Up to Six Units of Charge and Twist-Boat Benzene Moieties: Alkali Metal Reduction of Phenyl-Perisubstituted Benzenes[1]

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Abstract: Phenyl-perisubstituted benzenes, tetraphenylbenzene (**1**) and hexaphenylbenzene (**2**), were reduced by lithium and sodium metal in THF-d_8 under high vacuum. The reduction process and the nature of the reduction products were studied by NMR. Tetraphenylbenzene was reduced by both metals to yield the corresponding dianionic salt. It was found that the addition of extra charge into the system, restricted the free rotation of the four phenyl substituents about the σ bond connecting them to the central ring ($G^{\ddagger}_{181} = 7.8 \pm 0.2$ kcal mol^{-1}). The reaction of the alkali metals with **2** yielded four diamagnetic species: the first three were assigned to the dianion, tetraanion, and the surprising hexaanion of **2**. These species were calculated using density functional theory (DFT) and were found to have central benzene rings with an unusual twist-boat geometry. Computational and experimental evidences show that each phenyl ring and its attached carbon of the central ring behave like a benzyl anion. We therefore view the hexaanion of **2** as a cyclohexa(benzylanion). The fourth diamagnetic species was a product of a double-sided cyclization, which yielded the dianion of dihydro-9,18-diphenylphenanthro[9,10-b]triphenylene (9,18-diphenyltetrabenz[a,c,h,j]anthracene dianion, **3**$^{2-}$). Reaction of the dianion with oxygen gave **3** in improved yields compared to literature preparations.

Introduction

Benzene, the basic subunit of π-conjugated systems, can only be reduced to a radical anion.[2] However, highly substituted benzenes can reach the dianionic state, for example, rings that contain four and six trimethylsilyl (TMS) substituents.[3]

Phenyl groups are also candidates to act as stabilizers to a benzene dianion, by means of extending its π-system. Biphenyl (**4**) is the smallest member in the family of phenyl-substituted benzenes, which may be regarded as a benzene substituted by one phenyl (*n* = 1). Its reduced species has been studied.[4,5] Other substituted benzenes of this family that were examined are *ortho*, *meta*, and *para*-terphenyl[5,6] (**5**, *n* = 2), and 1,3,5-triphenylbenzene[7] (**6**, *n* = 3). These were reduced by alkali metals up to a radical anion or a dianion. Additional systems which are substituted by a greater number of phenyl groups

attached to benzene are tetraphenylbenzene (**1**, *n* = 4) and hexaphenylbenzene (**2**, *n* = 6).[8] The complete reduction of **1** and that of **2** which is thoroughly studied in this contribution[9] is therefore of great interest, particularly due to their key role together with other perisubstituted benzenes in various fields of research.[10,11]

Some general guidelines can be taken from the perisubstituted phenyl benzene systems that have been investigated. The substituent phenyl groups usually exhibit a pronounced charge

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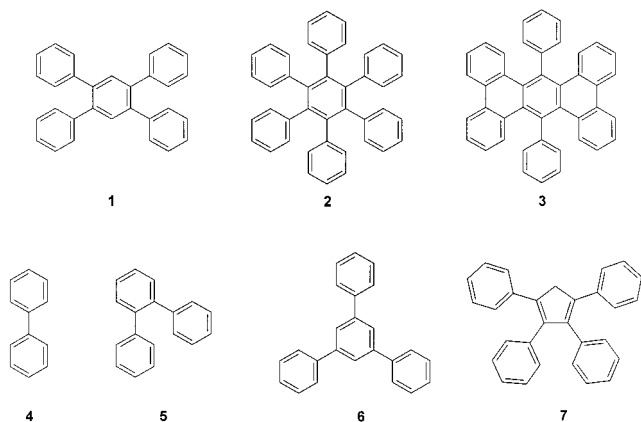
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Table 1. NMR Chemical Shifts of for the Li and Na Salts of $\mathbf{1}^{2-}$

compound		ortho	meta	para	ipso	central	a
$\mathbf{1}^{2-}$/2Li$^+$	δ_H	6.22	6.61	5.84	-	-	7.23
(240K)	δ_C	121.7	127.0	109.7	139.8	108.1	137.2
$\mathbf{1}^{2-}$/2Na$^+$	δ_H	6.18	6.64	5.93	-	-	7.31
(220K)	δ_C	121.1	127.1	111.5	139.2	106.4	129.4

