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# Alkali Metal Salts of Dianions: A Theoretical and Experimental Study of $(C_6H_4)^{2-}M^+$ (M = Li and Na)

**Steven M. Bachrach,*,[†] Michael Hare,[‡,§] and Steven R. Kass*,[‡]**

*Contribution from the Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115, and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455*

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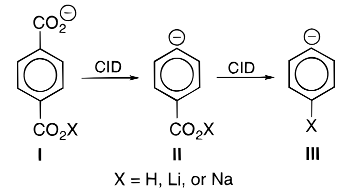
**Abstract:** Ab initio molecular orbital calculations have been carried out on the lithium and sodium salts of doubly deprotonated benzene. Full geometry optimizations of the three isomeric bare dianions and their corresponding lithium and sodium adducts were performed at the HF/6-31+G(d) and MP2/6-311+G(d,p) levels. The resulting structures are discussed. Deprotonation energies for phenyllithium and phenylsodium are reported. Phenyllithium is more acidic than benzene, while phenylsodium is only 3 kcal/mol less acidic. Alkali metal bridging and the formation of ion triplets can be extremely stabilizing and can lead to enhanced second deprotonations. Electrospray ionization mass spectrometry of terephthalic acid ($p$-$C_6H_4(CO_2H)_2$) followed by collision-induced dissociation of the resulting alkali metal salts of the dicarboxylate (**I**) affords $C_6H_4{}^{2-}Li^+$ and $C_6H_4{}^{2-}Na^+$. Formation of these species corroborates the theoretical prediction that alkali metal salts of dianions should be stable in the gas phase.

Organolithium compounds are notable for their oftentimes remarkably unusual structures.[1] Replacement of a hydrogen in a hydrocarbon with lithium usually leads to a very different geometry. Instead of the covalent C−H bond, the C−Li bond is largely ionic in nature. The dominance of electrostatic interactions leads to structures where the lithium bridges anionic centers, resulting in cyclic species with small angles. Streitwieser's ion triplet model explains these geometries as simply the arrangement that minimizes the electrostatic potential energy.[2] This ability of lithium (and sodium as well, but this has been examined to a much lesser extent) to bridge has important chemical consequences. In particular, the ability to interact with multiple anionic centers can lead to enhanced acidity.[3]

Recent advances in mass spectrometry, especially electrospray ionization (ESI), enable multiply charged ions, solvated ions, and metal-coordinated species to be formed in the gas phase.[4] The conjugate bases of compounds such as phenyllithium and phenylsodium, however, are unknown.[5] Spraying ions of this type directly into the gas-phase poses a considerable experimental challenge, while the aggregation and lack of volatility of phenyllithium has prevented us from generating $C_6H_4Li^-$ in a Fourier transform mass spectrometer via laser desorption or deprotonation of a heated sample.[6] An attractive alternative approach can be envisioned in which collision-induced dissociation (CID) of a $RCO_2X$ containing ion leads to the loss of carbon dioxide and the attachment of X to R. For example, multiple stages of CID starting with **I**, where X = H, gives rise to phenyl anion (Scheme 1), and similar behavior might be observed when X = Li or Na.

**Scheme 1**



Given the proclivity of lithium to enhance acidity and the attractiveness of the approach outlined in Scheme 1, we decided to examine the lithium and sodium salts of doubly deprotonated benzene from both a computational and experimental perspective. The calculations presented here indicate that phenyllithium is more acidic than benzene and phenylsodium has almost the same acidity as benzene. They also suggest that both conjugate bases are apt to be stable in the gas phase, which is in accord with the production of $C_6H_4{}^{2-}Li^+$ and $C_6H_4{}^{2-}Na^+$ via negative ion electrospray mass spectrometry.

## Methodology

**Computational Methods.** Accurate deprotonation energies (DPEs) can be obtained via computation provided that (a) the basis set contains polarization and diffuse functions, (b) cor-

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[†] Northern Illinois University.

[‡] University of Minnesota.

[§] Current address: Department of Chemistry, Ohio University, Athens, OH 45701.

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(5) In the liquid phase, all three $C_6H_4Li_2$, isomers have been synthesized. See: (a) Wittig, G.; Bickelhaupt, F. *Chem. Ber.* **1958**, *91*, 883−894. (b) Fraenkel, G.; Dayagi, S.; Kobayashi, S. *J. Phys. Chem.* **1968**, *72*, 953−961. (c) Fossatelli, M.; den Besten, R.; Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 527−528.

