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# Deprotonation of Lithiated Benzenes

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The deprotonation energies of all possible lithiobenzenes ($C_6Li_nH_{6-n}$, $n = 0-5$) were computed at B3LYP/6-311+G(d,p). Based on natural population analysis, the conjugate bases can be thought of as salts between a polyanionic phenyl core and associated lithium cations. The most stable structures maximize the electrostatic attraction between these two species, typically by positioning the lithium cations to bridge in the ring plane across two adjacent carbanion centers. Favorable deprotonation occurs when the formal carbanion centers are adjacent to each other and then the proton is removed from an adjacent carbon. The deprotonation free energies range from 365.0 to 397.2 kcal mol$^{-1}$, with most of them less than the deprotonation free energy of benzene (391.8 kcal mol$^{-1}$).

## Introduction

Organolithium compounds, besides being extremely useful reagents in organic synthesis,[1] possess novel structures that test our notions of bonding.[2] The C−Li bond is essentially ionic, and lithium frequently is found bridging carbanion centers to maximize their electrostatic attractions.[3−10] Among the interesting properties of organolithium compounds, we recently reported on the anomalously low deprotonation energy of phenyllithium;[11] the deprotonation energy of phenyllithium is in fact less than that of benzene.

Attempts to polylithiate benzene, prompted by our work, failed to exchange more than two protons with lithium in 1,3,5-trifluorobenzene.[12] We then examined the structures and energies of the polylithiated benzenes ($C_6Li_nH_{6-n}$, $n = 1-6$, **1**−**6**).[13] Sequential replacement of a hydrogen atom with a lithium atom is best accomplished by ortho lithiation. The meta lithiation demanded in the approach taken by Schlosser fails to take advantage of the favorable ion triplet electrostatic stabilization because the carbanion centers are too far apart to be effectively bridged. Our computations suggested that disproportionation of phenyllithium to hexalithiobenzene is exothermic for every step along the pathway.

One possible pathway for creating polylithiated benzenes is the sequential removal of a proton followed by lithium cation capture. In this paper, we present DFT computations of the deprotonation energy of the lithiobenzenes **1**−**5**, shown in Scheme 1. We have also computed the lithium cation affinity of the lithiobenzene conjugate bases **1cb**−**5cb**, shown in Scheme 2.

## Computational Methods

While organolithium structures can be predicted with relatively simple computations,[3] calculation of deprotonation energies (DPEs) requires accurate treatment of the conjugate base. This requires inclusion of electron correlation, polarization functions and diffuse functions.[14−16] We have therefore optimized all structures using the B3LYP/6-311+G(d,p) method.[17] We have previously demonstrated the appropriateness of this method for computing organolithium structures and deprotonation energies of hydrocarbons[18] and phenyllithium.[11]

In our previous work,[13] we computed many structures of the polylithiated benzenes (**1**−**6**) and reproduce here in Figure 1 just the lowest energy configurations. Many possible configurations of the conjugate bases are possible. We have completely optimized a number of them, using the structures of the neutral species as a guide. Care was taken to ensure proper restriction of the optimizations to appropriate point groups. The optimized structures of the conjugate

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[1] Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988.

[2] *Lithium Chemistry. A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; J. Wiley: New York, 1995.

[3] Streitwieser, A.; Bachrach, S. M.; Dorigo, A.; Schleyer, P. v. R. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1995; p 1−45.

[4] Streitwieser, A.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778−4784.

[5] Bachrach, S. M.; Streitwieser, A. *J. Am. Chem. Soc.* **1984**, *106*, 5818−5824.

[6] Waterman, K. C.; Streitwieser, A. *J. Am. Chem. Soc.* **1984**, *106*, 3138−3140.

[7] Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1985**, *107*, 1919−1921.

[8] Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909−5916.

[9] Mierzwicki, K.; Berski, S.; Latajka, Z. *Chem. Phys. Lett.* **2000**, *331*, 538−546.

[10] Ponec, R.; Roithova, J.; Girones, X.; Lain, L.; Torre, A.; Bochicchio, R. *J. Phys. Chem. A* **2002**, *106*, 1019−1025.

[11] Bachrach, S. M.; Hare, M.; Kass, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 12646−12649.

[12] Schlosser, M.; Guio, L.; Leroux, F. *J. Am. Chem. Soc.* **2001**, *123*, 3822−3823.

[13] Bachrach, S. M.; Miller, J. V. *J. Org. Chem.* **2002**, 7389−7398.

[14] Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1990**, *112*, 6514−6517.

[15] Saunders, W. H., Jr. *J. Phys. Org. Chem.* **1994**, *7*, 268−271.

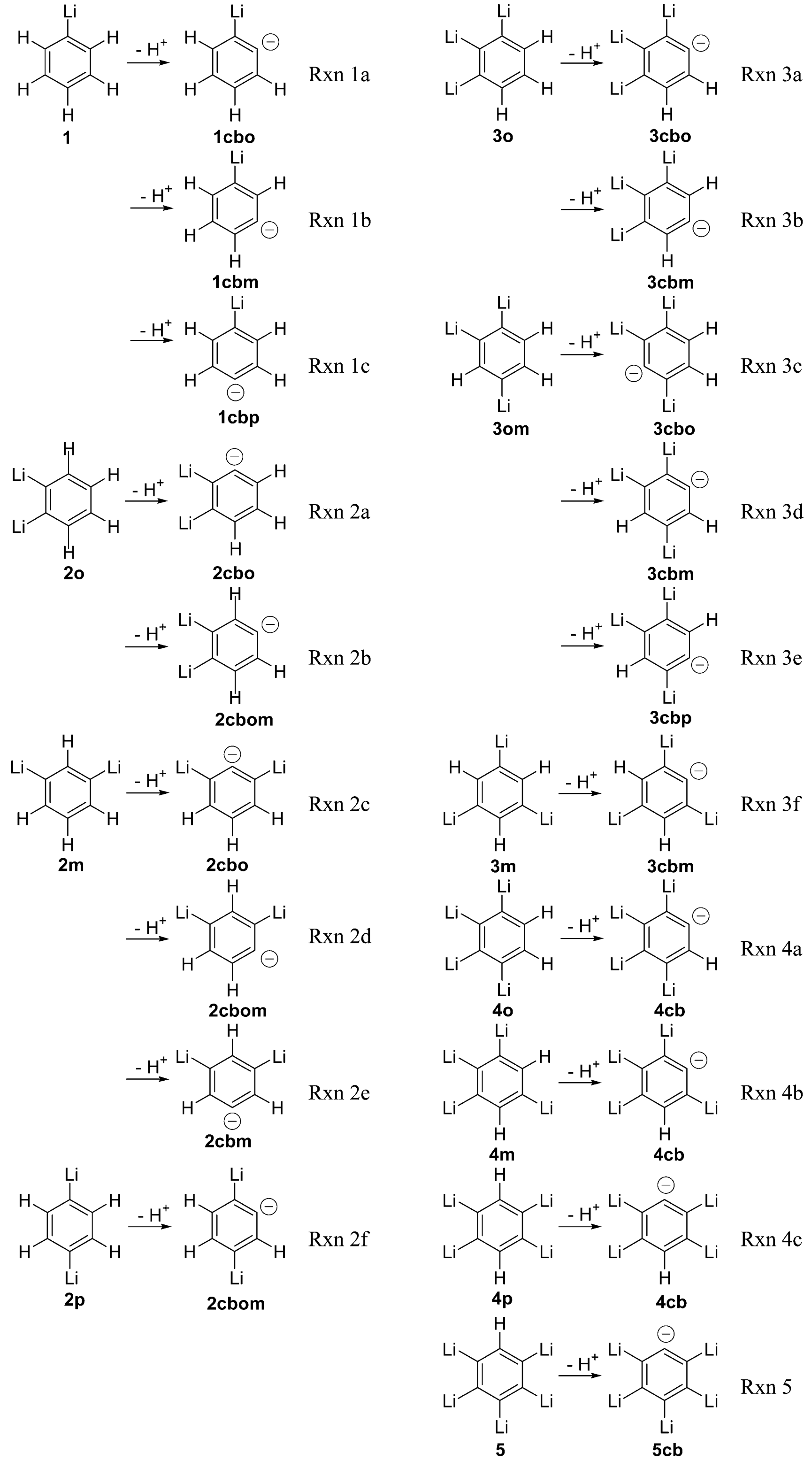
[16] Merrill, G. N.; Kass, S. R. *J. Phys. Chem.* **1996**, *100*, 17465−17471.

