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Structures and Relative Energies of Polylithiated Benzenes

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The geometries of dilithiobenzene, trilithiobenzene, tetralithiobenzene, pentalithiobenzene, and hexalithiobenzene were optimized at the B3LYP/6-311+G** level. The lowest energy structures can be understood in terms of maximizing the electrostatic interactions between carbanions and lithium cations. In particular, in-plane lithium cations bridging ortho dianions is a geometric arrangement that is repeatedly found, as epitomized in the star-shaped D_{6h} hexalithiobenzene structure **11a**. Disproportionation reactions involving phenyllithium leading to polylithiated benzenes are exothermic, suggesting that it may be posible to prepare highly lithiated aromatic species.

Introduction

Organolithium compounds frequently possess structures radically different from their hydrocarbon analogues.[1] Lithium tends to bridge across carbon centers, bridge between carbon and hydrogen atoms, and coordinate above rings. Examples include dilithioacetylene,[2−4] which has a diamond shape (instead of being linear like acetylene itself), *trans*-1,2-dilithioethene,[1,5,6] where the Li−C−C angle is less than 90°, allowing for lithium to interact with the *syn*-hydrogen, and cyclopentadienyllithium,[7] where lithium sits above the ring on the C_5 axis. The structures of organolithium compounds can be understood simply in terms of electrostatic interactions. The C−Li bond is largely ionic; lithium cation bridges carbanion centers to maximize this favorable electrostatic interaction.[1,8,9] Streitwieser[10] has argued that the propensity for lithium to bridge carbon atoms results from a favorable electrostatic attraction of the ion triplet structure, as shown in **A**.

A

We recently noted that the preference of lithium to bridge carbanion centers can favorably stabilize dianions.[11] Removal of a proton from the ortho or para positions of phenyllithium gives a dianion with a bridging lithium cation, with favorable electrostatic interactions. In fact, it is less endothermic to remove a proton from phenyllithium than from benzene!

Schlosser et al. attempted to replace the hydrogens in 1,3,5-trifluorobenzene with lithium, but were able to only interchange at most two of them at the same time.[12] We therefore decided to examine the structures and energetics of all of the possible polylithiated benzene compounds using computational techniques. These are 1,2-dilithiobenzene (**1**), 1,3-dilithiobenzene (**2**), 1,4-dilithiobenzene (**3**), 1,2,3-trilithiobenzene (**4**), 1,2,4-triilithiobenzene (**5**), 1,3,5-trilithiobenzene (**6**), 1,2,3,4-tetralithiobenzene (**7**), 1,2,3,5-tetralithiobenzene (**8**), 1,2,4,5-tetralithiobenzene (**9**), 1,2,3,4,5-pentalithiobenzene (**10**), and 1,2,3,4,5,6-hexalithiobenzene (**11**).

Computational Methods

Organolithium structures are reasonably well obtained with fairly limited computational methods; even HF with small basis sets will produce structures with adequate geometries.[1] However, since a future goal is to quantify the acidities of the polylithiated benzenes, and these calculations require inclusion of electron correlation, polarization functions, and diffuse

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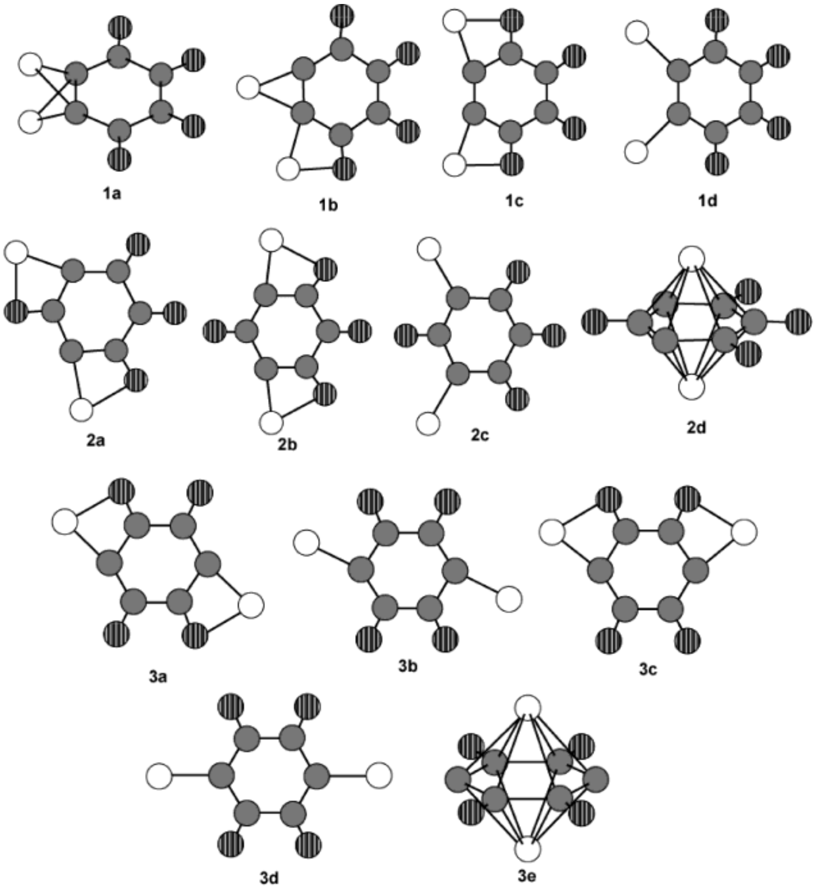

FIGURE 1. Optimized geometries of the various configurations of dilithiobenzenes (**1**−**3**). Carbons indicated as solid circles, lithiums as empty circles and hydrogens as striped circles.

functions,[13−15] we have chosen to examine compounds **1**−**11** at B3LYP/6-311+G**.[16] We have successfully employed this method to examine the acidity of phenyllithium and it should be appropriate here as well.[11]

A large number of structures are possible for **1**−**11**. We have completely optimized many of these, being careful to restrict optimizations within appropriate point groups where applicable. Sketches of the optimized structures are shown in Figures 1−5. Complete descriptions of all geometries are available in the Supporting Information.