NMR was proved to be a powerful tool for the study of structural as well as of electronic and magnetic phenomena of diamagnetic species.[17] Species with a symmetry of C_3 or higher may possess a triplet ground state for their dianions due to the degeneracy of their LUMO π-orbitals. Such is the case for 1,3,5-triphenylbenzene dianion, for example, which does not show NMR spectra.[18] However, due to a Jahn–Teller effect,[19,20] diamagnetic dianions of highly symmetrical molecules with singlet ground states are obtained, showing NMR spectra.[21] The high symmetry (D_6) of **2** might therefore raise difficulties in studying its charged species by NMR should a triplet state be a dominant one. Here we report that we have achieved a stepwise reduction of **1** and **2** by the reaction with lithium or with sodium in THF-d_8 under high vacuum and the process follow-up by NMR. The diamagnetic products of these reactions were analyzed by NMR techniques and were selectively calculated using the density functional theory[22] (DFT).

Results and Discussion

Reduction of Tetraphenylbenzene (1). Reaction of **1** with sodium or lithium yields a thermochromic diamagnetic species, blue at room temperatures, which within a few hours turns red at −78 °C. The centers of gravity[23] of the ¹H NMR and ¹³C NMR of the new species are shifted to higher fields with an overall change in ¹³C chemical shift ($\Sigma\delta_C$) of 283 ppm, in line with a formation of a dianion (Table 1). The chemical shift of the *ortho* protons broadens and decoalesces (180.5 K; 5.94 ppm) into two broad signals at lower temperatures (165 K; 4.90, 6.93 ppm). In contrast, the spectrum of the neutral molecule does not show any spectral temperature dependence (¹³C and ¹H NMR) even at 165 K. This behavior is attributed to an enhanced barrier of rotation of the phenyls due to reduction, that is, 7.8 ± 0.2 kcal mol⁻¹ at the coalescence temperature compared to an upper limit of 5.0 ± 0.2 kcal mol⁻¹ for the neutral

alternation effect.[12] The *ortho* and *para* positions carry a negative charge, while the *meta* and *ipso* positions serve as almost neutral or slightly positive positions. An alternate distribution of charge on phenyl groups was also observed in heterocyclic dianions bearing phenyls.[13]

The barrier of rotation of the phenyl ring substituents about the single bonds, which connect them to the central benzene ring, was found to rise as a result of reduction, suggesting that the motif of conjugation is increased; thus, the π-bond order between the benzene rings is higher.[5] For the same reason the calculated torsional angle between the phenyl substituents and the central benzene ring in the ground state of the perturbed systems is decreased upon charging.

Reduction may also drive the molecule to a new conformation of the central benzene ring. This behavior was found for hexakis-(trimethylsilyl)benzene dianion by Sakurai et al.[3a] The benzene ring loses the moderate chair conformation (torsional angle of 9.8°) seen in the neutral molecule, and adopts a boat conformation with localized double bonds in the dianion lithium salt as shown by X-ray crystallography.[3b] This is in accord with theoretical predictions for benzene dianion lithium complexes.[14] On the other hand, the central benzene ring of 1,2,4,5-tetrakis-(trimethylsilyl)benzene[3c] and the tethered hexasilyl derivated benzene,[3d] which are planar, maintain their planarity in their dianion lithium salts, thus creating an 8π electron system, which has antiaromatic characteristics as shown by an extremely low field ⁷Li NMR chemical shift (10.7 ppm). However, the effective charge on the benzene in these systems should actually be smaller than two electrons due to the electron-withdrawing TMS groups.

In light of these findings, special notice should be given to any conformational changes of the tested molecules due to their reduction. Unlike **1**,[15] the solid-phase structure of **2** was characterized by Bart et al. by X-ray crystallography.[16] They showed that the central benzene ring is planar and the six attached phenyl groups form a propeller conformation ($\Phi \cong 67°$) with a D_6 symmetry. The elongation of the C−C bonds between the central ring and each of the substituting phenyls to merely a single bond (1.47−1.53 Å) is evidence for only partial conjugation.

