Ab Initio Analysis of Pentadienyllithium, Pentadienylsodium, and the Pentadienyl Ions

Lawrence M. Pratt[†] and Andrew Streitwieser*

Department of Chemistry, University of California, Berkeley, California 94720-1460

Ab initio calculations were used to determine the equilibrium geometries and rotational barriers of the pentadienyl cation, anion, and metalated pentadienes. Pentadienyllithium and pentadienylsodium are most stable in a U-shaped structure. This geometry is a higher energy local minimum for the pentadienyl anion and is not a stationary point for the pentadienyl cation. The atomic and group charges were analyzed by natural population analysis and were determined for each of the conformations studied.

Introduction

Molecules containing conjugated double bonds have been the subject of much research over the past century. Numerous studies have been undertaken to determine the origin of the increased stability of conjugated molecules and ions, such as benzene, its heterocyclic analogues, and the allylic ions. Various schemes have been proposed to separate the contributions from the σ and π orbitals, and the relative contributions of each is a topic of continuing debate.[1–6] Other studies have investigated the structure and bonding in allylic systems containing heteroatoms.[7–13] It was found that heteroallylic cations containing electropositive elements behave as conjugated systems, but little conjugation was observed in the corresponding anions. Lithioimines and related molecules were found to have the lithium atom coordinated to all three atoms of the π system,[14] whereas lithium enolates show less coordination of the lithium atom to the vinyl carbons.[11] Much less work has been done on simple conjugated systems larger than allyl. An extensive debate on the extent of conjugation in carboxylate ions[15–20] has

been extended to related vinylogous ions.[21,22] A careful theoretical study has been made of the pentadienyl radical.[23] In this paper the structures, bonding, and charge distributions are reported for various conformations of pentadienyllithium, pentadienylsodium, and the pentadienyl ions. Three conformations of pentadienyllithium and pentadienylpotassium have been published previously at a low level of theory (STO-3G).[24]

Computational Methods

All ab initio calculations were performed using either the Gaussian 94[25] or Spartan 4.1[26] programs on an IBM RS6000 workstation. Semiempirical PM3 calculations were performed with Spartan, except for the molecules containing sodium, which has no PM3 parameters. The optimized semiempirical geometries were used as the initial geometries for the ab initio calculations. Ab initio geometry optimizations were performed at the Hartree–Fock level using the 3-21G and 6-311+G* basis sets and at the MP2 level with the larger basis set. Density functional (DFT)[27] geometry optimizations were also performed with the 6-311+G* basis set, using the Becke three-parameter hybrid method (B3LYP).[28,29] The pentadienylsodium calculations were performed only at the Hartree–Fock level because the number of basis functions made post-Hartree–Fock opti-

[†] Department of Chemistry, Fisk University, Nashville, TN 37208.
(1) Glendening, E. D.; Faust, R.; Streitwieser, A.; Vollhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952–7.
(2) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275–86.
(3) Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61–72.
(4) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc* **1989**, *111*, 4178.
(5) Jug, K.; Koster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.
(6) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344–51.
(7) Pratt, L. M.; Hogen-Esch, T. E.; Khan, I. M. *Tetrahedron* **1995**, *51*, 5955.
(8) Pratt, L. M.; Khan, I. M.; Hogen-Esch, T. E. *Macromol. Chem. Phys.* **1996**, *197*, 3555.
(9) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9287–93.
(10) Gobbi, A.; Yamaguchi, Y.; Frenking, G. *Chem. Phys. Lett.* **1995**, *244*, 27–31.
(11) Abbotto, A.; Streitwieser, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 11255–68.
(12) Glaser, R.; Streitwieser, A. *Pure Appl. Chem.* **1988**, *60*, 195–204.
(13) Glaser, R.; Streitwieser, A. *J. Am. Chem. Soc.* **1989**, *111*, 7340–8.
(14) Glaser, R.; Streitwieser, A. *J. Org. Chem.* **1991**, *56*, 6612–24.
(15) Siggel, M. R. F.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360.
(16) Siggel, M. R. F.; Streitwieser, A.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022–8.
(17) Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A. *J. Mol. Struct., Theochem* **1988**, *165*, 309–318.