All reported energies are electronic energies with unscaled zero-point vibrational energies. Analytical frequencies were determined to characterize all structures and obtain the zero-point vibrational energies. All computations were performed with GAUSSIAN-98.[17]

Results and Discussion

Dilithiobenzenes (1−3). We located four configurations of 1,2-dilithiobenzene (**1**), which are shown in Figure 1. Their relative energies are listed in Table 1. **1d** is the most "classical" of the four structures, the one expected from direct substitution of two hydrogen atoms with two lithium atoms. This structure is, however, a transition state that connects **1b** with its equivalent where lithium interacts with H_6 instead of H_3. **1b** has a lithium atom bridging in-plane the ortho dianion; the second lithium atom bridges a carbon anion and a neighboring hydrogen. Significantly less stable is **1c**, which has both lithium atoms bridging a carbanion center and a neighboring hydrogen. The most favorable structure is **1a**, lying 1.6 kcal mol^{-1} below **1b**. **1a** has both lithium atoms bridging the ortho dianion.

The configurations of 1,3- and 1,4-dilithiobenzene (**2** and **3**) parallel one another (see Figure 1 and Table 1). The "classical" structures **2c** and **3d** are local energy minima but are not the lowest energy configurations. Breaking the symmetry of each by swinging each lithium toward a neighboring hydrogen leads to a lower energy configuration, namely **2a** and **2b** and **3a** and **3c**. (**3b** is a hilltop having two imaginary frequencies.) Highest in

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TABLE 1. Relative Energies (kcal mol^{-1}) and Number of Imaginary Frequencies (NIMAG) for the Dilithiobenzenes (1−3)[a]

	1a	**1b**	**1c**	**1d**
E_{rel}	0.0	1.57	13.41	17.20
NIMAG	0	0	0	1

	2a	**2b**	**2c**	**2d**
E_{rel}	5.76	8.65	10.22	19.37
	(0.0)	(2.89)	(4.46)	(13.61)
NIMAG	0	0	0	0

	3a	**3b**	**3c**	**3d**	**3e**
E_{rel}	6.30	6.54	6.99	9.38	16.32
	(0.0)	(0.24)	(0.69)	(3.08)	(10.02)
NIMAG	0	2	0	0	0

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

energy are the bridging structures **2d** and **3e**. Unlike in **1a**, where the lithium cations can effectively interact with the two geminal carbanion centers, in **2d** and **3e** these lithium cations must reside above and below the rings and are quite removed from each carbanion (2.207 Å in **2d** and 2.242 Å in **3e**). The electrostatics advantage of bridging—each cation interacting with each anion—cannot be effectively achieved and the more classical structures are favored, though again lithium bridging across a carbanion and adjacent hydrogen is more favorable than simply an interaction between carbon and lithium alone.

The trends witnessed here will appear throughout the discussion of the polylithiated benzenes. Lithium prefers to bridge across adjacent carbanion centers, and the next best arrangement is where the lithium bridges a carbanion and an adjacent hydrogen. The structural feature of doubly bridged ortho dianions as in **1a** is often not the most favorable arrangement in other polylithiated benzenes (see below). This doubly bridging situation places the two lithium cations in near proximity, an unfavorable electrostatic arrangement, which can usually be avoided by an alternative configuration. However, for **1**, the only other alternative that preserves at least some ortho bridging is **1b**, but reducing the repulsion energy by moving the lithiums farther apart also means loss of favorable attractions to the carbanions: **1a** is therefore the lower energy configuration. Inferior is the situation where lithium interacts with a single carbanion center. A simple electrostatic model accounts for this trend. If one considers organolithium structures to be predominantly ionic, i.e., a carbanion/lithium cation pair, a Li^+ bridging across adjacent carbanion centers affords excellent favorable electrostatic interactions. Bridging across a carbanion and hydrogen is less favorable due to the diminished negative charge on hydrogen compared to a carbanion. Least favorable is the single Li^+-C^- interaction found in head-on σ-bonding interactions, such as in **1d**, **2c**, and **3d**.

The relative energy ordering of the dilithiobenzene isomers can thus be understood in terms of balancing unfavorable electrostatic repulsions between the carbanion centers (which would order **3** < **2** < **1**) against the favorable electrostatic interactions between the carbanions and the lithium cations. The lowest energy isomer is **1a**, in which the favorable bridging arrangement more than compensates for the repulsion of the ortho dianions. Even having one lithium cation bridging the ortho carbanions is enough to produce a favorable situation; **1b** is the second lowest energy isomer. The meta isomer **2a** is lower in energy than the para isomer **3a**, but the difference is small.

Trilithiobenzenes (4−6). The “classical” configuration of 1,2,3-trilithiobenzene **4f** is actually the highest energy isomer we located and is in fact a transition state connecting mirror images of **4b** (see Figure 2 and Table 2). The isomer **4b** has two in-plane lithium cations bridging neighboring carbanions. The third lithium bridges a carbanion and neighboring hydrogen. **4b** is about 35 kcal mol^{-1} more stable than **4f** due to the favorable bridging of the lithium cations. However, an even more favorable configuration can be obtained, that of **4a**, where the third lithium sits above the benzene ring and can favorably interact with all of the carbon atoms. This configuration allows for maximal electrostatic interaction between all three lithium cations and the three carbanions. **4c** is an interesting isomer where all three lithium cations bridge ortho carbanions. Generally ortho bridging is favorable, but here it requires two lithium cations to bridge the same pair of ortho carbanions and this brings them into close contact and induces an unfavorable electrostatic repulsion. Isomer **4d** is a local minimum lying 29.4 kcal mol^{-1} above **4a**. Compared to the lowest energy structure **4a**, **4d** moves one of the ortho-bridging lithium cations into a position below the benzene ring. This π-type ring interaction is less favorable than the ortho-bridging position because the distances between the cation and anion are greater. **4e** is the transition state connecting mirror image structures of **4d**, and it lies 15.94 kcal mol^{-1} above **4d**.

