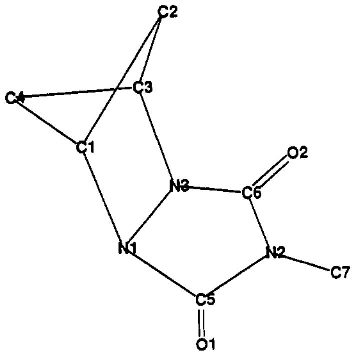
Table VII. Photoelectron Spectroscopic Data for Bicyclic Fused Triazolidinediones

compd	VIP, eV (width at half height, eV) [rel intensity][a]
3	{8.60 (0.50) [1.0], 9.00 (0.40) [1.0]} {10.15 (0.60) [1.0], 11.00 (0.70) [1.0]}
5	{8.48 (0.50) [1.0], 8.90 (0.55) [1.0]} {10.12 (0.60) [1.0], 11.07 (0.45) [1.0]}
6	{8.42 (0.45) [1.0], 8.78 (0.53) [1.2]} {10.15 (0.50) [1.0], 11.05 (0.35) [0.7]}
7	{8.15 (0.55) [1.0], 8.55 (0.55) [0.25]} {9.81 (0.45)}
8	{7.90 (0.50) [1.0], 8.25 (0.60) [0.5]} {9.64 (0.50)} {10.85 (0.30) [1.0], 11.25 (0.40) [1.9]}

[a] Regions fit together are enclosed in braces.

bond lengths and bond angles are listed in Tables V and VI, respecitvely, using the crystallographic numbering system shown below:



pK_a Determination of Azo Compounds. Reagent-grade concentrated sulfuric acid was standardized by titration with standardized NaOH solution and diluted by weight with triply distilled water to make solutions of lesser concentration. Azo compounds (0.1 mmol) and 80 mg of $Me_3NH^+HSO_4^-$ as reference were dissolved in 10 mL of each concentration of aqueous H_2SO_4, and proton NMR spectra were obtained on the solutions. A Bunnett-Olsen[12] analysis was used, in which pK_a is the intercept of plot of log (I) + (H_0 versus H_0 + log (C_H+), where H_0 is the Hammett acidity function, C_{H^+} the concentration of H$^+$, and I is the ionization ratio, assumed to be $(\delta_n - \delta_o)/(\delta_o - \delta_{nH^+})$, where δ_n is the observed chemical shift of neutral azo compound, δ_{nH^+} that of fully protonated azo compound, the δ_o the chemical shift observed in a given solution. Percentages of sulfuric acid required for half-protonatin were found to be 47 (**9**), 42 (**4**), 29 (**10**), and 4 (**11**). **12** was too basic to use the NMR method, and it was titrated potentially in 0.1 M tetraethylammonium perchlorate using 0.01 M $HClO_4$, on an Orion 811 meter with an Orion 917002 glass electrode.

Photoelectron spectra were run on a Varian IEE-15 spectrometer, modified as previously described.[23] Peak potentials were estimated by superimposing sums of Gaussian curves of adjustable position, width, and intensity over the unsmoothed data points on the screen of an IBM-PC-XT, using locally written software by P.A.P.) based on ASYST programming. The first ionization bands of **3**, **5**, and **6**, although broad, are quite symmetrical, and the VIP values quoted for these compounds in Table II are 0.65–0.7 eV wide single Gaussian fits. For comparison, two Gaussian fits to these data are included in Table VII, along with fits for the other bands up to 11 eV for **3** and **5–8**.

Acknowledgment. We thank the National Science foundation for partial support of this work under grants CHE-84-15077 and CHE-88-10588 and the National Institutes of Health under grant GM-29549. We also thank Jocelyn C. Schultz for recording the photoelectron spectrum of **6**. We thank Timothy Clark and James Stewart for supplying the semiempirical programs employed.

Registry No. **2**, 13274-43-6; **3**, 78715-55-6; **3x**, 121574-11-6; **3y**, 121574-10-5; **4**, 72192-13-3; **4** H$^+$, 130408-52-5; **4** H$^+$BF$_4^-$, 121574-09-2; **5**, 54168-24-0; **5x**, 90046-50-7; **5y**, 90046-47-2; **6**, 54168-25-1; **6u**, 78790-57-5; **6x**, 90046-49-4; **6y**, 90046-42-7; **7**, 54168-26-2; **7x**, 121574-15-0; **7y**, 121574-13-8; **8**, 54168-19-3; **9**, 117066-41-8; **9** H$^+$, 130466-86-3; **9** H$^+$BF$_4^-$, 121652-16-2; **10**, 2721-32-6; **10** H$^+$, 90046-46-1; **10** H$^+$BF$_4^-$, 106875-41-6; **11**, 3310-62-1; **11** H$^+$, 106875-40-5; **12**, 43195-77-3; **12** H$^+$, 130408-53-6; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; 4-methylurazole, 16312-79-1.

---

(23) Nelsen, S. F.; Rumack, D. T.; Meot-Ner(Mautner), M *J. Am. Chem. Soc.* 1988, *110*, 7945.