[17] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5650. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

[18] Bachrach, S. M. *J. Phys. Chem. A* **2003**, *107*, 4957−4961.

10.1021/jo035265l CCC: $27.50

**SCHEME 1**



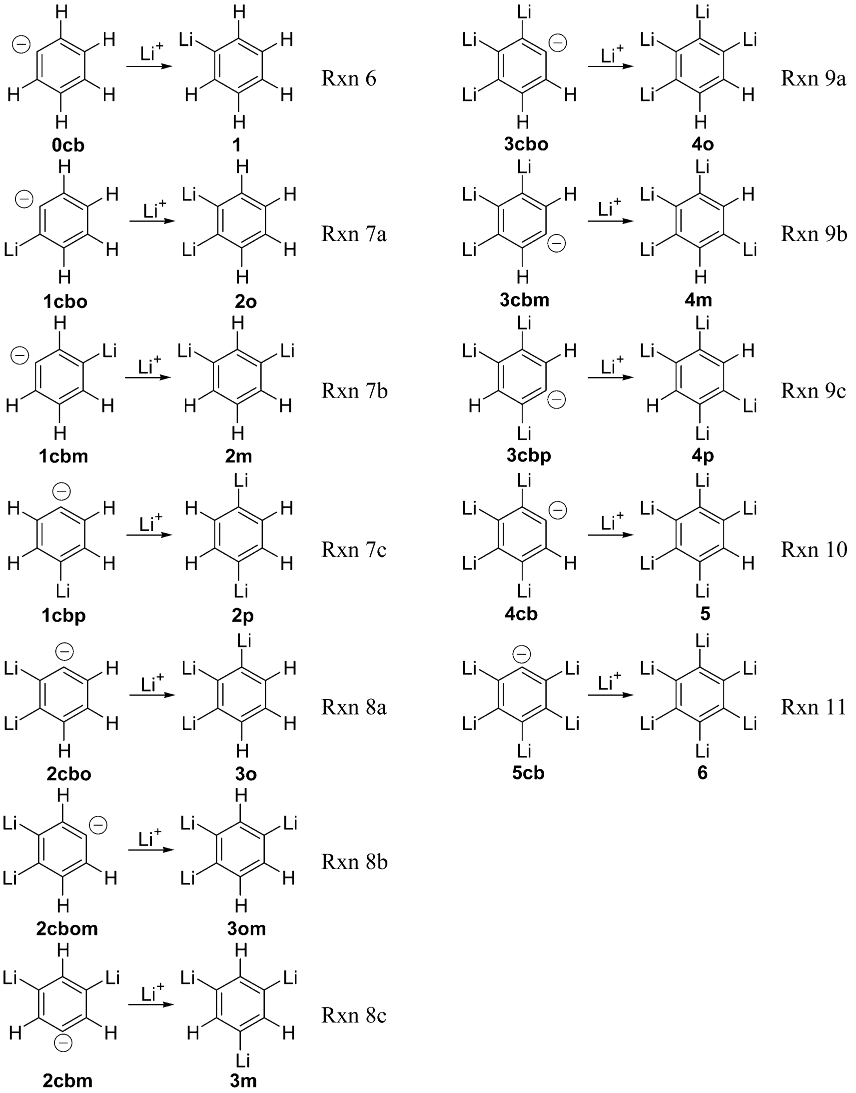
bases **1cb**−**5cb** are drawn in Figures 2−6. Complete descriptions of all geometries are available in the Supporting Information.

Analytical frequencies were computed to confirm the nature of all structures. These frequencies were used without scaling to determine 298 K thermal contributions to the free energies using standard partition-function approximations.[19] These free energies are reported throughout this paper. All computations were performed with GAUSSIAN-98.[20]

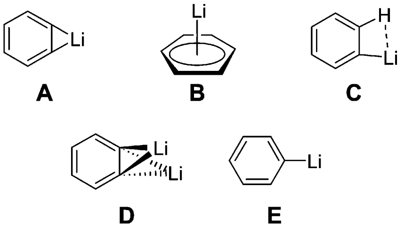
## Results and Discussion

**General Structural Trends in Polylithiated Benzenes.** In our study of phenyllithium anion[11] and polylithiated benzenes,[13] we were able to draw some general conclusions about these structures. The structures are dominated by the need to maximize the electrostatic attraction between carbanions and lithium cations while

**SCHEME 2**



minimizing repulsions between the carbanion centers and between the lithium cations. The most favorable structures possess the maximum number of lithium cations in the ring plane bridging two adjacent carbanion centers (**A**). The next two most favorable arrangements place a lithium cation above the center of the benzene ring (**B**) or have the lithium cation bridge a carbanion and the hydrogen on an adjacent carbon (**C**). Less favorable is to have two lithium cations bridging the same pair of ortho carbanions (**D**). The least favorable structure is the $\sigma$-interaction of a lithium cation with one carbanion (**E**). We will use these trends to guide our discussion of the polylithiated benzene anions.



**Conjugate Bases of Phenyllithium (1cb).** Analysis of the structures and energetics of the conjugate bases of phenyllithium was presented in our earlier article.[11] We reproduce the optimized structures and relative energies of the three isomers in Figure 2. The *ortho* isomer **1cbo** is the most stable configuration. The *para* isomer **1cbp** is 10.81 kcal mol$^{-1}$ higher in energy, while the *meta* isomer **1cbm** is the least stable form, lying 14.43 kcal mol$^{-1}$ above **1cbo**. The lithium cation effectively bridges across the adjacent carbanions in **1cbo**, balancing off the repulsion of the two formal anions. The bridging in the *para* isomer is the least effective of the

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(19) Cramer, C. J. *Essentials of Computational Chemistry. Theories and Models*; John Wiley: Chichester, UK, 2002.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, version A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

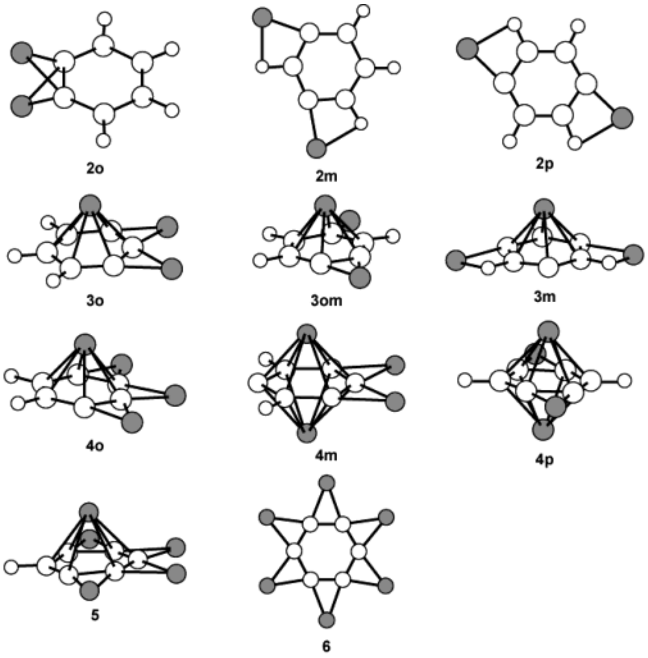


**FIGURE 1.** Optimized structures of **1**−**6**. Carbon is indicated by the large empty circle, hydrogen by the small empty circle, and lithium by the large shaded circle.