The optimized geometries of 1,2,4-trilithiobenzene **5** are shown in Figure 2 and their relative energies are listed in Table 2. The lowest energy structure is **5a**. This structure has one lithium cation bridging the ortho carbanions, the second sits above the ring, and the third is σ-bonded to the C4 carbanion. About 1 kcal mol^{-1} higher in energy is **5b**, which moves the σ-bonded lithium into the position below the ring. **5c** and **5d** have a lithium bridging the ortho carbanions and the other two bridge a carbanion and a neighboring hydrogen. The highest energy configuration is **5e**, which has two lithium cations bridging the ortho carbanions where their mutual repulsion makes the overall structure unfavorable.

We located six configurations of 1,3,5-trilithiobenzene **6**, shown in Figure 2. Again, the “classical” structure **6f** is the highest energy isomer. The two lowest energy structures are nearly degenerate: **6a** has one lithium above the ring plane, able to interact with all three carbanion centers, and the other lithium cations bridge a carbanion and neighboring hydrogen, while in **6b** all three lithium cations bridge a carbanion and neighboring hydrogen. **6c** differs from **6a** in the relative position of the in-plane lithium cations; they are farther apart in **6a** and this results in its greater stability. **6d** has two lithium cations above and below the ring and one σ-bonding lithium. **6e** is 1.5 kcal mol^{-1} more stable than **6f** due to the bridging interaction with the hydrogen atoms.

Comparing the most stable configuration of the three trilithiobenzene isomers, **4a** is 15.28 kcal mol^{-1} lower in

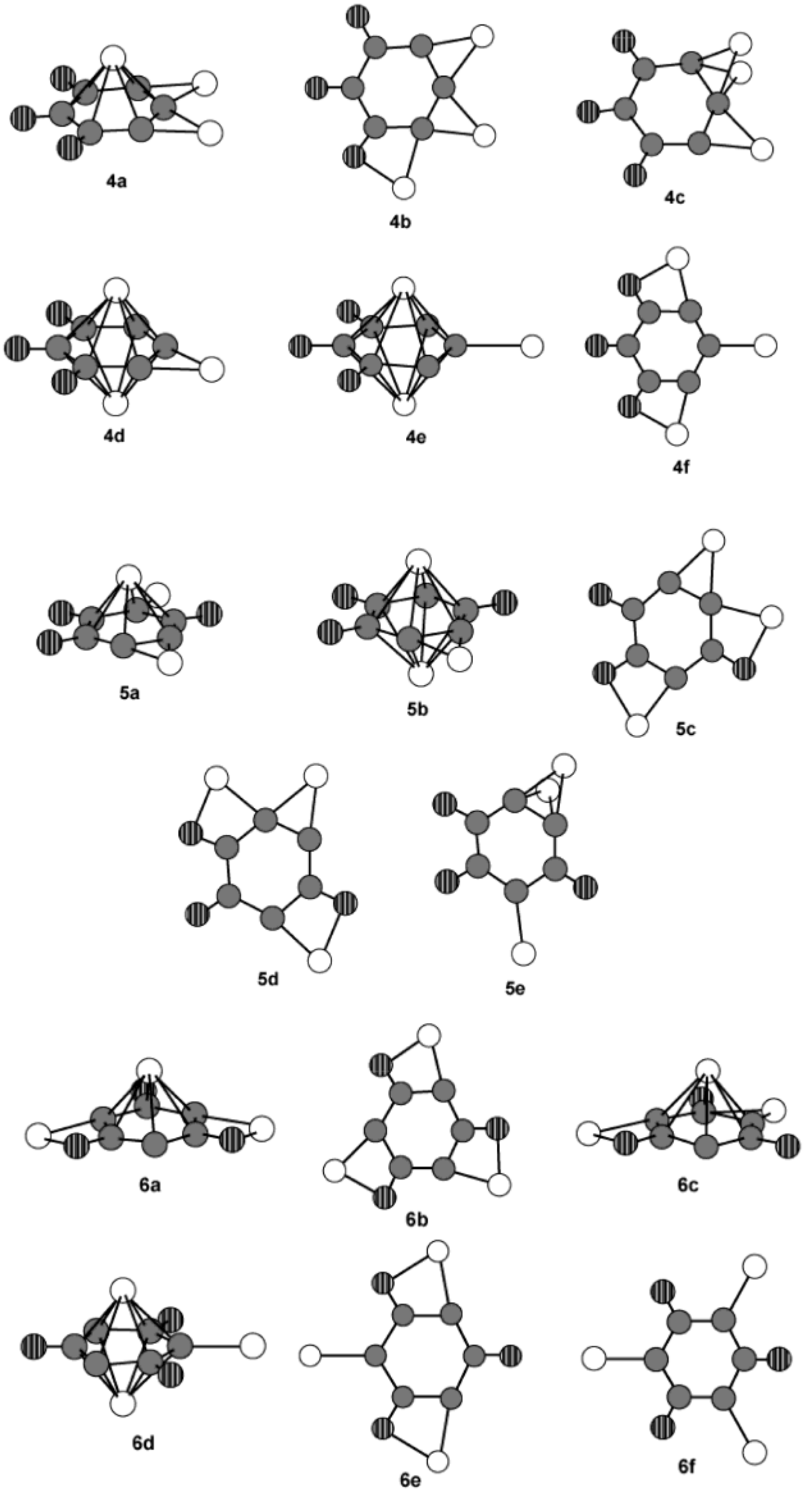

FIGURE 2. Optimized geometries of the various configurations of trilithiobenzenes (**4**−**6**).

energy than **5a**, which is nearly 16 kcal mol^{-1} below **6a**. If one considers the bare trianions, the 1,3,5-isomer would be the most stable since it avoids any ortho dianion repulsion and the 1,2,3-isomer would be the least stable. This is the exact opposite energy ordering of the salts. The ortho dicarbanion relationship can be very effectively bridged by a lithium cation, forming the very stable ion triplet arrangement. This leads to the very stable **4a** isomer. While the 1,3,5 arrangement of the carbanions minimizes their mutual repulsions, they are too far apart for a lithium cation to effectively bridge and therefore cannot recover enough electrostatic attraction.