(6) No evidence for gaseous phenyllithium was obtained. Reed, D.; Kass, S. R. Unpublished results.

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relation is included at least through the MP2 level, and (c) zero-point energy corrections are made. We and others have found that calculations using this model will provide DPEs for carbon acids within a couple of kilocalories per mol of the experimental results.[7] Therefore, all structures examined here were fully optimized at the HF/6-31+G(d) and MP2/6-311+G(d,p) levels using the appropriate symmetry constraints. Analytical frequencies were determined at the HF/6-31+G(d) level to confirm the nature of each stationary point and to provide zero-point energies (ZPEs) and temperature corrections. Final energies were obtained by correcting the MP2 results from 0 to 298 K and incorporating the HF ZPEs; Hartree−Fock frequencies and ZPEs were scaled by 0.8929 and 0.9135, respectively.[8] To judge the adequacy of the computational method employed, the energies of the lithium salts were obtained at MP4/6-311+G(d,p) (to test the effect of further electron correlation) and MP2/6-311+G(2df,2pd) (to test the effect of a larger basis set) using the MP2/6-311+G(d,p) optimized geometry. As an additional test, the structures of the Li salts were reoptimized at B3LYP/6-311+G(d,p) and the energies corrected for ZPE and temperature using unscaled vibrational frequencies evaluated at this same level. All calculations were performed using the GAUSSIAN-94 code.[9]

## Experimental Methods

Electrospray mass spectra were obtained with a Sciex API III triple-quadrupole instrument. In this device the spray process is assisted by a flow of nebulizer gas which obviates many of the problems with electrical discharges encountered in negative ion electrospray.[10] Air was used as the nebulizer gas in this work, and oxygen served as a scavenger of stray electrons. Approximately a 100 $\mu$M solution of terephthalic acid dissolved in a 1:1 (v/v) mixture of methanol and water or acetonitrile and water was made slightly basic with sodium or lithium hydroxide. It was then sprayed into the mass spectrometer with the aid of a syringe pump so as to maintain a solution flow rate of 1−5 $\mu$L/min. Collision-induced dissociation (CID) spectra were obtained by selecting an ion of a given mass-to-charge ratio with Q1, fragmenting this ion with argon in Q2, and mass analyzing the products with Q3. In some cases ions were purposely broken apart in the extraction region and a resulting fragment was mass selected and subjected to a second CID event.

## Results and Discussion

Our aim is to determine the deprotonation energy of phenyllithium and phenylsodium using a computational approach. The comparison of these energies with the DPE of benzene is of greatest interest, but the latter quantity can also serve as a measure of the accuracy of the calculations since it has been determined a number of times. Davico et al. recently measured this energy very precisely by an equilibrium technique, and the DPE of benzene was determined to be 401.7 ± 0.5 kcal mol$^{-1}$.[11] The MP2/6-311+G(d,p) calculated value is 400.0 kcal mol$^{-1}$ at 298 K, which is in very good agreement with the experimental result. Since DPEs of carbon acids commonly are reproduced to within 2−3 kcal mol$^{-1}$,[7] we anticipate that the calculated results reported below will be equally reliable.

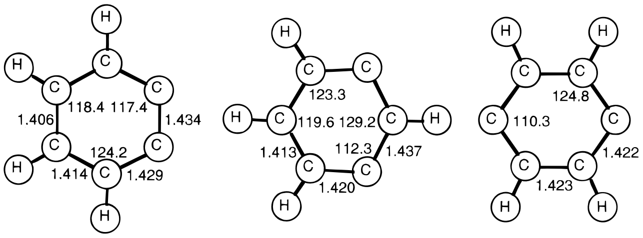
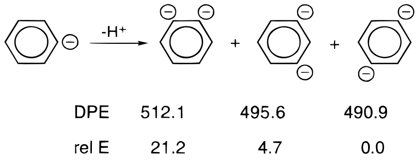


**Figure 1.** MP2/6-311+G(d,p) optimized structures of the ortho, meta, and para isomers of $C_6H_4^{2-}$. All distances are in angstroms, and all angles are in degrees.