**TABLE 1. Relative Free Energies (kcal mol$^{-1}$) and Number of Imaginary Frequencies (NIMAG) for the Conjugate Bases of Dilithiobenzene (2cb)**[a]

| | **2cbo-1** | **2cbo-2** | **2cbo-3** | **2cbo-4** | **2cbo-5** | **2cbo-6** |
|---|---|---|---|---|---|---|
| $\Delta G_{\mathrm{rel}}$ | 0.0 | 20.24 | 20.41 | 24.04 | 27.26 | 47.34 |
| NIMAG | 0 | 0 | 0 | 0 | 0 | 1 |

| | 2cbom-1 | 2cbom-2 | 2cbom-3 |
|---|---|---|---|
| $\Delta G_{\mathrm{rel}}$ | 10.90<br>(0.0) | 19.16<br>(8.26) | 34.18<br>(23.28) |
| NIMAG | 0 | 0 | 0 |

| | 2cbm-1 | 2cbm-2 | 2cbm-3 | 2cbm-4 |
|---|---|---|---|---|
| $\Delta G_{\mathrm{rel}}$ | 22.42<br>(0.0) | 32.39<br>(9.97) | 34.10<br>(11.68) | 36.76<br>(14.34) |
| NIMAG | 0 | 1 | 0 | 0 |

[a] Free energies relative to the most stable configuration of that isomer are in parentheses.

three isomers, due to the long distance separating the carbanions, but **1cbp** is more stable than **1cbm** due to the greater repulsion between the carbanions in the latter.

**Conjugate Bases of Dilithiobenzene (2cb).** There are three geometric isomers of the conjugate bases of dilithiobenzene. A simple method for distinguishing these isomers is to consider just the benzene ring, the hydrogen atoms, and the formal position of the anions. In the first isomer **2cbo**, the three hydrogens are on adjacent positions. The second isomer **2cbom** has two adjacent hydrogen atoms with the third separated by one intervening anionic carbon. The last isomer **2cbm** has alternating hydrogen atoms and anion around the benzene ring. One can thus consider the conjugate bases as the salt formed by these anions and two lithium cations. (More generally, all of the conjugate bases discussed in the article can be decomposed in this way—a salt formed of a polyanionic benzene core and the appropriate number of lithium cations.)

We located six configurations of **2cbo**, which are presented in Figure 3, and their relative energies are listed in Table 1. The suffix of their identifiers indicates their relative energetic order. As expected, based on the general structural trends, the lowest energy configuration is **2cbo-1**, which has the two lithium cations each bridging adjacent carbanions. This is not just the lowest energy configuration of **2cbo** but of all conjugate bases of dilithiobenzene. While positioning the three carbanion centers at adjacent positions (as in all the **2cbo** configurations) maximizes their electrostatic repulsions, the very favorable ion triplet bridging in **2cbo-1** more than compensates for this unfavorable phenyl tri-anion core.

The next two configurations **2cbo-2** and **2cbo-3** have nearly the same energy, lying about 20 kcal mol$^{-1}$ above **2cbo-1**. In **2cbo-2**, one lithium cation bridges ortho carbanions and the second lies above the ring. The two lithiums bridge the same pair of ortho carbanions in **2cbo-3**, leaving the third carbanion without any gegenion nearby. **2cbo-4** has the ortho bridging lithium cation and a lithium bridging a carbanion and an adjacent hydrogen atom. The lithium cations are $\sigma$-bonded to the outer two carbanions, leaving the central carbanion without gegenion, in **2cbo-5**. The highest lying configuration is **2cbo-6** and has one imaginary frequency, corresponding to motion of the lithium atoms into the ring plane, preserving only the $C_2$ axis.

We identified three configurations of **2cbom**, shown in Figure 3. Since one carbanion center is isolated from the others, there is no way for a lithium cation to effectively bridge to it. The lowest energy configuration