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Table 2. Experimental and Calculated (GIAO B3LYP/6-31G*//B3LYP/6-31G*) NMR Chemical Shifts of for the Li and Na Salts of 2^{2-}, 2^{4-}, and 2^{6-}

compound			*ortho*	*meta*	*para*	*ipso*	central
2^{2-}/2Li$^+$ (200 K)	δ_H		6.42	6.55	6.18	-	-
	δ_C		128.4	127.2	116.4	144.9	117.1
2^{2-}/2Na$^+$ (220 K)	δ_H		6.34	6.55	6.16	-	-
	δ_C		128.3	127.4	115.8	143.8	117.5
2^{2-} − calculated^a	δ_H		6.39	5.89	5.21	-	-
	δ_C		114.7	111.8	97.8	133.8	119.5
2^{2-}/Li(dimethyl ether)$_2^+$ (calculated)^a	δ_H		7.67	7.17	6.49	-	-
	δ_C		117.4	116.2	106.6	134.9	112.5
2^{4-}/4Li$^+$ (200 K)	δ_H		5.56	6.25	5.37	-	-
	δ_C		121.7	127.3	103.4	140.4	99.5
2^{4-}/4Na$^+$	δ_H		5.35	6.30	5.13	-	-
	δ_C		-	-	-	-	-
2^{4-} (calculated)	δ_H		5.02	4.74	2.83	-	-
	δ_C		112.7	109.0	77.5	106.6	147.7
2^{6-}/6Li$^+$ (180 K)	δ_H	ABB′CC′	3.78	6.28	4.49	-	-
		ABCDE	4.64, 4.79	6.35, 6.00	4.55	-	-
	δ_C		-	-	-	-	-
2^{6-}/6Na$^+$ (180 K)	δ_H	ABB′CC′	3.47	6.19	4.27	-	-
		ABCDE	4.55, 4.81	6.36, 5.96	4.35	-	-
	δ_C	ABB′CC′	120.6	125.9	87.9	124.6	96.2
		ABCDE	117.5, 107.5	130.1, 127.7	88.4	123.5	93.4
2^{6-} (calculated)	δ_H	ABB′CC′	4.74	4.68	2.86	-	-
		ABCDE	5.06, 5.25	4.95, 4.60	2.81	-	-
	δ_C	ABB′CC′	117.3	109.4	78.1	117.5	169.0
		ABCDE	106.4, 114.3	111.6, 106.0	77.2	101.2	137.1

^{a} Averaged values are presented to facilitate the comparison with the experimental data. Optimized TMS isotropy (D$_2$d: ^{1}H: 31.92; ^{13}C: 183.73).
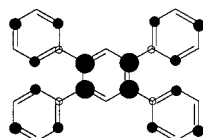
Figure 1. Experimental (^{13}C NMR) charge distribution in 1^{2-}.

compound.[24] Such behavior is absent for the *meta* protons, probably because the difference between the magnetic environments of the two sites is not too large.[25] Reaction of the reduced species with D$_2$O yielded the dideutero derivative ($m/z = 386$), while quenching with oxygen regenerated the starting material **1**. Due to these findings, we assign this species to the dianion of **1** (1^{2-}).

Charge distribution in 1^{2-}. The charge distribution was calculated from the change in the ^{13}C NMR chemical shifts upon reduction (see experimental).[26] The two charge units are evenly distributed between the four phenyls and the four carbons of the central ring to which they are attached (Figure 1). The substituent phenyl groups exhibit a pronounced charge alternation effect. The two carbons of the central benzene, which do not carry phenyls, serve as noncharged nodes between the two pairs of carbons which are substituted by phenyls, thus completing an overall charge alternation pattern.