**Scheme 2**



Deprotonation of phenyl anion to produce the dianion of benzene was examined next. Three isomers can be formed in this process: ortho, meta, and para dianions as shown in Scheme 2. The smallest DPE (490.9 kcal mol$^{-1}$) is for the production of the para dianion, which is 4.7 kcal mol$^{-1}$ less than for forming the meta dianion. The largest DPE (512.1 kcal mol$^{-1}$) is for making the ortho dianion. All of these DPEs are substantially larger than for the first deprotonation of benzene. This is not surprising since two full negative charges are formed and they experience the entire brunt of the electrostatic repulsion between each other without any compensating factors. The para dianion is favored simply because the negative charges are farthest apart; the ortho dianion is highest in energy due to the strong repulsion between the adjacent anionic centers. This is seen in the distorted geometries of these dianions shown in Figure 1. The bond distances to the anionic carbons are long, particularly the C−C distance between the two charged carbons in the ortho isomer and the bonds between the anionic carbons and C2 in the meta isomer. The angles about the deprotonated carbons are all considerably smaller than the usual 120° found for a formal sp$^2$ center, while the angles at some of the other carbon centers expand above 120°. These angular distortions serve to further separate the charges from each other.

Without some substantial assistance, removal of two protons from benzene is highly unlikely, and the resulting product undoubtedly would be unstable with respect to electron loss. This process can be facilitated, however, by a species which can stabilize a dianion. Metal cations can serve this function, and if they are small enough, bridging between the two charge centers can occur to form an ion triplet. Streitwieser has shown that the ion triplet is a very stable arrangement for the charges.[2] Lithium and, to a lesser extent, sodium are prime candidates for providing the necessary stabilization. Consequently, the structures of all three benzene dianions complexed with a lithium or sodium cation were examined.

The optimized structures of the three dianions complexed with lithium cation are drawn in Figure 2, while Figure 3 shows the sodium complexes. The lithium and sodium structures are very similar; the only notable difference is the longer C−Na distances

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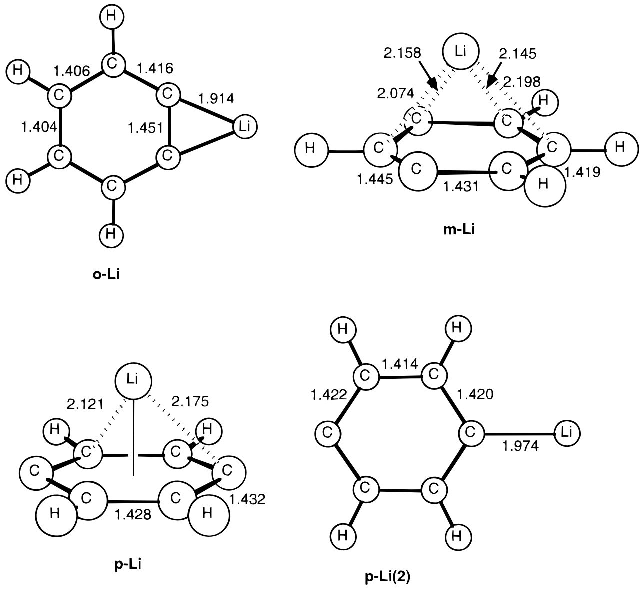


**Figure 2.** MP2/6-311+G(d,p) optimized structures of the isomers of $C_6H_4{}^{2-}Li^+$. All distances are in angstroms, and all angles are in degrees.

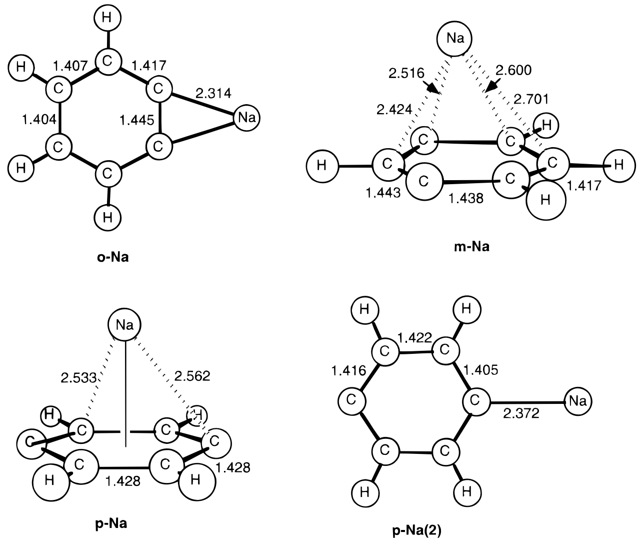


**Figure 3.** MP2/6-311+G(d,p) optimized structures of the isomers of $C_6H_4{}^{2-}Na^+$. All distances are in angstroms, and all angles are in degrees.