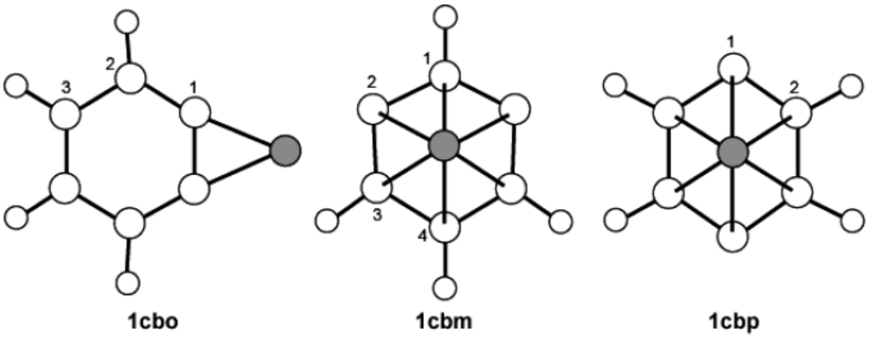


**FIGURE 2.** Optimized Structures of **1cb**. See Figure 1 for legend.

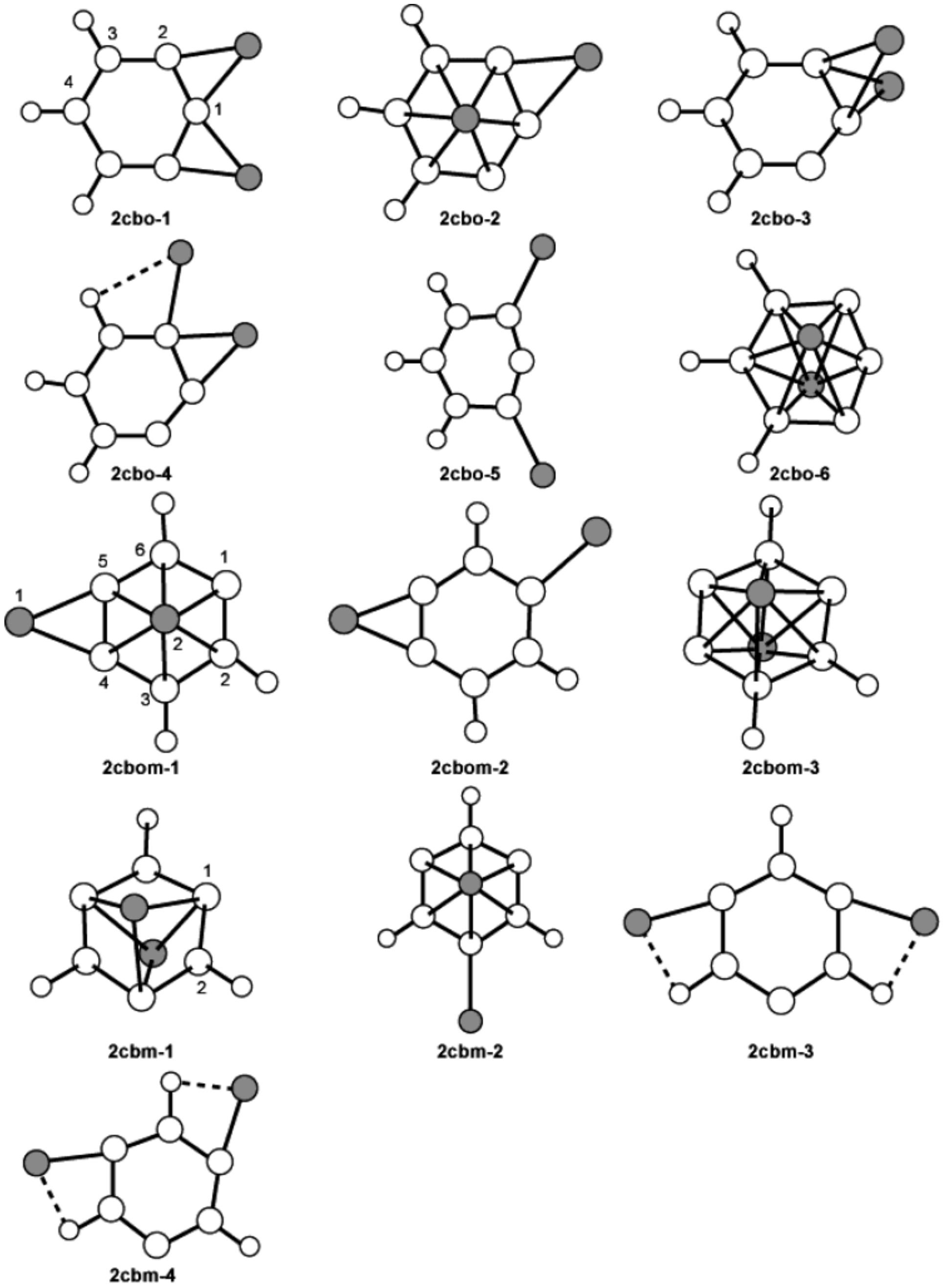
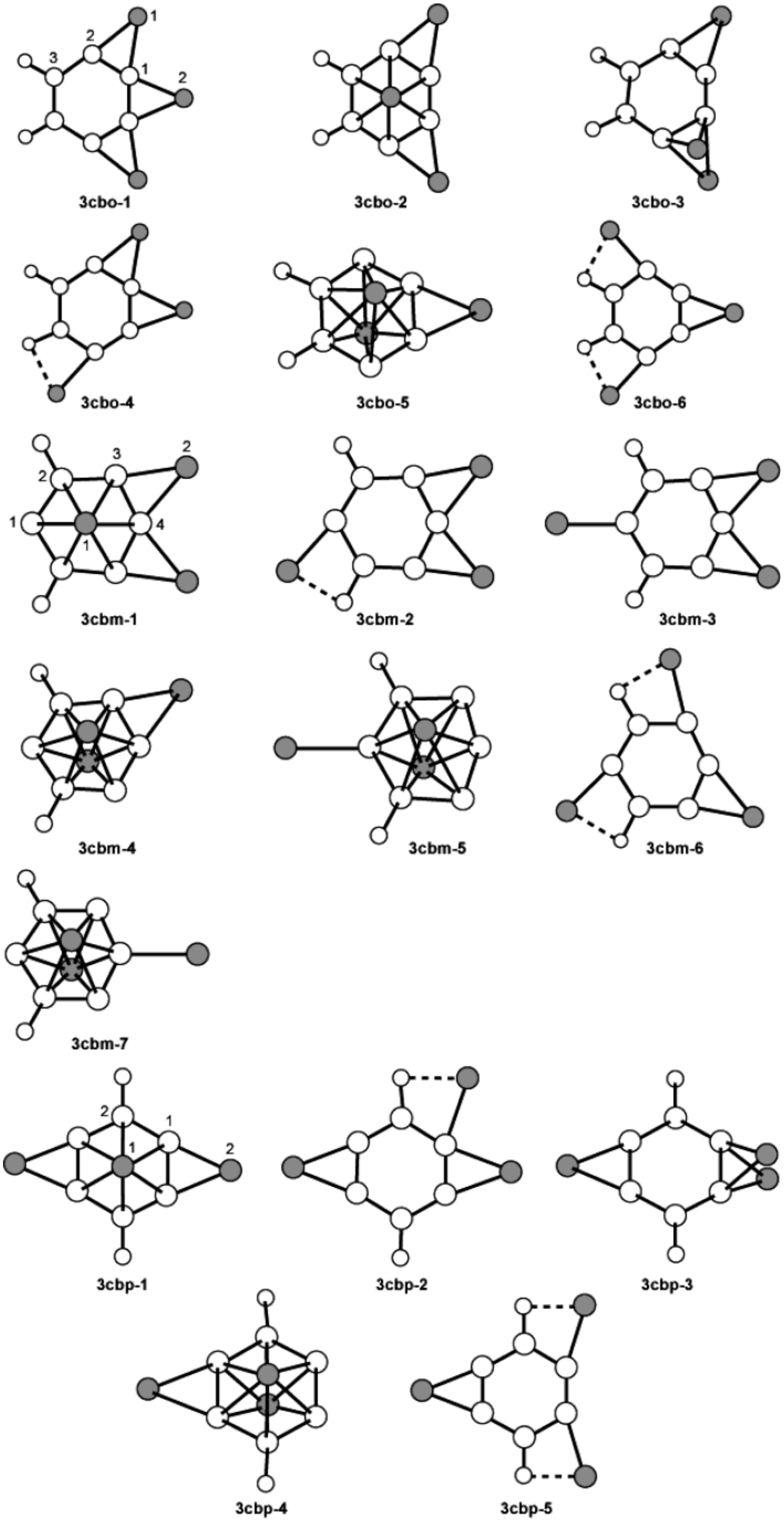


**FIGURE 3.** Optimized structures of **2cb**. See Figure 1 for legend.

**2cbom-1** has one lithium cation in the favorable ortho bridging position and the other lies above the ring. This isomer is 10.90 kcal mol$^{-1}$ above **2cbo-1**. Lying 8.3 kcal mol$^{-1}$higher in energy is **2cbom-2**, where the second lithium $\sigma$-bonds to the isolated carbanion. The highest lying configuration **2cbom-3** has the lithium cations above and below the ring center. This configuration is not as destabilized as **2cbo-6** is relative to **2cbo-1**; the repulsions among the carbanions are less severe in **2cbom** than in **2cbo** due to the isolation of one the carbanions.

The four configurations of **2cbm** (see Figure 3) are quite energetic. Since the carbanions are meta to each other, the lithium cations can only poorly bridge them by lying above the ring center. The lowest energy configuration **2cbm-1** has the cations above and below the ring center. Even though the repulsions between the carbanions is the weakest in this isomer, the electrostatic attractions between these centers and the lithium cations is also weak, resulting in it lying 22.42 kcal mol$^{-1}$ above **2cbo-1**. Having just one cation above the ring and one $\sigma$-bonded to a carbanion gives **2cbm-2**, which is nearly 10 kcal mol$^{-1}$ less stable than **2cbm-1**. The last two configurations have the lithium cations in the ring plane but bridge a carbanion and an adjacent hydrogen.

**Conjugate Bases of Trilithiobenzene (3cb).** Once again, there are three isomers of the conjugate base of trilithiobenzene, where the two remaining hydrogen atoms are ortho **3cbo**, meta **3cbm**, or para **3cbp**. Based simply on the electrostatic repulsions within the tetra-