Reduction of Hexaphenylbenzene (2). Reduction of the colorless solution of **2** in THF-d_8 by lithium metal first affords a green solution. The ^{1}H NMR spectrum broadens—possibly

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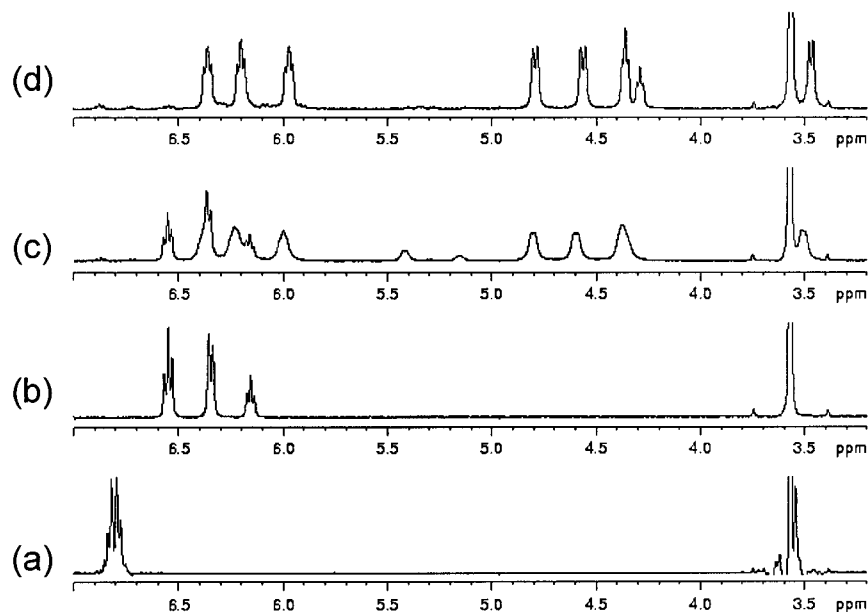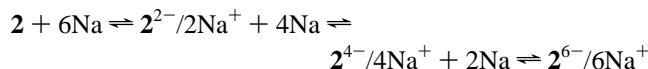
due to the formation of a radical anion. Further contact with the metal changes the color of the solution to brown, and a new ^{1}H NMR spectrum (Table 2) evolves, with a typical phenyl pattern (ABB′CC′), which is shifted to a higher field (6.20−6.59 ppm) compared to the ^{1}H NMR of the neutral **2**. The ^{13}C NMR spectrum is also shifted to a higher field with $\Sigma\delta_C$ of 240 ppm, a typical value for doubly charged aromatic polycyclic systems. When this species is quenched with molecular oxygen, the parent **2** is recovered, while reaction with D$_2$O yields dideuteriohexaphenylbenzene ($m/z = 538$). We therefore assign this species to the dianion (2^{2-}).

When the brown dianion solution is kept in contact with the lithium wire, a new ^{1}H NMR spectrum appears with no apparent change in the color of the solution. The new ^{13}C and ^{1}H NMR spectra show the same pattern as the former (i.e., ABB′CC′); however, all lines are shifted upfield (^{1}H NMR center of gravity = 5.79 ppm, $\Sigma\delta_C = 510$ ppm). The 2-fold shielding effect of the NMR spectra and the formation of tetradeutero**2** upon quenching with D$_2$O (as a major product; $m/z = 542$), as well as the recovery of **2** upon reaction with O$_2$, all point to the assignment of this species as the tetraanion of **2** (2^{4-}).

When **2** in THF-d_8 is reduced by sodium (Figure 2), the first stages of reduction are very similar to that of lithium reduction. The neutral spectrum broadens, the color changes to green and afterward to brown, and the spectrum of the 2^{2-} appears with only minor differences (Figure 2b). However, the next step differs somewhat. After a continuous and prolonged contact of the solution with the metal, a third set of spectral lines appears beside those of 2^{2-} and of 2^{4-} (Figure 2c). As the third set rises, the pattern of 2^{2-} declines while that of 2^{4-} remains as a steady-state intermediate between the 2^{2-} and the third species. When the reaction with the metal is carried out at temperatures higher than room temperature or at −78 °C, then the dianion and the traces of the tetraanion disappear, and the spectrum consists solely of the third set of lines (Figure 2d). In contrast

Figure 2. Na reduction of **2** followed up by ^{1}H NMR at 190 K. (a) **2**; (b) **2**[2−]; (c) **2**[2−], **2**[4−], and **2**[6−] in equilibrium; (d) **2**[6−].

to the former charged species, the ^{13}C and ^{1}H NMR spectra of this new species exhibit a lower symmetry, which includes two types of phenyls with ABCDE and regular ABB′CC′ NMR patterns in the ratio of 2:1, respectively. The ^{13}C NMR possesses 12 different peaks including four quaternary carbons. This observation suggests that the central benzene ring also loses its total (D_6) symmetry and one can identify two different types of the central ring carbons in the ratio of 2:1 as well.