The Structure of 7,12-Dilithio-7,12-dihydropleiadene: An Investigation by ^{13}C NMR Spectroscopy and MNDO Calculations

Brian Wind,[1a] Andrzej Sygula,[1a,b] Usha Govindarajan,[1a] Ulf Edlund,*[,1c] Ingmar Sethson,[1c] and Peter W. Rabideau*[,1a,d]

Department of Chemistry, Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana 46205, and Department of Organic Chemistry, Umea University, S-901 87 Umea, Sweden

Received April 18, 1990

MNDO calculations have been carried out on 7,12-dihydropleiadene dianion, disparkle (point positive charges), and dilithio derivatives. Calculations predict a planar geometry for the dianion in contrast to the neutral hydrocarbon where ring folding results in an angle of ϕ = 122° between the planes containing the two aromatic ring systems. The disparkle derivative, where sparkle represents a point positive charge, is also predicted to be planar with the sparkles located symmetrically over and under the central ring. The dilithio derivative, on the other hand, is predicted to be folded (ϕ = 153°) with significant pyramidalization at the anionic centers. However, when three waters of solvation are included for each lithium, the calculations predict a significantly flatter structure. The ^{13}C NMR spectrum of the dilithio derivative shows alternating upfield shifts, characteristic of highly delocalized anions, with somewhat greater shifts observed in the naphthalene moiety. A slightly nonplanar geometry with sp^2 hybridization is proposed for the dilithio species in solution, with one or both lithiums positioned more closely to the naphthalene ring. Comparison of the ^{13}C NMR data for both the dilithium and dipotassium salts suggests the presence of ion triplets.

The structure of organolithiums, as well as other organometals and carbanions, is of great importance due to the intermediacy of these species in numerous chemical reactions.[2,3] We have been interested in benzannelated,

0022-3263/91/1956-0618$02.50/0 © 1991 American Chemical Society

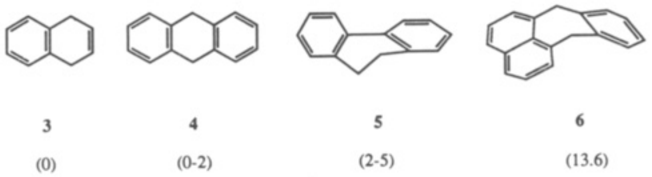
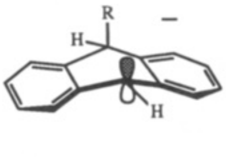


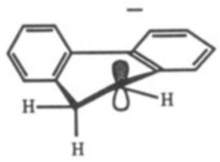
Figure 1. Dihydroaromatics and their ring-inversion barriers (kcal/mol).

carbocyclic ring systems, and especially in how the geometry of the ring changes when one or more hydrogens are replaced with lithium or sodium, affording monoanions and dianions.

9,10-Dihydroanthracene (DHA) has been regarded as a boat-shaped molecule,[4] and early stereochemical results from alkylation and protonation studies of 10-alkyl-9,10-dihydroanthracene 9-anions led to the suggestion of a similar, boat-shaped structure for the monoanion with sp^3 hybridization at the anionic center.[5] More recently, ^{13}C NMR[6] and alkylation studies[5] have suggested a relatively flat central ring for 9-lithio-9,10-dihydroanthracene and 9-alkyl-10-lithio-9,10-dihydroanthracene with sp^2 hybridization at the anionic center (i.e., **1**); a model that has been supported by semiempirical molecular orbital calculations.[7] Presumably, less flattening occurs with the deprotonation of the isomeric 9,10-dihydrophenanthrene to afford the monoanion **2**.[8]



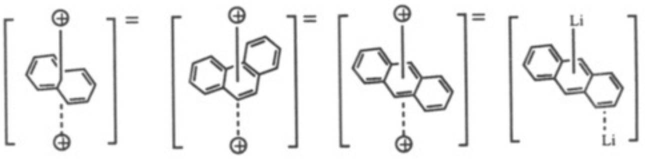
1



2

The flattening process during anion formation in these six-membered rings is more or less complete with the removal of a second proton to produce the dinegative species. Formation of these dianions can be surprisingly easy. For example, the pK_a of DHA monoanion is only 3.8 units higher than DHA itself, presumably due to ion triplet formation.[9] Indeed, MNDO calculations support ion triplets for the dianions of anthracene, naphthalene, and phenanthrene.[10] The structures are symmetrical when point positive charges are used as the counterion, but unsymmetrical arrangements are predicted for the dilithio compounds (as illustrated).

In each of the above cases, however, the dihydroaromatic compounds, which may be regarded as precursors to the dianions, (i.e., **3**, **4**, and **5**) have ring inversion barriers that are too low to be measured experimentally[4] (see Figure 1), and consequently, resistance to the formation of planar dianions due to ring strain is expected to be minimal. For this reason, we were interested in investigating the structure of a dianion generated from a carbocyclic ring system where planarity would be more difficult. 7,12-Dihydropleiadene (**6**) provides such a case since greater energy is required to convert its seven-membered, central ring to the planar form as compared to the six-membered rings. This is supported by the observed barrier of $\Delta G^‡ = 13.6$ kcal/mol for the interconversion of boat structures in **6**.[11a] Hence **6** is expected to be an excellent model for an evaluation of the balance between electronic effects (overlap of aromatic rings) and strain energy involved in dianion formation. What follows is a study of the dianion structure of **6** and its dilithium salt by both MNDO calculations and ^{13}C NMR spectroscopy.