Tetralithiobenzenes (7−**9).** The structures of 1,2,3,4-tetralithiobenzenes are sketched in Figure 3 and their relative energies are listed in Table 3. **7f** corresponds to the most “classical” structure, and this expresses some of the nonclassical behavior previously discussed: none of the lithium atoms are σ-bonded to a single carbon, but

TABLE 2. Relative Energies (kcal mol^{-1}) and Number of Imaginary Frequencies (NIMAG) for the Trilithiobenzenes (4–6)[a]

	4a	**4b**	**4c**	**4d**	**4e**	**4f**
E_{rel}	0.0	11.67	11.82	29.40	45.36	46.31
NIMAG	0	0	0	0	1	1

	5a	**5b**	**5c**	**5d**	**5e**
E_{rel}	15.28 (0.0)	16.33 (1.05)	22.58 (7.30)	23.01 (7.73)	24.23 (8.95)
NIMAG	0	0	0	0	0

	6a	**6b**	**6c**	**6d**	**6e**	**6f**
E_{rel}	31.16 (0.0)	31.19 (0.03)	34.23 3.07)	35.52 (4.36)	37.50 (6.34)	38.98 (7.82)
NIMAG	0	0	0	0	0	0

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

rather two bridge across ortho carbanion centers and the other two bridge a carbanion and an adjacent hydrogen. Most importantly, it lies 43.16 kcal mol^{-1} above the lowest energy structure **7a**. This lowest configuration has three lithium atoms bridging the ortho dicarbanions while the last lithium lies above the plane, interacting with all of the carbon atoms. **7b** is 14.4 kcal mol^{-1} higher in energy, though it differs from **7a** only in having the last lithium bridging a carbanion and an adjacent hydrogen instead lying above the ring. The next two lowest isomers **7c** and **7d** have the lithium bridging ortho carbanions only, with a pair of lithium cations (one above the plane and one below) bridging the same two carbanions. In **7e**, two lithium cations bridge ortho carbanions while the other two are above and below the plane. The most unfavorable structure we located is **7g**, a structure having four imaginary frequencies.

We located nine configurations of 1,2,3,5-tetralithiobenzene shown in Figure 3 and their relative energies are listed in Table 3. The two lowest energy structures, **8a** and **8b**, are very close in energy, differing by only 0.36 kcal mol^{-1}. Their structures are quite similar: both have two lithium cations bridging the two pair of ortho carbanions and one lithium cation above the ring plane. Their slight energetic difference is a consequence of the position of the fourth lithium atom: in **8a** it lies below the ring plane and can interact with all of the carbon atoms, while in **8b** it is σ-bonded to C5. The most "classical" structure is **8i**, the highest lying configuration, and it also happens to be a transition state. Relaxing the symmetry constraint of **8i** leads to **8c**, which lies 10.45 kcal mol^{-1} above **8a**. In **8c**, two lithium cations bridge the ortho carbanions and two bridge a carbanion and an adjacent hydrogen. Related to this structure are **8e** and **8f** where the difference is location of the lithium that bridges to a hydrogen. **8e** is disfavored relative to **8c** since it positions two lithium cations about a single carbanion, while **8f** is higher still in energy because it leaves a bare carbanion (C5). **8g** and **8h** are related to **8a** in that all three have two lithium cations in positions above and below the ring plane. Relative to the ground state **8a**, **8g** takes one of the ortho bridging lithium cations and σ-bonds it to C5, while in **8h** both of the ortho bridging lithium cations are σ-bonded instead; this arrangement is actually a transition state that interconverts **8g** and its mirror image.

Figure 3 shows six optimized configurations of 1,2,4,5-tetralithiobenzene and their relative energies are listed in Table 3. The "classical" structure, **9f**, in fact possesses two imaginary frequencies and is the highest energy structure we located, 68.24 kcal mol^{-1} above **9a**. The lowest energy structure **9a** has D_{2h} symmetry: two lithium atoms bridge across the ortho carbanions and the other two lie above and below the center of the ring. This structure allows for effective ion triplet interactions along with Li–ring interactions, while minimizing the repulsion among the lithium cations. **9b** and **9c** have similar arrangements, with two lithium cations bridging the ortho carbanions and two bridging a carbanion and a neighboring hydrogen. They differ in whether the these latter bridging lithium cations are para (**9b**) or meta (**9c**), with the former being 5.15 kcal mol^{-1} more stable due to lesser repulsion between these cations. **9d** is characterized by having all four lithium cations bridging the ortho carbanions in an out-of-plane fashion. This is less effective since it brings two cations in near proximity, resulting in **9d** being 24 kcal mol^{-1} less stable than **9a**. Last, **9e** has two lithium cations bridging the same pair of ortho carbanions, and the other two cations bridging a carbanion and an adjacent hydrogen. This structure lies 37.5 kcal mol^{-1} above **9a**.

The most stable tetralithiobenzene is **7a**, followed by **9a**, **7b**, and **8a**. These can be readily understood in terms of ion triplet interactions. The most stabilizing interaction is when a lithium cation bridges ortho dianions, and **7a** and **7b** have three of these, while others have just two. **9a** makes up for one less of these types of interactions with two lithium–benzene ring interactions. The configurations of **8** are higher due to the lack of an effective way for lithium to strongly bridge the C5 carbanion and any other carbanion.