compared to the C−Li distances. We will, therefore, primarily discuss the geometries of the lithium species, and note only some particular features of the sodium compounds.

The complex formed between the lithium cation and the ortho dianion (labeled ***o*-Li**) has $C_{2v}$ symmetry. In this species, the lithium cation bridges the two formal charge centers and lies within the plane of the phenyl ring. The distance between the two anionic carbons is very long (1.451 Å), 0.017 Å longer than in the bare dianion. This lengthening results from a shifting of the negative charge toward the lithium cation, thereby forcing the carbon centers to move further apart in order to minimize the charge repulsion. In the sodium salt this effect is not as dramatic due to the longer C−Na distance, which reduces the electrostatic attraction between the cation and dianion and lessens the concentration of charge.

The most stable complex between $Li^+$ and the meta dianion (***m*-Li**) has the lithium above the plane of the ring bridging the $\pi$ system of the aromatic ring. This complex has $C_s$ symmetry, and the lithium resides nearly above the center of the ring. It actually is closer to C2 and C4 than to the carbanion centers (C1 and C3), indicating that the lithium interacts with the entire ring system. It is displaced, nevertheless, toward C1 and C3 to better interact with the excess charge at this end of the molecule. In the sodium analogue, the sodium cation is less symmetrically situated above the ring and is displaced much more toward the C2 end of the molecule. Given the greater size of this cation, there are poorer electrostatic interactions with the ring electrons and this enhances the ionic interaction with the formal lone pairs of electrons at C1 and C3.

**Table 1.** Deprotonation Energies[a] (kcal mol$^{-1}$) of Phenyllithium Using Various Computational Methods

| product | MP2/6-311+ G(d,p) | MP4/6-311+ G(d,p) | MP2/6-311+ G(2df,2pd) | B3LYP/6-311+ G(d,p) |
|---|---|---|---|---|
| ***o*-Li** | 389.5 | 390.5 | 389.7 | 389.8 |
| ***m*-Li** | 401.3 | 401.4 | 403.7 | 404.3 |
| ***p*-Li** | 396.8 | 397.4 | 399.2 | 400.2 |

[a] Energies calculated using the MP2/6-311+G(d,p) geometries (except B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)) and include temperature and ZPE corrections (see Methodology).

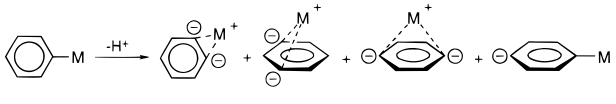
The lowest energy structure of the complex formed between $Li^+$ and the para dianion (***p*-Li**) has $C_{2v}$ symmetry. Lithium lies above the center of the ring, effectively bridging the two anionic centers and also interacting with the other carbon atoms. Due to the distortion of the ring, which serves to separate the two anionic centers (the C1−C4 distance is 3.05 Å in the bare dianion, ***p*-Li** and ***p*-Na**), the cation lies slightly closer to the formally neutral carbon atoms than to the charge-bearing ones. Both of the latter atoms (C1 and C4) are slightly bent out of the ring plane (0.062 Å in ***p*-Li** and 0.070 Å in ***p*-Na**, or put another way, the pucker angle is 175.6° in ***p*-Li** and 175.0° in ***p*-Na**) toward the lithium cation.

Another $C_{2v}$ structure for the complex with the para dianion (***p*-Li(2)** and ***p*-Na(2)**) was located. In this compound the lithium cation lies in the ring plane and is coordinated with just one of the anionic centers. Since this structure lacks the desirable bridging interactions, it is significantly higher in energy ($\Delta E$ = 22.7 kcal mol$^{-1}$) than the bridging structure ***p*-Li**.