MNDO. For this discussion, we will describe compound geometries in terms of two angles which are calculated using vector analysis of the computationally derived atomic coordinates. Ring folding is defined as ϕ, the angle between the bisecting planes which contain the naphthalene and the benzene rings, respectively. The other angle, θ, represents the degree of planarity at the anionic centers, C-7 and C-12. That is, the deviation from the sp^2 plane; the angle between the plane defined by carbon atoms C-6a, C-7, and C-7a, and the bond between C-7 and its attached hydrogen. Hence, **6** dianion with a planar central ring and a trigonal, coplanar anionic center (i.e., sp^2) would have $\phi = 180°$ and $\theta = 0°$.

7,12-Dihydropleiadene. A calculated energy profile for the parent hydrocarbon, **6**, is given in Figure 2a. It shows a minimum energy at $\phi = 122°$ with 15.9 kcal/mol required for conversion to the planar form. However, this energy profile represents a symmetry-constrained folding process, and the actual interconversion of boat conformations need not necessarily occur through a planar transition state. However, the use of a saddle calculation (see the Experimental Section) also provided a nearly planar transition state, albeit with a slightly lower inversion barrier (15.7 kcal/mol). In any event, the calculated barrier is only slightly higher than the experimental value of 13.6 kcalmol measured by dynamic NMR.[11] The calculated angle of 104.2° between the methylene hydrogens is also quite reasonable in view of the slight compression expected due to the larger C–C–C angle in the seven-membered ring.

Dianion. Figure 2b shows a similar analysis for the 7,12-dihydropleiadene dianion (6^{2-}). There is a very shallow minimum at $\phi = 180°$ with only 1.8 kcal/mol required for a 25° change in either direction. Hence calcu-

---

(1) (a) Indianapolis. (b) Permanent address, Department of Chemistry, Jagiellonian University, Krakow, Poland. (c) Umea. (d) Correspondence to this author should be addressed to the Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803.

(2) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979.

(3) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983, Vols. 2 and 3.

(4) *The Conformational Analysis of Cyclohexenes, Cyclohexadienes and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH: New York, 1989; Chapter 4.

(5) Mooney, J. L.; Marcinow, Z.; Rabideau, P. W. *J. Org. Chem.* **1986**, *51*, 527. See references therein for earlier studies suggesting sp^3 hybridization.

(6) Rabideau, P. W.; Wetzel, D. M.; Husted, C. A.; Lawrence, J. R. *Tetrahedron Lett.* **1984**, *25*, 31.

(7) Sygula, A.; Rabideau, P. W. *J. Org. Chem.* **1987**, *52*, 3521.

(8) Rabideau, P. W.; Harvey, R. G. *J. Org. Chem.* **1970**, *35*, 25.

(9) Streitweiser, A. *Acc. Chem. Res.* **1984**, *17*, 353.

(10) Sygula, A.; Lipkowitz, K.; Rabideau, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 6602.

(11) (a) Lansbury, P. T.; Bieron, J. F.; Klein, W. *J. Am. Chem. Soc.* **1966**, *88*, 1477. (b) Further investigations into the calculated energy barrier for ring inversion in **6** are in progress.

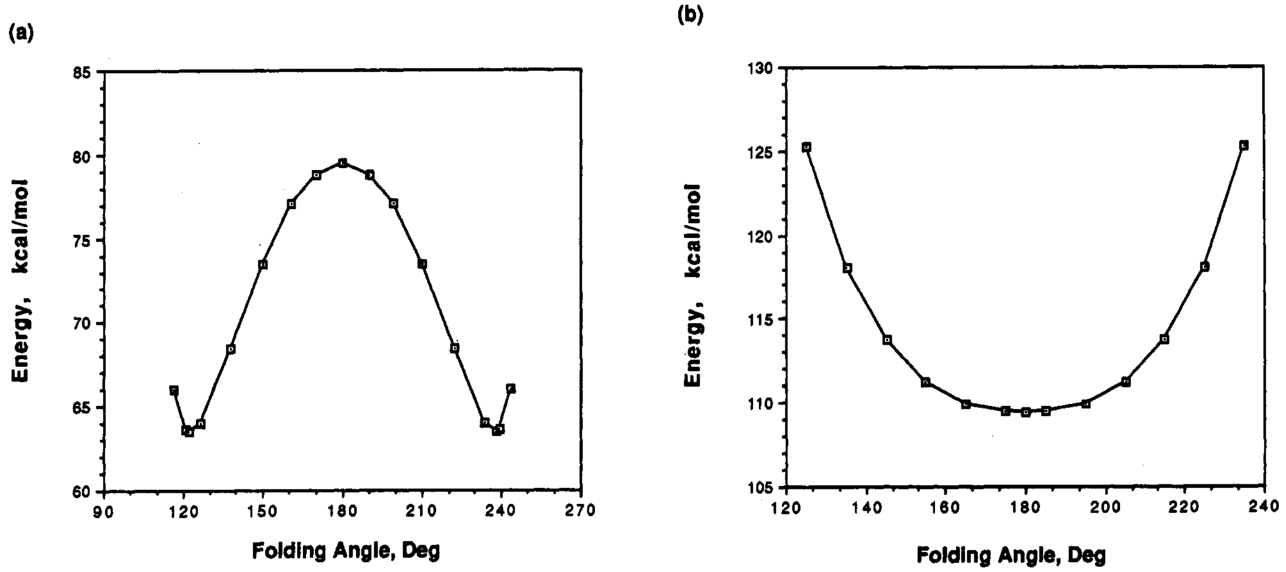
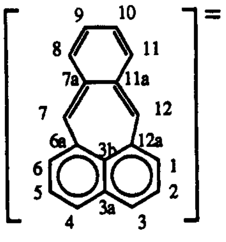