(18) Thomas, T. D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1945–8.
(19) Exner, O. *J. Org. Chem.* **1988**, *53*, 1810.
(20) Hibert, P. C.; Byrman, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 9875.
(21) Wiberg, K. B.; Ochterski, J.; Streitwieser *J. Am. Chem. Soc.* **1996**, *118*, 8291–9.
(22) Dewar, M. J. S.; Krull, K. L. *J. Chem. Soc., Chem. Commun.* **1990**, 333–4.
(23) Fort, R. C., Jr.; Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **1993**, *58*, 211–6.
(24) Yasuda, H.; Tatsumi, K.; Nakamura, A. *New Aspects of Carbanion Chemistry. Structure of Pentadienyl Anions and Butenediyl Dianions and their Roles in Organic and Inorganic Syntheses*; Elsevier Science Publishing Co., Inc.: New York, 1987; pp 59–71.
(25) *GAUSSIAN 94, Revision C3*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, N. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.
(26) *Spartan, version 4.1*; Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715.
(27) *Modern Density Functional Theory. A Tool for Chemistry Theoretical and Computational Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: New York, 1995; Vol. 2.
(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
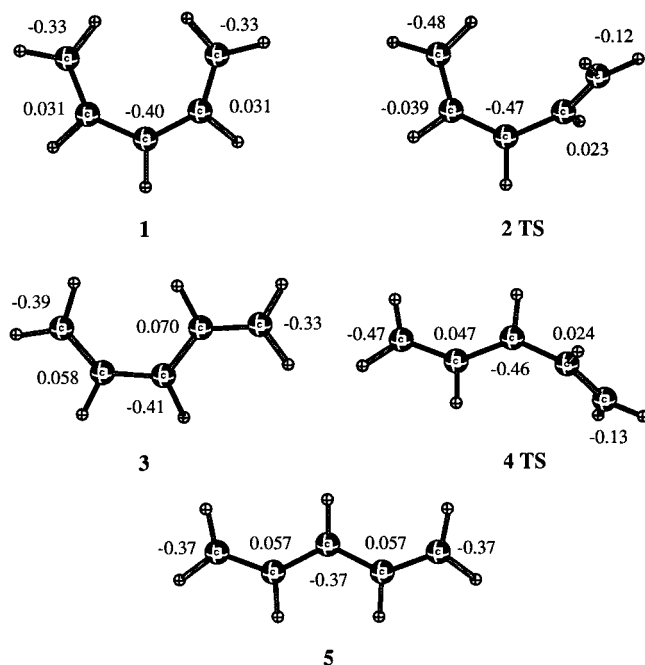(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

Figure 1. NPA charge distributions of pentadienyl anions (HF/6-311+G*).

Table 1. Relative Energies of Pentadienyl Anion Conformations (kcal/mol)

method	1	2 (TS)	3	4 (TS)	5
PM3	3.4	14.8	1.0	13.7	0
HF/3-21G	5.0	20.6	3.6	20.7	0
HF/6-311+G*	2.5	17.5	2.1	18.9	0
B3LYP/6-311+G*	2.9	20.0	2.2	20.8	0
MP2/6-311+G*	1.2	16.2	2.1	18.2	0

mizations prohibitively large. Atomic charges for each of the molecules were calculated at the Hartree−Fock level with the 6-311+G* basis set using the natural population analysis (NPA)[30] method. "Atomic charges" are not physical observables, and there are accordingly many definitions of such charges. In our experience, the NPA generally correspond with chemical expectations and are used in this paper; however, we do not expect the principal conclusions to be changed importantly with other definitions of charge distribution. The computed structures and energies are summarized in the Supplemental Information with the exception of the 3-21G data.

Results and Discussion

The optimized geometries of the pentadienyl anion are shown in Figure 1. Rotation about the two middle carbon−carbon bonds generated three local minima and two transition structures. The relative energies are given in Table 1. The most stable conformation is a W-shaped structure (**5**). The sickle-shaped conformation (**3**) is less stable by about 2.1 kcal/mol. The highest energy local minimum is the U-shaped structure (**1**), which was calculated to be 2.5 kcal/mol higher in energy than the W conformation at the Hartree−Fock level. At the MP2 level of theory, the U-shaped structure was calculated to be more stable than the sickle conformation.