Pentalithiobenzene (10). In Figure 4 we present eleven configurations of pentalithiobenzene. Their relative energies are listed in Table 4. The most "classical" structure is **10k**, which (as we have seen before) is the highest energy structure. It is also a transition state, connecting **10i** (lying nearly 17 kcal mol^{-1} lower in energy) and its mirror image. The lowest energy configuration that has even remotely "classical"-like structure is **10b**; this configuration has four lithium cations bridging ortho carbanions and one lithium bridging a carbanion and its neighboring hydrogen atom. But **10b** is not the lowest energy form, rather it is **10a**, which has maximized the number of lithium cations bridging the ortho carbanions (which is four) and places the last lithium above the ring plane, able to interact with all carbons. **10c** and **10e** have two lithium cations above and below the ring, but this reduces the number of ortho-bridging lithium cations, resulting in higher energy structures. **10g** is the transition state connecting **10c** with its mirror image. The remaining configurations have at least one pair of lithium cations bridging the same pair of ortho carbanions. This type of interaction positions these two cations in near proximity and increases their mutual repulsion.

Hexalithiobenzene (11). Hexalithiobenzene **11** has been synthesized and characterized by Lagow.[18,19] The

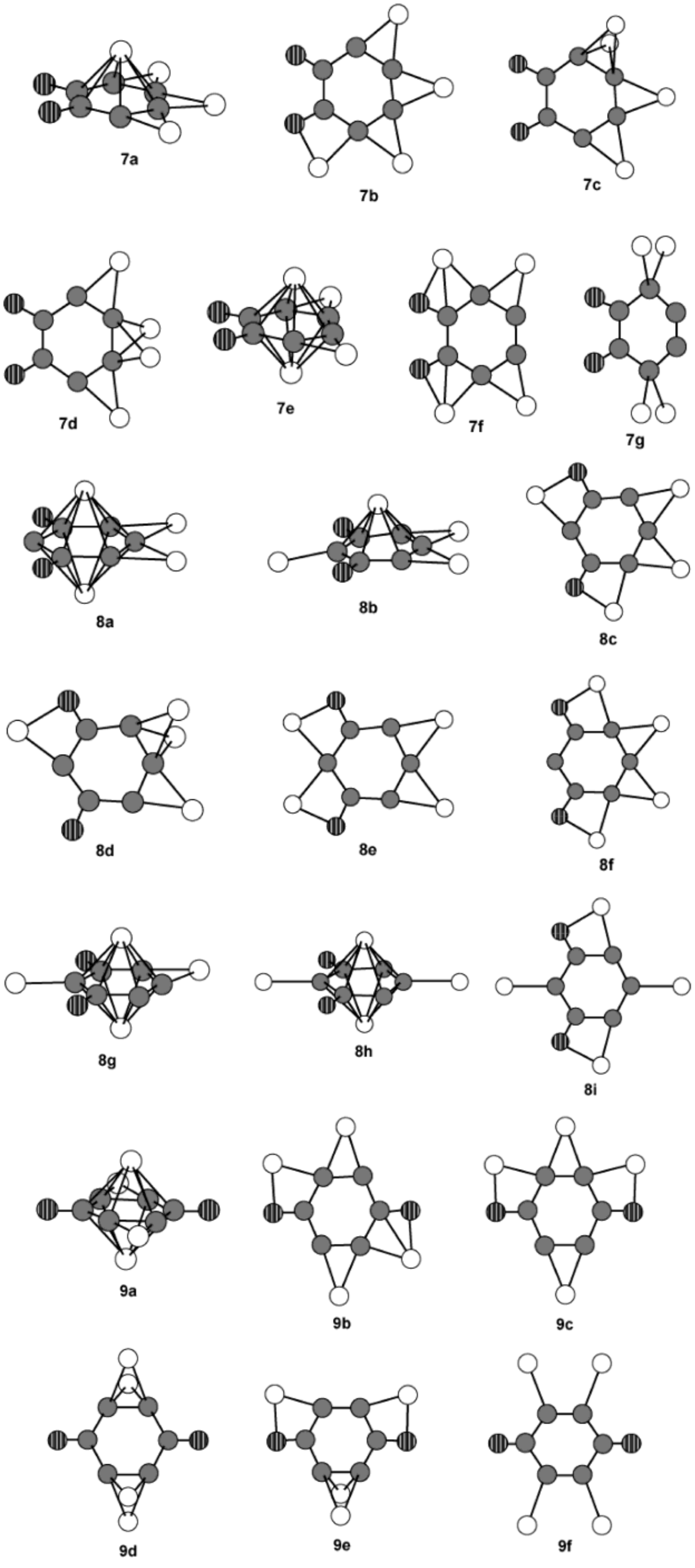

FIGURE 3. Optimized geometries of the various configurations of tetralithiobenzenes (**7**–**9**).

TABLE 3. Relative Energies (kcal mol^{-1}) and Number of Imaginary Frequencies (NIMAG) for the Tetralithiobenzenes (7−9)[a]

	7a	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**
E_{rel}	0.0	14.36	16.48	17.01	18.33	43.16	82.02
NIMAG	0	0	0	0	0	0	4

	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8i**
E_{rel}	14.94 (0.0)	15.30 (0.36)	25.39 (10.45)	31.39 (16.45)	32.58 (17.64)	33.94 (19.00)	39.03 (24.09)	56.50 (41.56)	64.79 (49.85)
NIMAG	0	0	0	0	1	0	0	1	1

	9a	**9b**	**9c**	**9d**	**9e**	**9f**
E_{rel}	10.06 (0.0)	27.04 (16.95)	32.16 (22.10)	34.08 (24.02)	47.59 (37.53)	78.30 (68.24)
NIMAG	0	0	0	0	0	2