Figure 2. MNDO calculated folding angles for (a) 7,12-dihydropleiadene and (b) its dianion.

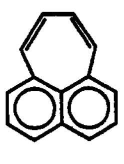
Table I. MNDO Calculations for Neutrals, Dianions, and Dilithio Derivatives

		geometries, deg					
		initial	final		ΔH_f,	bond lengths, Å	
compd	counterion	ϕ	ϕ	θ	kcal/mol	C_{6a}-C_7	C_7-H
6	-	180	122.1	52.1	63.5	1.5205	1.1160
6^{2-}	none	180	180.0	0	110.2	1.4065	1.0990
6^{2-}	sparkle	180	180.0	0	-112.2	1.4084	1.1000
7	-	180	176.8	0.6	103.8	1.4662	1.1022
8	Li	180	173.1	10.0	40.3	1.4905	1.1042
8	Li	150	153.1	26.6	33.9	1.4867	1.1037
8	Li	130	131.4	37.4	34.8	1.4797	1.1048
8	Li[a]	180	180.0[b]	0.0[b]	-374.7	1.4082	1.1001
8	Li[a]	180	172.9	2.0	-375.1	1.4456	1.1046
8	Li[a]	153	164.0	7.2	-375.3	1.4510	1.1046
9	Li	180	155.6	20.0	36.7	1.4233	1.1033
9	Li	150	137.9	25.0	35.2	1.4348	1.1023
9	Li	130	139.8	29.2	34.7	1.4330	1.1048

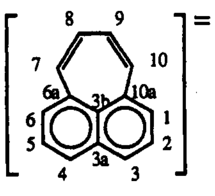
lations predict a planar dianion, but it appears that very little perturbation would be necessary to cause some degree of folding in the central seven-membered ring.



$6^=$



7

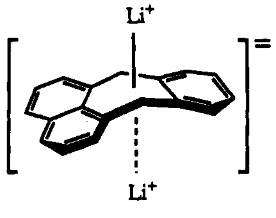


$7^=$

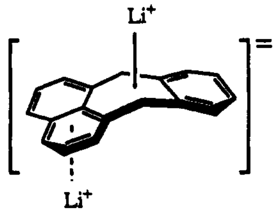
Examination of the carbanionic centers of the fully optimized, planar geometry shows $\theta = 0°$, indicating sp^2 hybridization at these carbons. As would be expected, both the C-7/C-6a (1.4065 Å) and the C-7/H-7 bond lengths (1.0990 Å) are shorter in the dianion than in 6 itself (1.5205 and 1.1160 Å, respectively) and are closer to the values for the related unsaturated hydrocarbon 7 (1.4662 and 1.1022 Å respectively).

Iron-Pairing Effects. It must be realized, of course, that these calculations apply to the gas phase and may not reflect the preferred geometries in solution that are subject to such effects as ion pairing and solvation. To learn something about the effect of counterions, calculations were carried out with the inclusion of two lithium cations. Schleyer and Setzer[12] have pointed out that this type of calculation, which excludes solvent molecules, provides an approximation of the solid-state structures. Taken together with the calculations above, this allows definition of the two limiting structures: the gas-phase dianion without counterion interaction and the organometal with strongly interacting lithium cations.

Although several dilithiated structures were studied with varying folding angles and lithium positions, only two lithium configurations were found to have significantly lower energies. The first, 8, has both lithium atoms trans to one another over and under the central ring, while the second, 9, has one lithium over the central ring, and the other lithium under the naphthalene moiety. Calculations