Conformations **2** and **4** correspond to transition structures, in which the pendant vinyl group is nearly perpendicular to the plane of the allylic system. The

rotational barriers of 15−20 kcal/mol demonstrate the importance of conjugation in the pentadienyl anion. These values are slightly lower than the rotational barrier of 23.1 kcal/mol reported by Gobbi and Frenking for the allyl anion.[2]

The C−C bond distances are comparable in all three of the 6-311+G* computations with agreement generally within 0.02 Å. For the fully conjugated conformations **1**, **3**, and **5** the terminal bonds are shorter than the internal bonds, 1.36−1.38 Å vs 1.41−1.42 Å. For the transition structures **2** and **4** the allyl moieties have bond lengths of 1.39−1.41 Å, and the pendent vinyl groups, twisted by dihedral angles of greater than 80°, have a double bond of length 1.32−1.35 Å separated from the allyl group by a bond of 1.47−1.49 Å.

Figure 1 shows the calculated atomic charges by the NPA method, with all of the hydrogen charges summed into the attached heavy atoms (regional charges). In each of the conjugated structures (**1**, **3**, and **5**), the methylene and methine group charges alternate from negative to slightly positive. Thus, the negative charge is concentrated on alternating atoms, which is consistent with the symmetry of the HOMO. A different charge distribution is seen in the transition structures **2** and **4**. Although the pendant vinyl group is formally neutral, the close proximity to the electropositive allylic anion is seen to induce charge polarization in the vinyl group, as shown by the substantial negative charge on the terminal carbon.

The optimized geometries of pentadienyllithium are shown in Figure 2. In each structure, the lithium atom is coordinated to three or more carbons, analogous to the known structure of allyllithium.[31−33] In addition to the U- (**6**), sickle- (**10**), and W-shaped (**12**) structures found for the pentadienyl anion, pentadienyllithium also has a distorted sicklelike structure in which the lithium atom is coordinated to four carbons (**8**). The relative energies of the pentadienyllithium conformations are shown in Table 2.

In contrast to the free anion, the most stable pentadienyllithium conformation is the U-shaped structure, which maximizes the electrostatic attraction between the cation and the anionic carbons. A similar structure has been described for cyclopentadienyllithium, in which the ring−lithium bonding is undoubtedly primarily ionic.[34] This interaction more than compensates for the steric strain between the hydrogens at the ends of the molecule. The energies of the local minima (structures **6**, **8**, **10**, and **12**) are lower than those of the transition structures (structures **7**, **9**, and **11**) by about 10−20 kcal/mol, indicating that, as in the free anion, conjugation is important in the pentadienyllithium molecule. A comparison of conformers **6** and **8** shows that when the coordination number of lithium is reduced from five to four, the energy increases by about 8 kcal/mol. The energy cost of going from structure **8** to structure **10** is about 4 kcal/mol, even though structure **8** has sacrificed some resonance stabilization to achieve the higher lithium coordination number.

(30) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(31) Brownstein, S.; Bywater, S.; Worsfold, D. J. *J. Organomet. Chem.* **1980**, *199*, 1.
(32) Decher, G.; Boche, G. *J. Organomet. Chem.* **1983**, *259*, 31.
(33) Neugebauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, *198*, 1.
(34) Waterman, K. C.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3138−40.
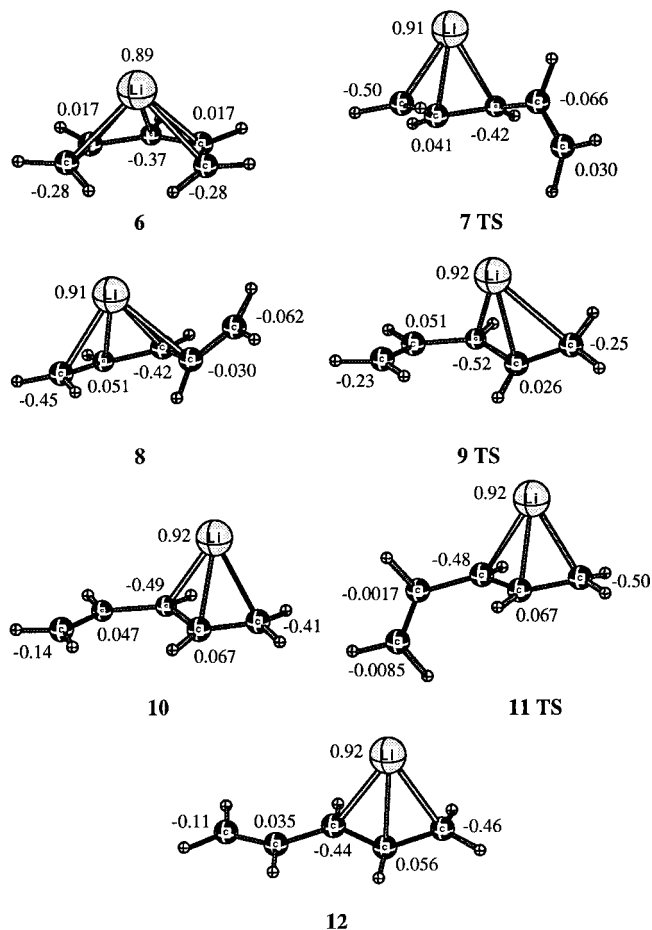
Figure 2. NPA charge distributions of pentadienyllithiums (HF/6-311+G*).