**3cbo-1** **3cbo-2** **3cbo-3**

**3cbo-4** **3cbo-5** **3cbo-6**

**3cbm-1** **3cbm-2** **3cbm-3**

**3cbm-4** **3cbm-5** **3cbm-6**

**3cbm-7**

**3cbp-1** **3cbp-2** **3cbp-3**

**3cbp-4** **3cbp-5**

**FIGURE 4.** Optimized structures of **3cb**. See Figure 1 for legend.

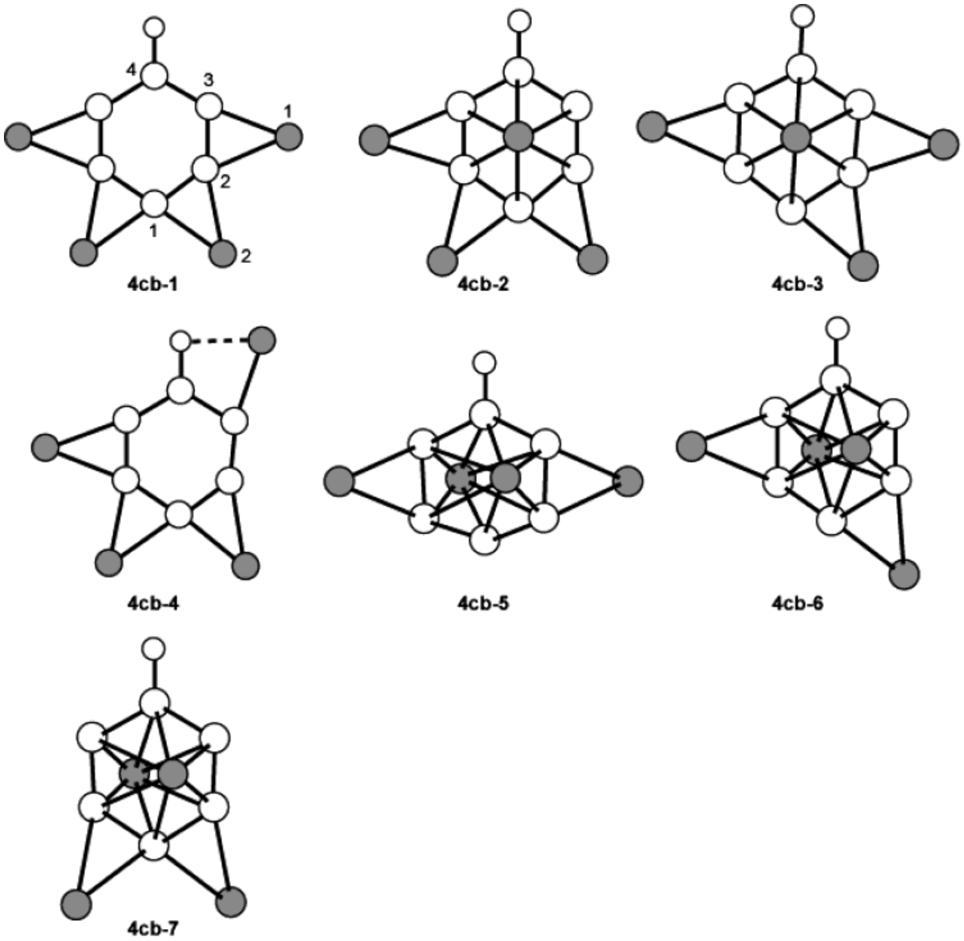


**FIGURE 5.** Optimized structures of **4cb**. See Figure 1 for legend.

**TABLE 2. Relative Free Energies (kcal mol$^{-1}$) and Number of Imaginary Frequencies (NIMAG) for the Conjugate Bases of Trilithiobenzene (3cb)**[a]

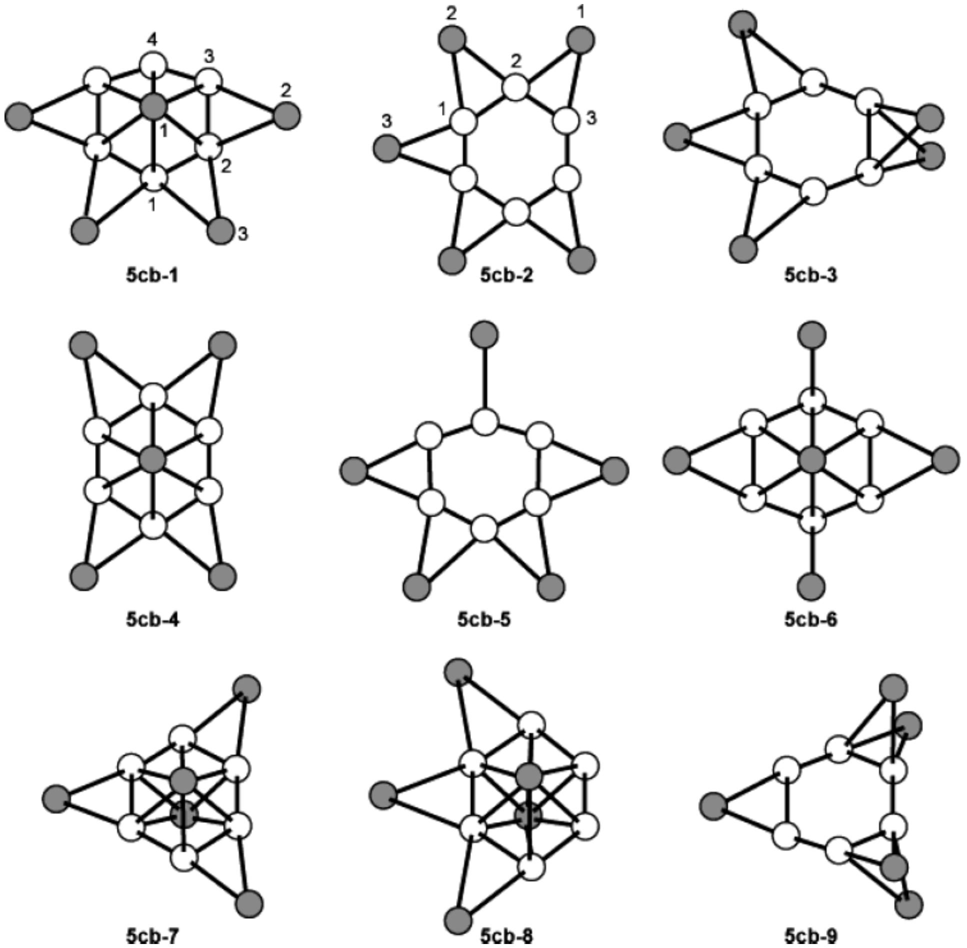
| | **3cbo-1** | **3cbo-2** | **3cbo-3** | **3cbo-4** | **3cbo-5** | **3cbo-6** | |
|---|---|---|---|---|---|---|---|
| $\Delta G_{\mathrm{rel}}$ | 0.0 | 12.60 | 21.57 | 21.77 | 29.62 | 47.52 | |
| NIMAG | 0 | 0 | 0 | 0 | 0 | 1 | |
| | **3cbm-1** | **3cbm-2** | **3cbm-3** | **3cbm-4** | **3cbm-5** | **3cbm-6** | **3cbm-7** |
| $\Delta G_{\mathrm{rel}}$ | 8.61<br>(0.0) | 18.48<br>(9.87) | 20.53<br>(11.92) | 22.40<br>(13.79) | 30.84<br>(22.23) | 36.67<br>(28.06) | 39.36<br>(30.75) |
| NIMAG | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| | **3cbp-1** | **3cbp-2** | **3cbp-3** | **3cbp-4** | **3cbp-5** | | |
| $\Delta G_{\mathrm{rel}}$ | 8.19<br>(0.0) | 17.67<br>(9.48) | 28.23<br>(20.04) | 29.17<br>(20.98) | 34.46<br>(26.27) | | |
| NIMAG | 0 | 0 | 0 | 1 | 0 | | |

[a] Free energies relative to the most stable configuration of that isomer are in parentheses.

anion core, the ortho isomer should be least stable and the para isomer should be most stable.

We located six configurations of the ortho isomer. These are drawn in Figure 4 and their relative energies listed in Table 2. The most stable isomer of **3cb** is **3cbo-1**, at least 8 kcal mol$^{-1}$ more stable than any other isomer or configuration. As expected on the basis of the general structural trends, this configuration has each lithium cation bridging in the molecular plane a pair of ortho carbanion centers. Even though the four formal carbanions are adjacent to each other, maximizing their repulsions, the three ion triplet structures formed by the bridging lithium cations realize substantial favorable electrostatic attraction, enough to make this the most stable salt.