8



9

were performed on both of these lithium arrangements

---

[12] Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

Table II. Carbon-13 Chemical Shifts for 7,12-Dihydropleiadene (6), Cyclohepta[*de*]naphthalene (7), and Their Dianions

compound	solvent	cation	C1	C2	C3	C7	C8	C9	C3a	C3b	C6a	C7a
6	THF[a]		126.6	125.3	127.8	43.0	127.3	126.2	130.9	135.2	139.5	135.6
6^{2-}	THF[a]	2 Li^+	112.7	125.5	107.3	76.2	116.4	114.1	136.9	117.2	149.7	142.2
6^{2-}	THF[b]	2 Li^+	112.5	125.6	106.9	77.3	116.6	114.2	136.8	117.3	150.1	142.7
6^{2-}	MTHF[a]	2 Li^+	114.4	126.1	110.5	72.3	117.1	115.4	137.1	116.5	147.7	139.6
6^{2-}	THF/DMPU[b,c]	2 Li^+	113.0	126.6	106.6	77.4	116.7	114.3	137.2	118.7	151.4	143.8
6^{2-}	THF[b]	2K^+	112.5	125.3	106.1	83.6	118.1	113.9	135.8	106.8	143.0	137.2
($\Delta\delta$, $6^{2-}/6$)	(THF[a])	(2 Li^+)	(−13.9)	(0.2)	(−20.5)	(−62.1[d])	(−10.9)	(−12.1)	(+6.0)	(−18.0)	(+10.2)	(+6.6)
7	THF[a]		128.8	127.1	128.9	140.0	127.7		139.2	140.2	140.3	
7^{2-}	THF[b]	2 Li^+	114.9	122.9	102.4	71.1	107.9		132.0	106.0	145.0	
7^{2-}	THF[b]	2 K^+	113.2	121.8	104.9	79.5	107.2		131.7	96.2	140.7	
($\Delta\delta$, $7^{2-}/7$)	(THF[a])	(2 Li)	(−13.9)	(−4.2)	(−26.5)	(−68.9)	(−19.8)		(−7.2)	(−34.2)	(+4.7)	

[a] Run at ambient temperature. [b] Run at −30 °C. [c] THF:DMPU = 2:1. DMPU = *N,N'*-dimethylpropyleneurea. [d] Calculated value: see text.

starting with three different folding angles (180°, 150°, and 130°), and the results appear in Table I. Interestingly, none of the lithium arrangements result in planar forms as the most stable conformation, but rather adopt boat conformations. However, all minima found are considerably flatter than neutral **6**.

The global minimum has the lithiums located over and under the central ring which has a folding angle of 153°. The angle θ for the C-7 and C-12 hydrogens is 26.6°, indicating increased sp^3 character as compared to the planar dianion calculation. As expected, the bond lengths C-7/C-6a and C-7/H-7 (1.4867 and 1.1307 Å, respectively) are also longer than observed with the dianion. Thus the dilithiated structure, in contrast to the dianion, is folded with hybridization between sp^2 and sp^3. However, it is well known that MNDO tends to overestimate carbon–lithium interactions,[13] especially in the absence of solvation. Calculations were carried out beginning with both planar (180°) and folded (153°) dilithium structures with the addition of three waters of solvation for each lithium. The planar structure folded to an angle of 173°, whereas the folded structure flattened to 164°. Although the latter structure was found to be slightly more stable by ca. 0.15 kcal/mol, it is evident that the MNDo potential surface is quite flat in the region of 164° to 173°. Moreover, the otherwise optimimized structure with a constraint holding the aromatic rings coplanar (180°) is only 0.6 kcal/mol less stable than the global minimum at 164°.

It has been suggested previously that the use of a "sparkle" (a +1 positive charge with an effective radius of 0.7 Å[13]) as a counterion may better approximate solvated ion pairs in solution.[10] We carried out sparkle calculations beginning with the two cation locations found above for lithium, and with folding angles of 180° and 150°; full geometry optimization was employed throughout. All four cases resulted in a planar dianion with the sparkles being located symmetrically above and below the seven-membered ring.

^{13}C NMR. ^{13}C NMR has proven to be a useful experimental technique for the study of ion pairing and charge distribution since for a series of closely related structures it can be shown that carbon shifts are linearly correlated to charge density on carbon.[14,15] However, such correlations must be treated with great care. Generally, the electron angular momentum term is the major contribution to the shielding through the paramagnetic term in the Ramsey equation.[15c] Therefore bonding variation must be considered before any shift–charge correlation is attempted. But if the angular momentum terms are roughly constant, as for a series of cyclic or polycyclic systems, then the $\langle r^{-3} \rangle_{pA}$ (i.e. the radius of the p orbitals) becomes dominating and the shift will consequently reflect charge provided that the average one-electron excitation term (ΔE) is large or constant.[15c] An increase in the electron density at a carbon will result in increased shielding (upfield chemical shift), and consequently, reduction of a parent hydrocarbon to an anion will result in an overall average upfield shift.

Early NMR studies of monocyclic, planar aromatics have shown the shift-charge correlation to be governed by a proportionality constant of approximately 160 ppm per electron (ppm/e).[14a] More recent studies have demonstrated that this value can be extended to acyclic carbon π-systems with good results,[14b,c] all in accordance with the expectations from systems having a large HOMO–LUMO gap (ΔE). However, in systems sustaining a paramagnetic ring current, this proportionality constant (K_C) has been shown to be quite variable and related to ^{1}H ring current anisotropy.[16] The most paratropic anions show K_C values close to zero since the "anisotropy" on carbon is counteracting the charge effect. Similar observations have been made in planar conjugated heteroatom systems.[16c] Field effects on carbon are also of significance, but not as important as the factors mentioned above.[14c]

To derive experimental charge densities from ^{13}C NMR chemical shifts, the shifts of the neutral precursor are subtracted from those of the charged compound.[14c,17] If the "tropicity" of the two systems vary significantly, a correction of the induced carbon shifts must be made as reported earlier.[16a] The shift differences can then be attributed to changes in electron density upon going to charged species. Care must be taken to ensure that the hybridization of each carbon in both the neutral and charged species are the same since changes in bond order greatly affect the shielding.