Table 2. Relative Energies of Pentadienyllithium Conformations (kcal/mol)

method	6	7 (TS)	8	9 (TS)	10	11 (TS)	12
PM3	0	10.7	6.6	10.9	0.007	10.5	7.2
HF/3-21G	0	19.2	8.0	14.4	12.1	18.5	10.2
HF/6-311+G*	0	17.9	7.7	13.4	10.7	16.8	8.5
B3LYP/6-311+G*	0	20.9	8.7	14.6	12.7	20.3	10.4
MP2/6-311+G*	0	20.8	10.2	16.6	15.2	21.6	13.2

In general, the structures of the pentadienyl moieties in the lithium compounds are similar to those of the corresponding free anion with differences that are readily understandable by the coordination to lithium. Structures **10** and **12**, for example, are vinylallyllithiums with allyl C−C bond lengths of 1.38−1.41 Å and a vinyl double bond, 1.33−1.36 Å, joined by a bond of 1.45−1.46 Å. The differences from the anions of several hundredths Ångstrom are in the expected directions. The transition structures **7**, **9**, and **11** are also similar to the corresponding anion structures except that the pendant vinyl group has slightly shorter double bonds attached by a slightly longer single bond, again indicative of decreased polarization in the lithium structures. The C−Li bonds are also unexceptional. In the allyllithium moieties of **10** and **12**, for example, the bonds to the external carbons are (at HF/6-311+G*) 2.11−2.15 Å with shorter bonds, for simple geometric reasons, to the central carbons. The fourth C−Li bond to the pendant vinyl group is longer, 2.39 Å at the same level, and in the more expanded U structure of **6** the comparable C−Li bond lengths are 2.30, 2.17, and 2.12 Å.
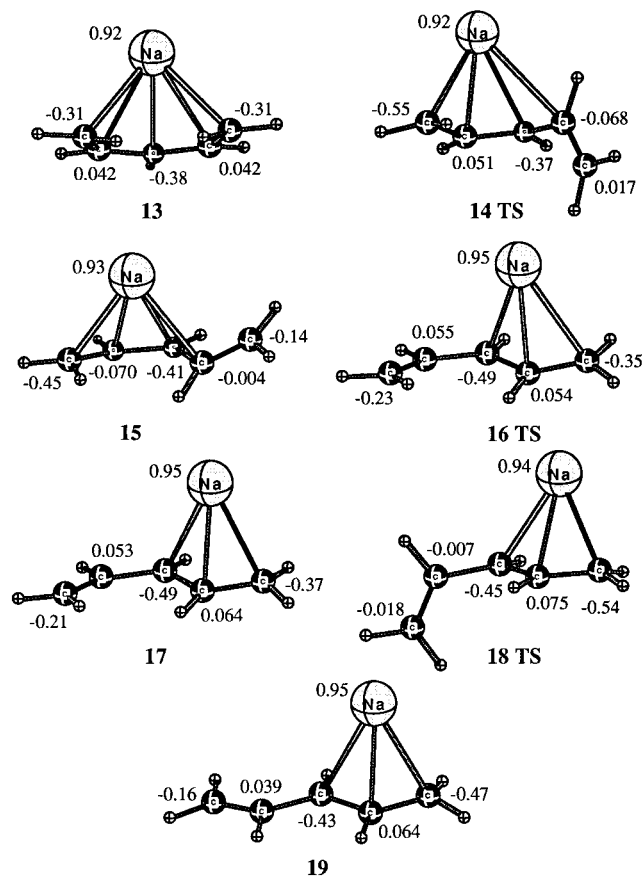

Figure 3. NPA charge distributions of pentadienylsodiums (HF/6-311+G*).