The second lowest configuration of the ortho isomer is **3cbo-2** where two lithium cations bridge in-plane and the third lies above the ring. In **3cbo-3**, all lithium cations bridge ortho carbanions, but here two bridge the same pair. This is less stable than **3cbo-1** because these two lithium cations are closer together, increasing their repulsion energy. **3cbo-4** differs from the most stable configuration by having one lithium bridging a carbanion and a hydrogen instead of bridging ortho carbanions. This



5cb-1 5cb-2 5cb-3

5cb-4 5cb-5 5cb-6

5cb-7 5cb-8 5cb-9

**FIGURE 6.** Optimized structures of **5cb**. See Figure 1 for legend.

configuration is 22 kcal mol$^{-1}$ above **3cbo-1**, indicating the strong preference for lithium bridging ortho carbanions. Less stable is **3cbo-5**, which has only one lithium cation bridging ortho carbanions while the other two lie above and below the ring. The last isomer **3cbo-6** has one lithium cation bridging ortho carbanions and the other two bridge a carbanion and an adjacent hydrogen. It is 47 kcal mol$^{-1}$ above **3cbo-1**, slightly more than twice the gap between **3cbo-4** and **3cbo-1**, which reflects the loss of only one ortho carbanion lithium bridge.

We optimized seven configurations of **3cbm**, drawn in Figure 4 with relative energies listed in Table 2. The configuration possessing maximum in-plane bridging is **3cbm-2**. It is, however, not the most favorable configuration. Lying almost 10 kcal mol$^{-1}$ below is **3cbm-1**, which positions two lithium cations in-plane bridging ortho carbanions and the third lies above the ring plane. This $\eta$-6 type bonding is preferential to lithium bridging a carbanion and an adjacent hydrogen atom, as seen also in the preference of **3cbo-2** over **3cbo-4**, **2cbo-2** over **2cbo-4**, and **2cbm-1** over **2cbm-4**. **3cbm-3** lacks the bridge to the adjacent hydrogen in **3cbm-2**; the energetic consequence of this bridging interaction is thus the difference in the energies of these two structures: 2.05 kcal mol$^{-1}$. **3cbm-4**, **3cbm-5**, and **3cbm-6** all have two lithium cations above and below the ring; they differ in the position of the third lithium cation. The most favorable is the lithium bridging adjacent carbanions (**3cbm-4**). **3cbm-6** differs from **3cbm-2** in having a lithium bridge a carbanion and a hydrogen in the former versus bridging ortho carbanions in the latter. The energetic consequence of this is again approximately 20 kcal mol$^{-1}$.

The configuration with maximum in-plane bridging of the lithium cations for the para isomer is **3cbp-2**, which again is not the lowest energy isomer. The $\eta$-6 type bonding is better than bridging a carbanion and an adjacent hydrogen, making **3cbp-1** 9.48 kcal mol$^{-1}$ lower than **3cbp-2**. Doubly bridging one pair of ortho carbanions (creating **3cbp-3**) raises the energy by 20 kcal mol$^{-1}$ above the best configuration, again reflecting the increased repulsions between the neighboring cations and reduced attraction between the lithium and the carbanions across the ring. Lithium capping above and below the ring **3cbp-4** is nearly isoenergetic with **3cbp-3**, while double bridging a carbanion and an adjacent hydrogen gives the least stable configuration **3cbp-5**.

**Conjugate Bases of Tetralithiobenzene (4cb).** The seven configurations of the conjugate base of tetralithiobenzene **4cb** that we found are shown in Figure 5 and their relative free energies are listed in Table 3. The most stable configuration **4cb-1**, consistent with the general structural trends, has all four lithium cations bridging in-plane pairs of ortho carbanions. The next two higher configurations (**4cb-2** and **4cb-3**) place one of the lithium cations above the ring, while the remaining three bridge

**TABLE 3. Relative Free Energies (kcal mol$^{-1}$) and Number of Imaginary Frequencies (NIMAG) for the Conjugate Bases of Tetralithiobenzene (4cb)**

| | 4cb-1 | 4cb-2 | 4cb-3 | 4cb-4 | 4cb-5 | 4cb-6 | 4cb-7 |
|---|---|---|---|---|---|---|---|
| $\Delta G_{rel}$ | 0.0 | 5.03 | 5.52 | 12.95 | 13.08 | 17.76 | 20.08 |
| NIMAG | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

ortho carbanions. These two configurations are very close in energy, lying about 5 kcal mol$^{-1}$ above **4cb-1**. **4cb-4** differs from the ground-state configuration by moving a lithium cation to bridge a carbanion and the adjacent hydrogen, rather than bridging ortho carbanions; this raises the energy by 13 kcal mol$^{-1}$, a lesser penalty than seen in **3cb**. The highest three configurations have one lithium cation above and one below the ring and two bridging ortho carbanions, differing in which carbanions are bridged. The best of these three configurations is **4cb-5** where the two in-plane lithium cations are on opposite sides of the ring and the formal bare carbanion is para to the carbon bearing a hydrogen. This arrangement places the lithium cations farther apart than in **4cb-6**. The last configuration **4cb-7** suffers from having the in-plane lithium cations near each other and two formal bare carbanions.

**Conjugate Bases of Pentalithiobenzene (5cb).** We were able to locate nine configurations of the conjugate base of pentalithiobenzene. These are drawn in Figure 6 and their relative energies listed in Table 4. We attempted to locate a number of other configurations, mostly related to the ones shown in Figure 6, but they invariably optimized to structures where the six-member carbon ring had been cleaved.

The configuration with maximum in-plane lithium bridging is **5cb-2**. Surprisingly, this configuration is not the lowest energy structure; it is not even a local minimum, having one imaginary frequency distorting the molecule from $C_2v$ to nearly $C_2$. The lowest energy configuration is **5cb-1**, which has one lithium cation above the ring and the others bridging ortho carbanions. The four in-plane lithium cations actually bend upward from the ring plane toward the capping lithium cation. A similar configuration, **5cb-3**, also has four lithium cations bridging ortho carbanions but having $C_2v$ symmetry. This configuration is 22 kcal mol$^{-1}$ above the minimum energy structure. All of the other configurations we located have at least one imaginary frequency. **5cb-4** and **5cb-9** have at least one pair of lithium cations bridging the same pair of ortho carbanions. **5cb-7** and **5cb-8** have lithium cations capping the top and bottom faces of the benzene ring, differing in which pair of ortho carbanions the remaining lithium cations bridge. The more stable configuration (**5cb-7**) places these lithium cations farther apart.

**Population Analysis.** Population analysis of organolithium compounds has a long and tortured history.[3,21] Mulliken populations of organolithium compounds are notoriously useless since the method dramatically overestimates the covalent nature of the bond; it neglects the spatial component of the orbitals.[22] Atoms-in-molecules (AIM)[23] charges indicate a near full transfer of an electron from lithium to carbon,[8,10] while natural population analysis (NPA)[24] suggests a very large charge transfer,[7,25,26] but not quite as large as with the AIM analysis. We choose to report here the NPA charges since they are fast to compute and provide a nice compromise between problems associated with AIM charges and the more traditional orbital approach.

In Table 5, we provide the NPA charges for carbon and lithium in the lowest energy configurations of the conjugate bases and the reference compounds phenyl anion, phenylithium **1**, and hexalithiobenzene **6**. The charge on lithium is usually quite large, for example, +0.90 in **1**, +0.79 in **6**, and greater than +0.76 for the majority of the conjugate bases. This agrees with previous charge distributions in a variety of organolithium compounds. For these cases, it is reasonable as a first approximation to consider the lithium as a full cation, having transferred an electron to the phenyl fragment. The rare exceptions are $Li_2$ in **3cbo-1**, $Li_2$ in **4cb-1**, $Li_3$ in **5cb-1** and $Li_2$ in **5cb-2**; here, these lithium atoms carry a charge of less than +0.6. These lithium centers are in the interior of a series of adjacent ortho bridging cations.