The ^{13}C NMR chemical shifts for **6** and its dilithio and dipotassium derivatives, together with similar data[18] for the related hydrocarbon **7**, are presented in Table II. For all cases but one, the carbon chemical shifts in neutral **6**

---

[13] (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. (b) Glaser, R.; Streitwieser, A. *J. Mol. Struct.* **1988**, *163*, 19. (c) Glaser, R.; Streitwieser, A. *J. Org. Chem.* **1989**, *54*, 5491.

[14] (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. (b) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (c) Fraenkel, G.; Hallden-Abberton, M. *Tetrahedron* **1982**, *38*, 71. (d) Review; Young, R. N. *Prog. NMR Spectr.* **1978**, *12*, 261. (e) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

[15] (a) Fliszar, S.; Cardinal, G.; Beraldin, M. *J. Am. Chem. Soc.* **1982**, *104*, 5287. (b) Fliszar, S. *Can. J. Chem.* **1976**, *54*, 2839. (c) Grutzner, J. B. In *Recent Advances in Organic NMR Spectroscopy*; Lambert, J. B., Rittner, R., Eds.; Norell Press: Landisville, NJ, 1987; p 17.

[16] (a) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937. (b) Eliasson, B.; Edlund, U. *Ibid* **1983**, 1837. (c) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **1988**, 31.

[17] Lambert, J. B.; Wharry, S. M. *J. Am. Chem. Soc.* **1982**, *104*, 5857.

[18] (a) Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 204. (b) Becker, B. C.; Huber, W.; Schnieders, C.; Müllen, K. *Chem. Ber.* **1983**, *116*, 1573. (c) Neumann, G. Dissertation, University of Cologne, 1985.

Table III. Proton Chemical Shifts for 7,12-Dihydropleiadene (6), Cyclohepta[*de*]naphthalene (7), and Their Dianions

compd	solvent	cation	H1	H2	H3	H7	H8	H9
6	THF[a]		7.2	7.2	7.6	4.2	7.2	7.1
6^{2-}	THF[a]	2 Li^+	5.8	6.4	5.8	3.6	5.5	5.5
6^{2-}	MTHF[a]	2 Li^+	6.1	6.6	6.1	3.9	5.8	5.7
6^{2-}	THF/DMPU[b,c]	2 Li^+	5.6	6.3	5.7	3.7	5.4	5.4
6^{2-}	THF[b]	2 K^+	5.7	6.5	5.7	3.8	5.3	5.2
7	THF[a]		6.6	6.9	7.2	6.0	5.3	
7^{2-}	THF[b]	2 Li^+	6.0	6.6	6.0	3.1	4.0	

[a] Run at ambient temperature. [b] Run at −30 °C. [c] THF:DMPU = 2:1. DMPU = *N,N'*-dimethylpropyleneurea.

were used as a reference to assess charge buildup in the dialkali salts. Since C-7 and C-12 experience a change in hybridization, a rough estimate can be obtained in the following manner: A base value of 140.0 was selected, corresponding to the chemical shift of C-7 in 7. A correction was then made for the absence of the additional benzene ring in 7, as compared to 6, by subtracing 1.7 ppm, the difference in chemical shift between C-9 in anthracene and C-1 in naphthalene. This provided a reference value of 138.3 ppm used as a "neutral but sp^2 hybridized" value for C-7/C-12.

When the sum of the chemical shift differences is divided by the charge introduced into each of the systems, an approximate K_C value of 109 ppm/e is obtained for 6[20] while the corresponding value for 7^{2-} is 149.3. Both values are somewhat low, and this is an indication that at least one (6^{2-}) of these $4n\pi$ systems (20 and 16 π electrons, respectively) have subcircuits that to some minor extent give a paramagnetic ring current contribution. The average carbon shifts of the dianions can also be estimated using a relationship introduced by O'Brien[14b] and applied to the cyclohexadienyl system by Fraenkel[14c]

$$\delta_{av} = -156.8\rho_{av} + 289.9$$

where ρ_{av} is the average π-electron density on carbon. This equation affords a calculated value of 115.7 ppm for 6^{2-} (experimental value 119.0) while the corresponding value for 7^{2-} is 110.7 (experimental value 111.9). The experimental values are both downfield from those calculated and support the K_c observations. The existence of a small but significant paramagnetic ring current contribution in 6^{2-} is also supported by the proton shift data that all are slightly upfield relative to 7^{2-} although the charge on the carbons of 6^{2-} are lower (see Table III). It should also be noted that the proton shifts are generally shifted upfield as the cation solvation increases or as the size of the cation gets larger.[19] In a given system, an increased tendency for "loose" ion pairing will increase the paratropicity of the system. To summarize, according to the induced carbon and proton chemical shifts, 6^{2-} can be classified as a weakly paratropic system while 7^{2-}, in the present ion pair state, is atropic or less diatropic than its neutral precursor.