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

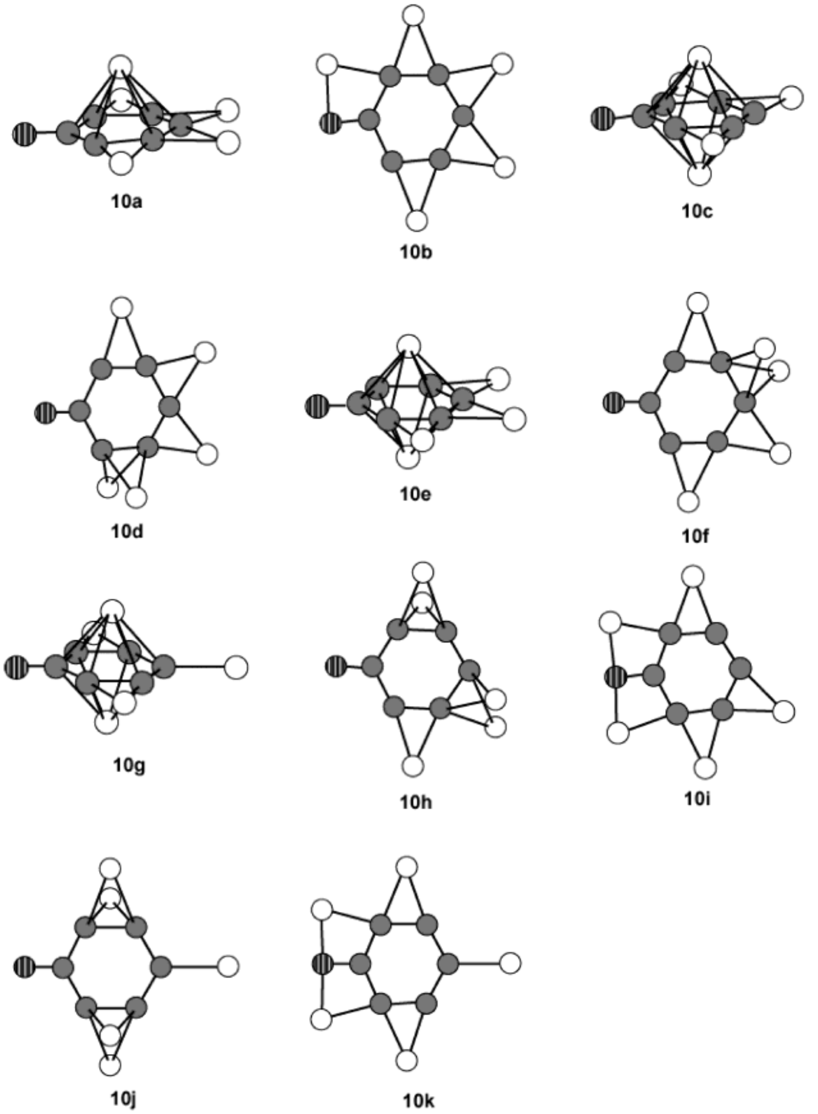

FIGURE 4. Optimized geometries of the various configurations of pentalithiobenzenes (**10**).

first computational study of **11** was the MP2/TZP//HF/TZP study of Xie and Schaefer.[20] They located four stable structures, corresponding to our **11a**, **11p**, **11r**, and **11s**. They found that **11a** is the lowest energy benzene structure and next is **11p** (64.4 kcal mol^{-1} above **11a**).

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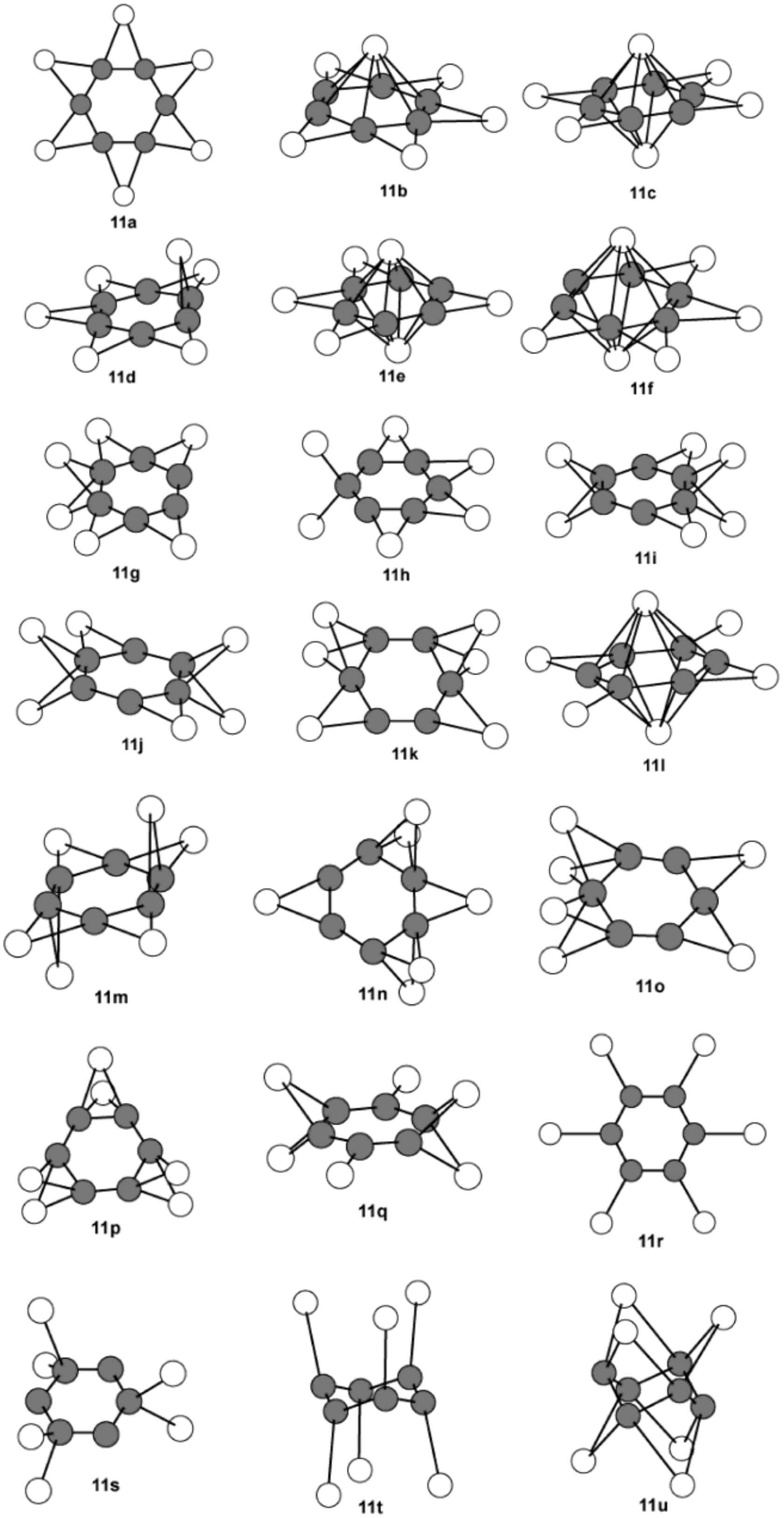