The proton chemical shifts of the *ortho* and the *para* positions are shifted to a very high field (3.47−4.81 ppm), while the *meta* protons are less affected (5.96−6.36 ppm). The total center of gravity moves to 5.04 ppm, which is approximately 0.7 ppm upfield compared to **2**[4−]. This is in the order of the difference between the centers of gravity of **2**[4−] and **2**[2−]. This suggests that after reduction to a dianion, which is followed by a tetraanion, the reduction finally results in a third species, which is the highly charged hexaanion of **2** that is, **2**[6−].[27] The ^{13}C NMR spectrum offers extra support to a hexaanion assignment, with $\Sigma\delta_C = 819$ ppm, that is, six charges that yield $K_C = 136.5$ ppm/e[26] which is in the same order as those of **2**[2−] and of **2**[4−]. This value shows a linear trend of higher K_C values as more electrons are added to the system. The possibility that the third species is a product of a chemical reaction that involves breaking or formation of new bonds is ruled out by the following observations: (a) the parent **2** is recovered after quench of with O_2; (b) a ROESY exchange cross-peak between the two types of *para* protons,[28] which indicates that the ABCDE is indeed a phenyl group, and not a fixed benzo substituent, and (c) there is no signal in the sp[3] region in the ^{13}C NMR spectrum indicating that it is not a protonation product or a cyclization intermediate.[29]

2[6−] is stable for days at −78 °C. However, when the solution containing **2**[6−] is not brought in contact with the metal, then the process reverts and the spectrum of **2**[2−] reappears until **2**[6−] totally vanishes while metallic-like dust appears. These observa-

tions lead us to suggest that **2**[2−] is in equilibrium with the higher reduced **2**[4−] (as a steady-state intermediate) and **2**[6−]. The coexistence of three diamagnetic species with only moderate broadening of their lines (up to approximately 10 Hz) is possible if the intermediary paramagnetic radical stages are of very low concentrations. The reduction process is therefore:

$$2 + 6\text{Na} \rightleftharpoons 2^{2-}/2\text{Na}^+ + 4\text{Na} \rightleftharpoons$$
$$2^{4-}/4\text{Na}^+ + 2\text{Na} \rightleftharpoons 2^{6-}/6\text{Na}^+$$

Unlike reduction of **2** with sodium, **2**[6−] lines can hardly be seen upon reduction with lithium only if the reduction is held above room temperatures or after weeks of charging at low temperatures. There is a 0.5 ppm difference in the chemical shifts of one of the ABCDE *ortho* protons of **2**[6−]/6Li[+] as compared to that of **2**[6−]/6Na[+] possibly due to different ion solvation equilibria.

The ^{7}Li NMR chemical shifts of the Li^{+} counterions at 200 K are −1.08, −1.45, and −2.54 ppm for the corresponding **2**[2−], **2**[4−], and **2**[6−] respectively. The appearance of the [7]Li bands in this region indicates that the cations are most likely solvent separated, despite the likelihood that highly charged systems such as the tetra and the hexaanions would attract the counter-cations to form contact ion pairs (CIP). In light of these findings we calculated the anions of **2** without considering countercations or solvent molecules. The calculations were done by using the DFT approach and employing Becke's three-parameter exchange functional[30] (B3) along with the nonlocal correlation functionals of Lee, Yang, and Parr[31] (LYP) and the 6-31G* basis set.[32] The most stable singlet states of the "bare" anions refer to minimum structures with a central benzene ring in a twist-boat conformation, which have D_2 (**2**[2−] and **2**[4−]) or C_2 symmetry (**2**[6−]; the deviation from D_2 symmetry is rather small). In contrast, the optimized structure of the uncharged **2** is character-ized by a propeller-style D_6 arrangement as has been found by

(27) It should be noted that reaction with MeI or with D_2O gave a mixture of unresolved products.

