated below generates a stereocenter, and so a stereoselective process aimed at the preparation of homochiral compounds would be highly desirable. The first example of such a process was reported

(1) (a) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275–316. (b) Beak, P.; Zajdel, W. J.; Reitz, D. B. *Ibid.* **1984**, *84*, 471–523.

0022-3263/89/1954-0175$01.50/0