FIGURE 5. Optimized geometries of the various configurations of hexalithiobenzenes (**11**).

The "classical" structure **11r** lies 122.2 kcal mol^{-1} above **11a** and it has 11 imaginary frequencies, while **11s** is 10.7 kcal mol^{-1} higher still, with 8 imaginary frequencies. Smith[21] later confirmed the relative ordering of **11a**, **11p**, and **11r** using DFT methods, along with locating a lower energy isomer that does not preserve the benzene framework. A recent computational study[22] has reported the remarkably large second hyperpolarizability of **11a**.

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TABLE 4. Relative Energies (kcal mol^{-1}) and Number of Imaginary Frequencies (NIMAG) for the Pentalithiobenzenes (10)

	10a	10b	10c	10d	10e	10f
E_{rel}	0.0	13.03	14.21	20.04	23.07	24.40
NIMAG	0	0	0	0	0	0

	10g	10h	10i	10j	10k
E_{rel}	30.96	40.95	48.20	59.01	65.23
NIMAG	1	0	0	1	1

TABLE 5. Relative Energies (kcal mol^{-1}) and Number of Imaginary Frequencies (NIMAG) for the Hexalithiobenzenes (11)

	11a	11b	11c	11d	11e	11f
E_{rel}	0.0	11.82	20.50	21.33	22.18	31.87
NIMAG	0	0	0	1	0	0

	11g	11h	11i	11j	11k	11l
E_{rel}	35.68	41.28	44.05	44.76	49.82	50.94
NIMAG	2	3	0	0	0	2

	11m	11n	11o	11p	11q	11r
E_{rel}	55.04	56.17	57.66	66.44	69.96	125.30
NIMAG	5	0	3	0	4	12

	11s	11t	11u
E_{rel}	130.02	132.76	136.97
NIMAG	8	5	2

In Figure 5 we present 21 computed configurations of **11** and list their relative energies in Table 5. The lowest energy configuration is **11a**, as found by Xie and Schaefer. This structure has all six lithium cations bridging ortho carbanions, an arrangement that effectively maximizes their electrostatic attractions. The "classical" structure **11r** lies well above the minimum structure (125.20 kcal mol^{-1}), very similar to what Xie and Schaefer report, though we find 12 imaginary frequencies. We also find **11p** to be a local energy minimum that lies 66.44 kcal mol^{-1} above **11a**. **11p** also has the lithium cations bridging ortho carbanions, but here they pair up into three sets, where in each set one lithium is above the ring plane and the other is below the ring plane. This configuration brings the lithium cations closer together than in **11a**, thereby destabilizing the structure.

Unlike Xie and Schaefer, we were able to locate eight additional local minima lower in energy that **11p**. The second most favorable configuration is **11b**, which differs from **11a** by having one lithium positioned above the benzene ring, interacting with all 6 carbons, instead of in the in-plane ortho-bridging position. **11b** is 11.82 kcal mol^{-1} less stable than **11a**. **11d** is the transition state connecting **11a** and **11b** and lies 21.33 kcal mol^{-1} above **11a**.

In **11c**, **11e**, and **11f** two lithium cations lie above and below the ring plane, while the remaining four bridge ortho carbanions, differing in which pair are bridged. **11f** is substantially less stable than the other two because one carbanion has no in-plane interaction with a cation. Related to these three configurations is **11l**, a structure having two imaginary frequencies that correspond to interchange among **11c**, **11e**, and its mirror image. In terms of electrostatics, **11l** is disfavored relative to these three configurations by having 2 σ-bound lithium cations instead of having them bridge ortho carbanions. The other local minima (**11i**, **11j**, **11k**, and **11n**) have two pair of lithium cations bridging ortho carbanions; the more favorable separate these pair as much as possible. **11o**, which has these two pairs in adjacent positions, has three imaginary frequencies. **11q** is a high-order saddle connecting **11i**, **11j**, and their mirror images. The two highest lying structures **11t** and **11i** have D_{3d} symmetry, which breaks the planarity of the six-membered carbon ring. This leads to their extraordinarily high energies.