To discuss the charges on carbon, we first turn to the reference compounds. In phenyl anion, the negative charge is distributed to some extent about the ring; the formal anionic carbon carries a charge of −0.41 while each of the remaining CH groups carry a charge of about −0.1. The charge is much more concentrated in phenyllithium **1**, where the charge on $C_1$ is −0.64, the two ortho CH groups have a charge of −0.08 and the other CH groups are nearly neutral. The lithium cation serves to polarize the charge toward itself. Last, the charge on carbon in **6** is −0.79, each carbon carrying significant negative charge.

The charge distributions in the conjugate bases of phenyllithium **1cb** are very instructive. In **1cbo** the two carbon atoms without an attached hydrogen, which may be formally thought as “anionic”, carry the bulk of the negative charge (−0.64 e), while the other four carbons carry about a tenth of an electron. In the other two isomers, the formally anionic carbons carry much less charge (just under a half of an electron). The bridging ortho lithium cation in **1cbo** polarizes the negative charge toward itself, building up charge on $C_1$. In the other two isomers, the lithium cation sits above the ring, interacting well with all six carbon atoms, leading to a more delocalized distribution. Strong ionic interactions require large nearby concentrations of opposite charge; this occurs in **1cbo** and explains why it is the most stable isomer.

For the isomers of the conjugate base of dilithiobenzene **2cb**, the adjacent, formally anionic carbons bridged by a

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[21] Bachrach, S. M. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 1994; Vol. 5, pp 171−228.

[22] Streitwieser, A.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, G. W. In *Electron Distribution and the Chemical Bond*; Coppens, P., Hall, M. B., Eds.; Plenum Press: New York, 1982; pp 447−473.

[23] Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, 1990.

[24] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

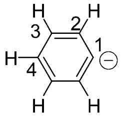
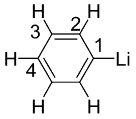
[25] Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1987**, *7*, 1597−1607.

[26] Bickelhaupt, F. M.; van Eikema Hommes, N. J. R.; Guerra, C. F.; Baerends, E. J. *Organometallics* **1996**, *15*, 2923−2931.

**TABLE 4. Relative Free Energies (kcal mol$^{-1}$) and Number of Imaginary Frequencies (NIMAG) for the Conjugate Bases of Pentalithiobenzene (5cb)**

| | **5cb-1** | **5cb-2** | **5cb-3** | **5cb-4** | **5cb-5** | **5cb-6** | **5cb-7** | **5cb-8** | **5cb-9** |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta G_{\mathrm{rel}}$ | 0.0 | 19.63 | 22.33 | 22.40 | 25.09 | 29.21 | 31.04 | 32.81 | 46.09 |
| NIMAG | 0 | 1 | 0 | 1 | 2 | 2 | 2 | 1 | 1 |

**TABLE 5. NPA Atomic Charges[a]**

| Compound | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $Li_1$ | $Li_2$ | $Li_3$ |
|---|---|---|---|---|---|---|---|---|---|
| **1cbo** | -0.64<br>(-0.64) | -0.28<br>(-0.12) | -0.28<br>(-0.11) | | | | 0.75 | | |
| **1cbm** | -0.45<br>(-0.29) | -0.48<br>(-0.48) | -0.40<br>(-0.24) | -0.33<br>(-0.16) | | | 0.87 | | |
| **1cbp** | -0.49<br>(-0.49) | -0.37<br>(-0.21) | | | | | 0.83 | | |
| **2cbo-1** | -0.77<br>(-0.77) | -0.62<br>(-0.62) | -0.29<br>(-0.13) | -0.27<br>(-0.10) | | | 0.69 | | |
| **2cbom-1** | -0.47<br>(-0.47) | -0.39<br>(-0.23) | -0.36<br>(-0.19) | -0.75<br>(-0.75) | -0.73<br>(-0.73) | -0.42<br>(-0.26) | 0.87 | 0.77 | |
| **2cbm-1** | -0.56<br>(-0.56) | -0.55<br>(-0.38) | | | | | 0.91 | | |
| **3cbo-1** | -0.78<br>(-0.78) | -0.60<br>(-0.60) | -0.28<br>(-0.12) | | | | 0.78 | 0.45 | |
| **3cbm-1** | -0.40<br>(-0.40) | -0.42<br>(-0.25) | -0.70<br>(-0.70) | -0.82<br>(-0.82) | | | 0.88 | 0.62 | |
| **3cbp-1** | -0.74<br>(-0.74) | -0.39<br>(-0.23) | | | | | 0.89 | 0.76 | |
| **4cb-1** | -0.84<br>(-0.84) | -0.69<br>(-0.69) | -0.60<br>(-0.60) | -0.29<br>(-0.12) | | | 0.72 | 0.54 | |
| **5cb-1** | -0.83 | -0.86 | -0.61 | -0.04 | | | 0.65 | 0.72 | 0.36 |
| **5cb-2** | -0.72 | -0.83 | -0.51 | | | | 0.77 | 0.47 | 0.65 |
|  | -0.41<br>(-0.41) | -0.29<br>(-0.14) | -0.26<br>(-0.10) | -0.29<br>(-0.12) | | | | | |
|  **1** | -0.64<br>(-0.64) | -0.25<br>(-0.08) | -0.23<br>(-0.03) | -0.23<br>(-0.03) | | | 0.90 | | |
| **6** | -0.79 | | | | | | 0.79 | | |

[a] Charges in parentheses are for the carbon and its bonded hydrogen together. For atom labels, see Figures 2−6.

lithium cation all carry large negative charge (~ −0.7 e), while the formally anionic carbons that are isolated carry much less charge, about −0.5 e. The large charge buildup on the adjacent anionic carbons of **2cbo-1** allow for maximal electrostatic interaction with the nearby bridging lithium cations, leading to its stability. The same trend is seen in the conjugate base of trilithiobenzene **3cb**. The adjacent formal carbon anions in **3cbo-1**, **3cbm-1**, and **3cbp-1** all carry large negative charge, while the isolated formal carbon anion in **3cbm-1** carries much less charge (−0.40 e). Again, **3cbo-1** is the most stable isomer due to the excellent electrostatic interaction between the highly charged carbanions near to the bridging lithium cations.

Another interesting trend is exemplified in **4cb-1**. Here all five of the formally anionic carbon atoms carry large negative charge; the most negative is $C_1$ followed by $C_2$ and then $C_3$. The more interior the formal carbanion, the more highly charged it is. Thus in **2cbo-1** and **3cbo-1** $C_1$ is more negative than $C_2$ and $C_4$ is more negative than $C_3$ in **3cbm-1**. This charge buildup is exactly opposite what occurs with the lithium counterion; here the interior lithium centers carry less charge than the ones on the end. This trend reflects the desire to maximize the electrostatic attractions between cation and anion while minimizing the repulsions between like charges.