Table 3. Relative Energies of Pentadienylsodium Conformations (kcal/mol)

method	13	14 (TS)	15	16 (TS)	17	18 (TS)	19
HF/3-21G	0	20.1	7.1	12.1	11.9	20.2	10.3
HF/6-311+G*	0	18.4	6.2	10.4	10.3	18.8	8.4

The calculated regional charges are also shown in Figure 2. The charge distribution in the U-shaped conformer (**6**) is similar to that of the free anion. Significant differences are found in the two sickle-like structures (**8** and **10**) with most of the negative charge concentrated on the carbons coordinated to the lithium. A similar charge distribution is found for the W-shaped structure (**12**) and for the transition structure **9** between **8** and **10**. The transition structures corresponding to bond rotation (**7** and **11**) have less double bond polarization in the pendant vinyl group compared to the free anion (**2** and **4**), again because polarization is electrostatically impeded by the lithium cation.

Figure 3 shows the relative energies and atomic charges of the pentadienylsodium conformations. The relative energies are similar to those of pentadienyllithium, but the calculated energy barriers for bond rotation are slightly higher for the pentadienylsodium (transition structures **14** and **18**) than for the corresponding pentadienyllithium structures (**7** and **11**) when calculated at the same level of theory. This trend is consistent with that for experimental energies of allyl compounds of alkali metals, with allyllithium having the lowest rotational barrier and allylcesium the highest.[35] These energies are summarized in Table 3.

(35) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459.
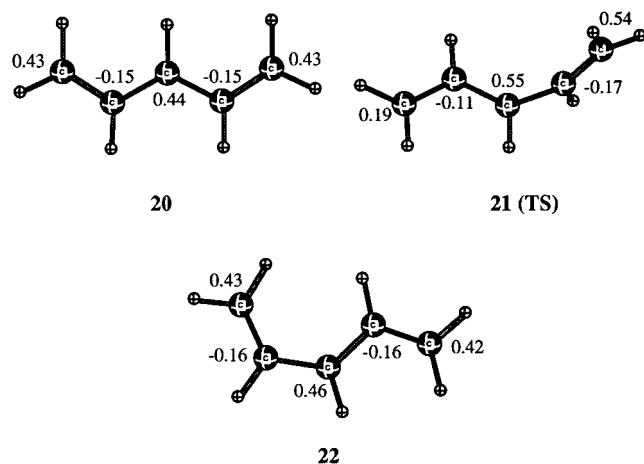
Figure 4. NPA charge distributions of pentadienyl cations (HF/6-311+G*).

Table 4. Conformational Energies of the Pentadienyl Cation (kcal/mol)

method	20	21 (TS)	22
PM3	0	10.3	1.2
HF/3-21G	0	18.5	3.5
HF/6-311+G*	0	18.4	3.9
B3LYP/6-311+G*	0	21.1	3.7
MP2/6-311+G*	0	19.7	3.8

Some experimental NMR data are available for comparison in THF solution.[24] Pentadienylpotassium shows a U conformation, whereas the lithium salt was found to exist in the W conformation. The difference was interpreted on the basis that the lithium salt is a solvent-separated ion pair.[24] The solvent-separated ion pair should more resemble the free anion, and these experimental results are thus not in disagreement with the present computations.

The organic structures of the sodium compounds are quite similar to those of the corresponding organolithiums; C–C bond lengths differ generally by no more than 0.01 Å at HF/6-311+G*. The C–Na bonds are unexceptional; most are 0.40–0.45 Å longer than their C–Li counterparts.