The charge distribution in π conjugated systems of these types are expected to show nonuniform alternating patterns.[20] With 6^{2-}, the positions of highest charge are expected to be carbons 1(6), 3(4), 3b, 7(12), 8(11), and 9(10). This pattern is nicely followed by the charge-induced differentials, including the α-carbons 7(12), if corrected for the hybridization effect as mentioned. A value of −62.1 ppm is obtained after this correction, which compares well with the value of −68.9 for the same positions in 7^{2-}. This resemblance between the carbon induced shifts in 6^{2-} and 7^{2-} are quite general, the only significant difference seems to be that the central carbon in 6^{2-} is less charged than in 7^{2-}.

Conclusions about hybridization and the extent of delocalization based on α-carbon chemical shifts are complicated by the fact that these positions are the most affected by the field of the cations and changes in ion pairing due to temperature and solvent effects.[14b,21] However, these effects are generally small compared to the major shift changes produced by rehybridization at these carbons upon going from sp^3 to sp^2. Browne et al.[22] have done an analysis of these effects and have suggested that systems with a high degree of sp^2 hybridization may show shift changes (uncorrected for hybridization change) at the α-carbon that vary from a low of +21.8 ppm to a high of +45.7 ppm. The value for dilithio-6 of +33.2 ppm (uncorrected) is well within this range, and, perhaps more significantly, compares quite favorably with the value of +34.4 ppm (uncorrected) for the somewhat structurally similar diphenylmethyl lithium.[22]

The para carbon chemical shifts have been taken as the most reliable indicator of charge delocalization since they experience the greatest shift change, and they are the least affected by direct effects from the cation.[21-23] Browne et al.[22] have suggested a range of −10 to −25 ppm for para carbon shifts, where −25 ppm represents maximum charge delocalization from an sp^2 hybridized anionic center. Furthermore, they claim that values less than −10 ppm should be attributed to purely inductive effects. This latter value is in reasonable agreement with the induced para carbon shift observed in phenyl-substituted group 4 element anions.[24] These pyramidal anions, where charge delocalization could safely be excluded, showed, depending on the degree of phenyl substitution, induced para carbon shifts in the range of −6 to −10 ppm relative to their neutral counterparts. In any event, the vaue of −20.5 ppm for the "para" carbon (C-3) in the naphthalene ring of dilithio-6 suggests considerable delocalization.

The upfield shift of the benzene C8–C11 carbons corresponds to a delocalization of approximately $^1/_3$ of an electron. A comparison with 7^{2-} reveals that the redistribution of charge caused by the annelation of a benzene ring mostly affects the nonproton-bearing positions in the naphthalene subunit; that is, C3a (+13.2 ppm) and C3b (+16.2) are both deshielded by adding a benzene ring. A change in cation solvation going from tetrahydrofuran (THF)/1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidi-

---

(19) Müllen, K. *Chem. Rev.* **1984**, *84*, 603.

(20) (a) Rabinovitz, M.; Cohen, Y. *Tetrahedron* **1988**, *44*, 6957. (b) Klein, J. *Tetrahedron* **1983**, *39*, 2733. (c) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **1988**, *110*, 4634.

(21) (a) Waack, R.; Doran, M. A.; Baker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 1272. (b) O'Brien, D. H.; Russel, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7427. (c) Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709. (d) Hoell, D.; Lex, J.; Müllen, K. *J. Am. Chem. Soc.* **1986**, *108*, 5983. (e) Bank, S.; Schepartz, A.; Giammatteo, P.; Zubieta, J. *J. Org. Chem.* **1983**, *48*, 3458. (f) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (g) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661.

(22) Browne, S. E.; Asher, S. E.; Corneall, E. H.; Frisoli, J. K.; Harris, L. J.; Salot, E. A.; Sauter, E. A.; Trecoske, M. A.; Veale, P. S., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1432.

(23) See also ref 6.

(24) Buncel, E.; Venkatachalam, T. K.; Eliasson, B.; Edlund, U. *J. Am. Chem. Soc.* **1985**, *107*, 303.

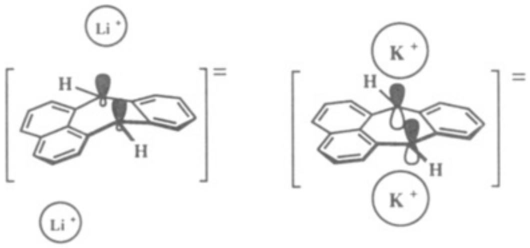


Figure 3. Ion triplets for dilithium and dipotassium 6^{2-}.

none (DMPU) to THF and finally to the less solvating 2-methyltetrahydrofuran (MTHF) causes a deshielding of the most charged protonated aromatic carbons as expected. The magnitude of this deshielding is equal to or larger than that observed in the planar indenyl anion system upon a similar solvent change.[25] A slightly larger effect is seen in the naphthalene subunit, and, together with the observed charge-induced shift upon reduction, this supports a situation where more charge is delocalized into the naphthenyl system than into the benzene ring.