While the MP2/6-311+G(d,p) method provides excellent DPEs for carbon acids,[7] these studies have dealt with monoanions, while here we are interested in (formally) dianions. To test the adequacy of the computational methods, we computed the three DPEs of phenyllithium at MP4/6-311+G(d,p) and MP2/6-311+G(2df,2pd) using the MP2/6-311+G(d,p) geometries and at B3LYP/6-311+G(d,p); these are listed in Table 1. The difference in DPEs computed at MP2 and MP4 with the same basis set is less than 1 kcal mol$^{-1}$, suggesting that further accounting of electron correlation will have little effect. The effect of expanding the basis set is slightly greater. There is no change in the DPE leading to ***o*-Li** when the larger basis is used, but the DPEs leading to the two other isomers increases by slightly more than 2 kcal mol$^{-1}$. The DPE leading to ***o*-Li** is essentially identical at MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p), though the DPEs to the other two isomers are higher by more than 3 kcal mol$^{-1}$ at the latter level. There is close agreement of the DPEs estimated by B3LYP and MP2 with the larger basis set. Since all of these variations result in minor changes in the DPEs, we believe that the MP2/6-311+G(d,p) method is appropriate, especially in terms of the ordering of the relative energies of the isomers. Further, the DPE leading to ***o*-Li**, the least endothermic (most acidic) process, is insensitive to the computational methods tested here.

The DPEs of phenyllithium and phenylsodium are given in Scheme 3 along with the relative energies of the different product ions. Two competing effects, electrostatic repulsion

**Scheme 3**



| | | | | | |
|---|---|---|---|---|---|
| M = Li | DPE | 389.5 | 401.3 | 396.8 | 419.5 |
| | rel E | 0.0 | 11.8 | 7.3 | 30.0 |
| M = Na | DPE | 402.8 | 411.3 | 407.5 | 415.5 |
| | rel E | 0.0 | 8.5 | 4.7 | 12.7 |

between the anionic centers and electrostatic stabilization of the ion triplet structures, account for the energy differences. The first of these is reflected in the relative energies of the bare dianions: $E_{\text{para}} < E_{\text{meta}} < E_{\text{ortho}}$. The latter effect depends on the distance between the complexing lithium cation and the deprotonated centers; as they get closer together the interaction increases, so $E_{\text{para}} > E_{\text{meta}} > E_{\text{ortho}}$. These competing trends manifest themselves in the relative energy of the series: $E_{\boldsymbol{o}-\mathbf{Li}} < E_{\boldsymbol{p}-\mathbf{Li}} < E_{\boldsymbol{m}-\mathbf{Li}} < E_{\boldsymbol{p}-\mathbf{Li(2)}}$. The same order is found for the sodium series. In ***o*-Li** and ***o*-Na**, the bridging metal strongly interacts with the two adjacent anionic centers and overcomes their mutual repulsion. The ion triplet stabilization in these ions is about 25−30 kcal mol$^{-1}$ greater than in ***p*-Li** and ***p*-Na** based upon the energy differences between the bare anions and the complexes. In contrast, the energy difference between ***p*-Li** and ***m*-Li** (and between ***p*-Na** and ***m*-Na**) is about the same as between the bare para and meta dianions, which suggests that their complexation energies are comparable.

Perhaps of most interest, however, is the value of the DPEs themselves, particularly in how they compare with the acidity of benzene.[12] The deprotonation energy of phenyllithium to afford ***o*-Li** is only 389.5 kcal mol$^{-1}$, or 10.5 kcal mol$^{-1}$ *less* than the DPE of benzene. The DPE leading to ***p*-Li** also is less than that of benzene, while the DPE leading to ***m*-Li** is only slightly greater than that of benzene. The deprotonation energies of phenylsodium are all greater than that of benzene, but the lowest value (that leading to ***o*-Na**) is only 2.8 kcal mol$^{-1}$ higher. Given the relative accuracy of these types of calculations we can assert that phenyllithium is more acidic than benzene.