For the most part, the atomic charges in the pentadienylsodium conformations are similar to those in pentadienyllithium. In the bond rotation transition structures (**14** and **18**), the pendant vinyl group shows more polarization than in the pentadienyllithium transition structures, but not nearly so much as in the free anion. Because carbon–sodium bonds are primarily ionic, the similarity in the charge distribution in the lithium and sodium compounds is further evidence of the ionic character of the lithium bonds in this system.

Unlike the pentadienyl anion and the corresponding lithium and sodium compounds, the pentadienyl cation did not optimize to a stable U-shaped structure. The optimized geometries are shown in Figure 4. The most stable conformations are the W form (**20**) and a sickle form (**22**) that is slightly higher in energy. These two structures interconvert via a nonplanar transition structure (**21**) that is analogous to that of the anion (**4**). The rotational barrier of about 18–20 kcal/mol is similar to that of the anion. The relative conformational energies and atomic charges are shown in Table 4.

The atomic charges on the pentadienyl cation nearly mirror those of the anion. In the most symmetrical

structure (**20**), partial positive charge resides on alternate carbon atoms, similar to the negative charge in the anion. Nearly the same charge distribution is found in the sickle-shaped conformer (**22**). In the transition structure (**21**), a substantial positive charge is induced onto the formally neutral pendant vinyl group, similar to the induced negative charge in the anion.

It is clear from the conformational energies of the pentadienyl anion and the pentadienylmetal compounds that the stabilization of the planar forms of the organometallic compounds results from both conjugation and electrostatic attraction between the negative carbons and the alkali metal cations. To determine the relative magnitude of these effects, the reaction energies were determined for the hypothetical reaction in eq 1. The

Table 5. Calculated Energies (kcal/mol) for the Formation of Pentadienyllithium Conformations from Li$^+$ and the Corresponding Anion Conformer (eq 1)
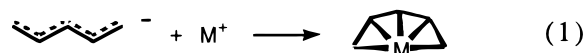
method	6	10	12
HF/3-21G	−180.6	−165.9	−165.4
HF/6-311+G*	−161.9	−150.8	−150.9
B3LYP/6-311+G*	−164.7	−151.6	−151.3
MP2/6-311+G*	−167.0	−152.8	−152.5

Table 6. Calculated Energies (kcal/mol) for the Formation of Pentadienylsodium Conformations from Na$^+$ and the Corresponding Anion Conformer (eq 1)

method	13	17	19
HF/3-21G	−154.4	−139.9	−139.2
HF/6-311+G*	−134.6	−123.9	−123.7

$$\text{(1)}$$

results are given in Tables 5 and 6. The reaction energies for the formation of pentadienyllithium are substantially greater than for pentadienylsodium, indicating a greater electrostatic attraction for the shorter lithium–carbon bonds. Between each pair of structures in which the metal is coordinated to three carbons (**10** and **12** for lithium, **17** and **19** for sodium), the energies are nearly equal, as would be expected in structures with nearly the same metal–carbon coordination. In these cases, steric effects have little influence on the coordination energies. In the free anion, the difference in energy between the sickle and W conformations is only about 2 kcal/mol. Much larger energy differences of about 8–13 kcal/mol (depending on the theory level) are found when comparing the U and W structures of pentadienyllithium and pentadienylsodium (**6** with **12** with **13** with **19**). Thus, we conclude that the electrostatic attraction between the alkali metal and the negatively charged carbons plays a major role in determining the relative stabilities of the conformations.

Conclusions

Pentadienyllithium and pentadienylsodium exist in several different conformations, the most stable of which is the U-shaped structure that results in maximum coordination of the metal cation to the pentadienyl anion. The stability of the pentadienyl organometallic compounds results from a combination of electron delocalization in the conjugated molecule and ionic bonding to the metal. The greater difference in conformational

energies of the organometallic compounds compared to the free anion is a result of this coordination to the metal.

In the planar pentadienyl ions, the charges are symmetrically distributed about the carbon skeleton. When one vinyl group is twisted out of the plane of the molecule, some charge polarization is still induced in the pendant vinyl group as a result of the proximity of the charged allylic system. This induced polarization is greatly reduced in pentadienyllithium and pentadienylsodium, an electrostatic inhibition of polarization. The relative conformational stabilities of the organometallic molecules results from a combination of delocalization stabilization and coordination to the metal.

Supporting Information Available: Energies and coordinates for compounds **1** to **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990674W