The last issue to consider is the relative stabilities of **5cb-1** and **5cb-2**. The lowest energy structure should be the one that maximizes the number of ortho-bridged lithium atoms: **5cb-2**. However, **5cb-2** is a transition state and **5cb-1** is much lower in energy. We believe the stability reversal of these structures results form a number of factors. First, **5cb** can be thought of, as a first approximation, as a hexaanion, a large amount of charge for a single species to carry. Ortho bridging of the lithium counterion can only assist so much; we note that the energy difference between the all-ortho-bridged isomer and the next lowest isomer decreases from about 10 kcal mol$^{-1}$ in **1cb** and **2cb** to 8 kcal mol$^{-1}$ in **3cb** and 5 kcal mol$^{-1}$ in **4cb**. Second, the structural deformation in **5cb-1** allows for negative charge to concentrate on five carbon atoms, instead of all six in **5cb-2**. This brings the charge

**TABLE 6. Deprotonation Energies (kcal mol$^{-1}$)**

| reaction | $\Delta G$ | reaction | $\Delta G$ |
|---|---|---|---|
| **1a** | 382.7 | **3a** | 387.1 |
| **1b** | 397.2 | **3b** | 395.7 |
| **1c** | 393.6 | **3c** | 372.6 |
| **2a** | 376.5 | **3d** | 381.2 |
| **2b** | 387.4 | **3e** | 380.8 |
| **2c** | 368.0 | **3f** | 365.0 |
| **2d** | 378.9 | **4a** | 393.1 |
| **2e** | 390.4 | **4b** | 377.4 |
| **2f** | 378.1 | **4c** | 381.9 |
| | | **5** | 378.3 |

**TABLE 7. Lithium Cation Affinity (kcal mol$^{-1}$)**

| reaction | $\Delta G$ | reaction | $\Delta G$ |
|---|---|---|---|
| **6** | −153.1 | **9a** | −159.7 |
| **7a** | −146.5 | **9b** | −162.7 |
| **7b** | −152.4 | **9c** | −156.7 |
| **7c** | −148.0 | **10** | −163.0 |
| **8a** | −155.2 | **11** | −152.7 |
| **8b** | −151.6 | | |
| **8c** | −146.9 | | |

nearer to the lithium cations, affecting stronger electrostatic attractions. C$_4$ of **5cb-1** carries no charge and is best thought of as a bent allenic center; in fact the C−C−C angle about it is 147.7°, much larger than in a typical phenyl ring.

**Deprotonation Energies.** The deprotonation free energies of the lithiobenzenes **1**−**5** are listed in Table 6, indexed by the reaction numbers given in Scheme 1. To benchmark the accuracy of the calculations, the computed free energy for deptrotonation of benzene is 391.8 kcal mol$^{-1}$,which compares very well the experimental value[27] of 392.9 kcal mol$^{-1}$. This is consistent with our (and other's) general experience that computed DPEs differ from experiment by about 1 kcal mol$^{-1}$.[11,16,28,29]

We previously discussed the deprotonation energies of **1** (reaction 1) at this computational level.[11] We include the values here for completeness and note that we report here $\Delta H$, rather than $\Delta H$, for deprotonation. The lowest DPE is to remove the ortho proton, leading to **1cbo**, and we note again that this is *less* than the DPE of benzene.

Loss of an ortho hydrogen in **2o** (reaction 2a) is much more favorable than loss of a more remote proton. The resulting anion, having three adjacent formal carbananions that allows for maximal lithium bridging (**2cbo**), is much more stable than the alternate (**2cbom**). Of the three possible deprotonations of **2m**, the proton between the two lithiums is much more acidic (by at least 10 kcal mol$^{-1}$), again due to the very favorable electrostatics that arise in **2cbo**. The smallest DPE for deprotonation of **2** is reaction 2c; this reaction starts with the least favorable isomer of dilithiobenzene and creates the most favorable conjugate base (**2cbo**). The largest DPE (least acidic proton) is for reaction 2e, where the meta proton is removed, forming the least stable conjugate base (**2cbm**).

There are two different protons that can be removed from **3o**. The more acidic is the proton adjacent to the lithium, reaction 3a, because the resulting conjugate base has four adjacent formal carbanions leading to extensive strong electrostatic attractions to the bridging lithium cations. Of the three possible deprotonation pathways from **3om**, the most favorable by at least 8 kcal mol$^{-1}$ is reaction 3c leading to **3cbo**, the same favorable isomer as for reaction 3a. There is only one deprotonation path for **3m** (reaction 3f); its DPE is the smallest of all possible deprotonations from trilithiobenzene. This is largely attributable to **3m** being the least stable isomer of trilithiobenzene.

Each isomer of tetralithiobenzene (**4o**, **4m**, and **4p**) has only one type of proton to lose, resulting in the same conjugate base **4cb**. Their DPEs thus reflect the stability of the different isomers, and since **4o** is the most stable isomer, its DPE is the largest (393.1 kcal mol$^{-1}$), while the least stable isomer, **4b**, has the lowest DPE (377.4 kcal mol$^{-1}$).

The DPE of pentalithiobenzene **5** is 378.3 kcal mol$^{-1}$, which lies well within the range of DPEs of the polylithiated benzenes examined here.

The DPEs do not trend upward or downward with increasing lithium substitution. The lack of an upward trend may strike some as surprising, since in the sense we have been arguing, each increase in lithium substitution means a greater build-up of negative charge upon the phenyl core, suggesting perhaps a more severe penalty to loss of a proton and further increase of negative charge. But this is not apparent; examination of the simple series of reactions 1a, 2a, 3a, 4a, and 5 (which have in common all lithium cations adjacent and removal of an adjacent proton) gives the DPEs 382.7, 376.5, 387.1, 393.1, and 378.3 kcal mol$^{-1}$, respectively.

One interesting point is that the majority of the DPEs of the lithiated benzenes are less than the DPE of benzene itself. The only DPEs above that of benzene (391.8 kcal mol$^{-1}$ at this computational level) are reactions 1b, 1c, 3b, and 4a, all cases where effective lithium bridging in the conjugate base cannot be attained.

**Lithium Cation Affinity.** The reactions listed in Scheme 2 define the lithium cation affinity for all of the conjugate bases examined here. The free energy changes for these reactions are listed in Table 7.

Reaction 6 defines our reference: the lithium cation affinity of phenyl anion. $\Delta G$ for reaction 6 is −153.1 kcal mol$^{-1}$. The lithium cation affinities of the conjugate bases of lithiated benzenes do not vary much from this reference value, ranging from −146.5 to −163.0 kcal mol$^{-1}$. The least exoergonic reaction is reaction 7a, the capture of Li$^{+}$ by **1cbo**. This reflects really the very great stability of **1cbo**, rather than any relative instability of **2o**. (For example, **1cbo** is 1.4 kcal mol$^{-1}$ more stable than **1cbo**, yet **2o** is only 8.5 kcal mol$^{-1}$ below **2m**.) The most exoergonic reaction is reaction 10.

## Conclusion

The DPE of the polylithiated benzenes can all be less than that of benzene itself, as long as the proton removed is adjacent to a carbon bearing a lithium. The lowest DPEs are always found when all of the formal carbanion centers of the conjugate base are adjacent. This arrange-

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[27] Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *117*, 2590−2599.

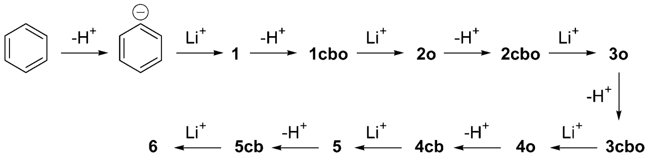
[28] Kroeker, R. L.; Bachrach, S. M.; Kass, S. R. *J. Org. Chem.* **1991**, *56*, 4062−4064.

[29] Hare, M.; Emrick, T.; Eaton, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 237−238.

ment of anions allows for optimum electrostatic interaction with the lithium counterions.

Tables 5 and 6 provide guidance toward the preparation of polylithiated benzenes. (A disclaimer must be proffered from the outset that these computations are for gas-phase chemistry, and great care must be used by anyone meaning to extrapolate them to solvent-phase chemistry.) If, for example, one was to sequentially deprotonate benzene and then capture the anion with lithium cation, the best sequence of intermediates is presented in Scheme 3. While this chemical pathway is highly idealized, it does point out one very important aspect toward the synthesis of polylithiated benzenes. Favorable ion triplet formation is quite stabilizing, enough to overcome the inherent destabilization of the polyanionic phenyl core, but only if the formal anionic centers are adjacent. Thus, attempts to create polylithiated benznes should target precursors and pathways that enable the formation of adjacent carbanions.

**SCHEME 3**



**Supporting Information Available:** Coordinates of all optimized B3LYP/6-311+G(d,p) structures, their absolute energies, and number of imaginary frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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