These energies indicate that removal of the second proton from benzene will be easier than the first as long as a lithium cation is present. Clearly, the ability of lithium to form an ion triplet structure and bridge adjacent anionic centers is extremely stabilizing. Sodium cation is not quite as effective due to the longer distances involved; even so, the second deprotonation is nearly isoenergetic with the first. A few previous calculations of lithium salts also have suggested an enhanced second deprotonation due to favorable ion triplet structures.[3]

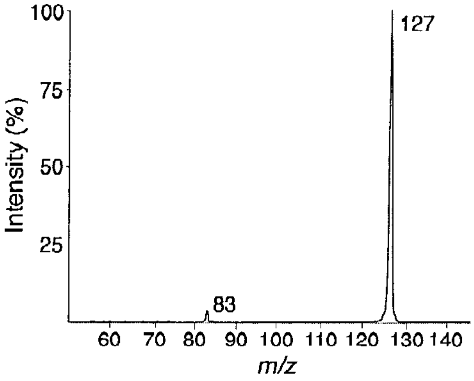


**Figure 4.** Collision-induced dissociation spectrum of $\mathrm{LiC_6H_4CO_2^-}$ (*m/z* 127). The fragment ion at *m/z* 83 corresponds to $\mathrm{C_6H_4Li^-}$.

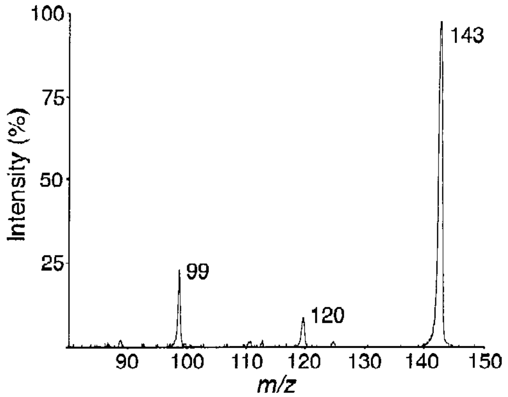


**Figure 5.** Collision-induced dissociation spectrum of $\mathrm{NaC_6H_4CO_2^-}$ (*m/z* 143). The fragment ions at *m/z* 99 and 120 correspond to $\mathrm{C_6H_4Na^-}$ and $\mathrm{{}^{\bullet}C_6H_4CO_2^-}$, respectively.

These results suggest that the dianion salts of benzene should be stable species in the gas phase. Evidence for their existence has been obtained using negative ion electrospray mass spectrometry. Alkali metal adducts of terephthalic acid (**I**, X = Li or Na, see Scheme 1) were observed as strong signals in the spectra of the dicarboxylic acid when lithium or sodium hydroxide was added to promote dianion formation. Collision-induced dissociation of these ions in the ion extraction region (or Q2) results in the loss of carbon dioxide and, presumably, affords a phenyl anion/carboxylate salt (**II**). Alternatively, **II** could be an isomeric phenyl salt/carboxylate anion, but this structure would require rearrangement concurrent with decarboxylation and this seems less likely to us at this time. Further fragmentation of **II**, where X = Li, leads to a second decarboxylation and the formation of a small signal at *m/z* 83 (Figure 4). This ion corresponds to the lithium salt of doubly deprotonated benzene (**III**, X = Li). In a similar fashion, CID of the sodium salt of **II** gives a stronger signal of the alkali metal adduct of doubly deprotonated benzene (**III**, X = Na; *m/z* 99) in addition to a fragment corresponding to $\mathrm{C_6H_4CO_2^-}$ (*m/z* 120, Figure 5). These experiments are in accord with the theoretical prediction that the lithium and sodium cation salts of the conjugate base of phenyl anion are stable.

## Conclusions

High-level ab initio calculations indicate that thermodynamic deprotonation of phenyllithium or phenylsodium will produce a bridged ortho dianion that is remarkably stable. The DPE of phenyllithium is predicted to be only 389.5 kcal mol$^{-1}$ or about 10 kcal mol$^{-1}$ less than that for benzene. The relative energies of the isomers of these salts is based on an interplay of competing effects: Coulombic repulsion of the dianions vs electrostatic stabilization of the ion triplet. Ions corresponding to $\mathrm{C_6H_4^{2-}Li^+}$ and $\mathrm{C_6H_4^{2-}Na^+}$ have been observed by electrospray mass spectrometry, thereby confirming their stability.

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[12] The computed acidity of benzene (400.0 kcal mol$^{-1}$) rather than the experimental value (401.7 ± 0.5 kcal mol$^{-1}$) was used in the following comparisons for consistencies sake.