SCHEME 1

$2\,C_6H_5Li \rightarrow C_6H_4Li_2 + C_6H_6$
$2\,C_6H_5Li \rightarrow \mathbf{1a} + C_6H_6$ $\Delta E = -0.86$ kcal mol^{-1}
$2\,C_6H_5Li \rightarrow \mathbf{2a} + C_6H_6$ $\Delta E = +4.90$ kcal mol^{-1}
$2\,C_6H_5Li \rightarrow \mathbf{3a} + C_6H_6$ $\Delta E = +5.43$ kcal mol^{-1}

$C_6H_4Li_2 + C_6H_5Li \rightarrow C_6H_3Li_3 + C_6H_6$
$\mathbf{1a} + C_6H_5Li \rightarrow \mathbf{4a} + C_6H_6$ $\Delta E = -22.81$ kcal mol^{-1}
$\mathbf{1a} + C_6H_5Li \rightarrow \mathbf{5a} + C_6H_6$ $\Delta E = -7.53$ kcal mol^{-1}
$\mathbf{2a} + C_6H_5Li \rightarrow \mathbf{5a} + C_6H_6$ $\Delta E = +2.58$ kcal mol^{-1}

$C_6H_3Li_3 + C_6H_5Li \rightarrow C_6H_2Li_4 + C_6H_6$
$\mathbf{4a} + C_6H_5Li \rightarrow \mathbf{7a} + C_6H_6$ $\Delta E = -12.93$ kcal mol^{-1}
$\mathbf{4a} + C_6H_5Li \rightarrow \mathbf{8a} + C_6H_6$ $\Delta E = +2.00$ kcal mol^{-1}
$\mathbf{5a} + C_6H_5Li \rightarrow \mathbf{9a} + C_6H_6$ $\Delta E = -18.15$ kcal mol^{-1}

$C_6H_2Li_4 + C_6H_5Li \rightarrow C_6HLi_5 + C_6H_6$
$\mathbf{7a} + C_6H_5Li \rightarrow \mathbf{10a} + C_6H_6$ $\Delta E = -10.27$ kcal mol^{-1}

$C_6HLi_5 + C_6H_5Li \rightarrow C_6Li_6 + C_6H_6$
$\mathbf{10a} + C_6H_5Li \rightarrow \mathbf{11a} + C_6H_6$ $\Delta E = -15.84$ kcal mol^{-1}

Disproportionation Energetics. Sequential replacement of hydrogen with lithium is one potential method for creating polylithiated benzene (and potentially other aromatic systems as well). We observed an activation of the ortho proton in phenyllithium due to the ability of lithium to effectively bridge the resultant ortho dianion.[11] In Scheme 1, we list reaction energetics for representative disproportionation reactions that provide a sequential pathway for creating the polylithiated benzenes **1**−**11**.

The reactions that produce the most stable form of each of the classes of lithiobenzenes, i.e., **1a** for $C_6H_4Li_2$, **4a** for $C_6H_3Li_3$, and **7a** for $C_6H_2Li_4$, are all exothermic. The diproportionation reaction of phenyllithium to form **1a** and benzene is the least exothermic of the set, $\Delta E = -0.86$ kcal mol^{-1}. The ion triplet produces a small net stabilization here since the two lithium cations need to bridge the same pair of carbons, and therefore must be in close proximity. From here on out, each subsequent replacement of hydrogen with lithium is very exothermic: -22.8 kcal mol^{-1} to add the third Li, -12.9 kcal mol^{-1} to add the fourth Li, -10.3 kcal mol^{-1} to add the fifth Li, and -15.8 kcal mol^{-1} to add the sixth Li.

It is very important that one carefully interprets these energies. All of these computations are for gas-phase reactions, and they imply that gas-phase phenyllithium will convert entirely to hexalithiobenzene and benzene at equilibrium. We are currently examining the barriers and intermediates for this gas-phase process. Phenyllithium solution in alkanes is stable and clearly coordination, aggregation, and solvation effects cannot be ne-

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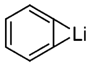
glected in considering solution-phase organolithium compounds. Nevertheless, the gas-phase results intriguingly suggest that polylithiation of aromatic species may be achievable.

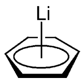
The calculations also suggest why the attempt to exchange all three protons in 1,3,5-trifluorobenzene failed.[12] Substituting in two lithium atoms creates an arrangement that is analogous to **2a** while the third substitution is analogous to **5a**. Disproportionation of two molecules of phenyllithium to **2a** and benzene is predicted to be endothermic. The reaction of **2a** with phenyllithium to give **5a** and benzene is also endothermic. Favorable ion triplet structures just cannot occur in these species due to the meta arrangement of the carbanions, which are too far apart to be effectively bridged by a lithium cation. Therefore, multiple hydrogen−lithium exchange is unlikely. The computations suggest that future attempts should point toward exchange of ortho positions.

Conclusions

The structures of the polylithiated benzenes can be understood in terms of maximizing the electrostatic interactions between the lithium cations and the carbanions imbedded within the benzene ring. A few simple structural patterns emerge. The most favorable arrangement is to have ortho dicarbanions singly bridged by a lithium cation, such as in **B**. Except for dilithiobenzene, the lowest energy structures all have maximal arrangements of this type. The next two best arrangements are placing a lithium cation above the benzene ring (**C**) or placing the lithium cation in a bridging arrangement across a carbanion and a neighboring hydrogen, as in **D**. Less favorable still is two lithium cations bridging the same ortho dicarbanions (**E**), which forces the two cations in near proximity, inducing some repulsion. The lowest energy structure of dilithiobenzene is of this type, because alternative configurations lack sufficient favorable electrostatic interactions between the lithium cations and the carbanion centers. The least favorable arrangement is a σ-bond between the carbon and lithium (**F**), the expected covalent bond that is not the preferred interaction in organolithium compounds. In fact, for all of the polylithiated benzenes examined, the classical covalent structure is extremely high in energy and often not a local minimum.



B



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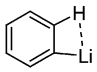

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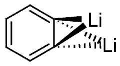
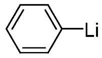


E



F

Sequential substitution of a hydrogen with a lithium from phenyllithium, using phenyllithium as the lithium source, is exothermic for each replacement. These results support further synthetic and computational study toward the preparation of polylithiated benzenes and aromatics in general, compounds that could hold synthetic promise.

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Supporting Information Available: Coordinates of all optimized B3LYP/6-311+G** 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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