The comparison between the shift data obtained for 6^{2-} in THF/DMPU, a solvent system known to favor solvent-separated ion pairs, and those obtained in THF using potassium as counterions is quite surprising. The deshielding of C7/12 and the shielding of the "para" carbons are most significant for the dipotassium salt, even through it must be classified as a contact ion pair. Hence, the anion appears to be more delocalized as a potassium salt. Similar observations have been made for 7^{2-} where increased solvation of the potassium salt (dimethoxyethane), or going to even larger cations (Cs^+), does not increase the delocalization of charge.[18c] In fact, the "para" positions are slightly deshielded by such a change. These findings are in sharp contrast to observations of other planar conjugated anions that have similar charge per carbon.[25] The shift data for the potassium salts of 6^{2-} and 7^{2-} show strong similarities with the shieldings of the central carbons being especially unexpected. We note that the one-bond ^1J (C_7-H) coupling of 6^{2-} increases from 138 Hz (Li/THF) to 143 Hz (K/THF), consistent with increased sp^2 hybridization.[26] It should also be mentioned that the size of the observed couplings is typical for charged sp^2 carbons (which are smaller than neutral counterparts), and close to the Cα-H ($\delta = 78.5$, $^1J = 142$ Hz) coupling observed for the lithium salt of diphenylmethane.[21a]

An attractive explanation is the presence of ion triplets.[9] With the solvent-separated dilithium salt, the seven-membered ring is slightly puckered with lessened sp^2 hybridization, and one, or both, of the lithiums is oriented closer to the naphthalene moiety. In going to the contact ion pair with the dipotassium salt, the counterions are held more tightly, and more symmetrically, forcing a flattening of the seven-membered ring and full sp^2 hybridization. This is shown pictorially in Figure 3.

Conclusions

The conclusions that may be drawn safely about the structure of dilithio-**6** are (1) considerable sp^2 hybridization exists at carbons 7 and 12, and (2) more charge is delocalized into the naphthalene ring than into the benzene ring. The question about planarity is a more difficult one. Although it is evident from the NMR data that the system is planar or almost planar, a slightly bent structure is quite likely for the dilithio derivatives, since, according to the observed shift and Cα-H one-bond coupling changes, the dipotassium derivative is the most delocalized and therefore the most planar structure. A slightly folded structure for the dilithium salt is also consistent with the calculations of the solvated structure.

Of course, none of the experiments or calculations herein address the possibility of aggregation, and this question remains unanswered. However, it has been suggested that with delocalized, benzylic carbanion ion pairs, the electrostatic stabilization provided by aggregate formation is insufficient to overcome the unfavorable entropy of association.[27]

Experimental Section

Calculations. The MNDO method was employed together with Thiel's lithium parameters[28a] using MNDOC[28a] and MOPAC (version 3.10).[28b] The saddle calculation of the inversion barrier of 7,12-dihydropleiadene, according to the method of Dewar, Healy, and Stewart,[29] was carried out with MOPAC.

NMR Measurements. Ether solutions of **6** in NMR tubes were initially degassed and subsequently disconnected from the vacuum line in an argon atmosphere. Typically, 2–4 equiv o concentrated *n*-BuLi (8–10 M) were added to the cooled samples, and, in one case, DMPU was also added at this stage. The NMR tubes were again evacuated and then sealed off from the vacuum line. The potassium salts were prepared using Lochmann-Schlosser reagent (*n*-BuLi/*t*-BuOK).[30] Assignment of the C-13 signals were obtained through selective decoupling, DEPT-90 or when necessary through 2D CH heteronuclear experiments. All measurements were obtained on Bruker AC-P 250 or AM-500 NMR instruments. The chemical shifts were measured relative to internal cyclohexane and then adapted to the TMS scale using δ (cyclohexane) = 27.70 ppm. The measurements refer to room temperature experiments if not stated otherwise.

Acknowledgment. Support from the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy to P.W.R. and from the Swedish Natural Science Research Council to Ulf Edlund are gratefully acknowledged. We are also indebted to Professor Klaus Müllen, Mainz, for valuable discussions.

---

[25] (a) Lejon, T.; Edlund, U. *Acta Chem. Scand.* **1989**, *43*, 275. (b) Eliasson, B.; Lejon, T.; Edlund, U.; Mueller, R. L.; Staley, S. W. *J. Phys. Org. Chem.*, in press.

[26] (a) McKeever, D.; Waack, R. *J. Organomet. Chem.* **1971**, *28*, 145. (b) Hogen-Esch, T. E.; Jenkins, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 3666.

[27] Kaufman, M. J.; Gronert, S.; Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 602. See also: Murdoch, J. R.; Bryson, D. F.; McMillen, D. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 600.

[28] (a) Thiel, W. *QCPE* **1983**, *15*, 438. (b) Stewart, J. P. *QCPE Bull.* **1983**, *3*, 455.

[29] Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 227.

[30] Boche, G.; Etzrodt, H. *Tetrahedron Lett.* **1983**, *24*, 5477.