(28) Appearance or lack of ROESY exchange cross-peaks between the *ortho* and *meta* protons does not indicate the existence of an exchange process because these protons also have NOE correlations.

(29) Formation of benzo[*ghi*]perylene dianion from [5]-helicene di-anion: Ayalon, A.; Rabinovitz, M. *Tetrahedron Lett.* **1992**, *33*, 2395−2398.

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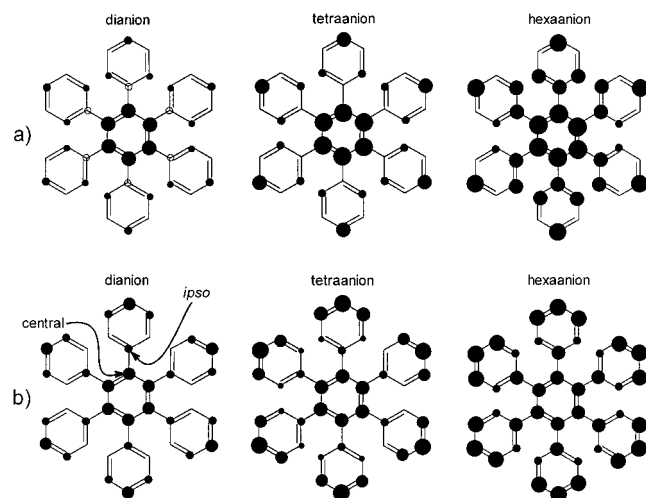
Figure 3. Charge distribution in the anions of **2**. (a) Experimental (^{13}C NMR); (b) calculated (NBO (B3LYP/6-31G*)). Due to the D_2 symmetry, there are several values with small differences for a specific position, but the calculated values of 2^{2-} and 2^{4-} were averaged to simplify the comparison with the experimental elucidation (which shows an average for these anions).

Table 3. Coupling Constants between Carbons of the Central Ring and the *ipso* Carbons of the Phenyl Substituents in the Anions of **2**

	neutral	2^{2-}	2^{4-}	2^{6-}
$^1J_{CC}$ (Hz)	36	58	63	-
% s (hybridization)	26 (sp³)	32 (sp²)	36 (sp²)	-

X-ray crystallography:[16] The carbon–carbon bond lengths within the central six-membered ring and between the central ring and each substituting phenyl amount to 1.41 and 1.50 Å respectively, and the dihedral angle between the substituting phenyls and the plane of the central ring is 65°.

Charge Distribution in the Anions of 2. We determined the charge distribution according to the differences between the ^{13}C NMR spectra of the anions and of the neutral compound (Figure 3a; see Experimental Section).[26] To establish the ^{13}C NMR assignment of the central ring carbons we synthesized a ^{13}C-enriched **2** in the 1,4 positions (**2**-$^{13}C_2$) by a Diels–Alder reaction between a ^{13}C-labeled tetraphenylcyclopentadienone and diphenyl acetylene. The labeling enabled the evaluation of the degree of conjugation between the phenyls by calculating the *s* character from the carbon–carbon coupling ($^1J_{CC}$) between the central ring carbons and the *ipso* carbons of the phenyls.[33] The results (Table 3) show an increase of the *s* character as the system carries more charge, thus indicating charge distribution via conjugation.

Elucidation of the charge distribution from the differences in the ^{13}C NMR spectra is based on the assumption that extra shielding is proportional to the additional charge carried by a specific carbon.[26] The high field shift of the carbons in all the three species may also result from the loss of the aromatic nature of the central benzene ring. The calculations mentioned above suggest that the central ring adopts a twist-boat conformation. It follows that the central six-membered ring is no longer a benzene ring as the π orbitals can merely overlap in such a conformation. For this reason instead of using **2** as the neutral reference, the chemical shifts of the hindered phenyls (and the carbon they are attached to) of tetraphenylcyclopentadiene (**7**)[34]

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(34) Schumann, H.; Janiak, C.; Zuckerman, J. *J. Chem. Ber.* **1988**, *121*, 207–218.
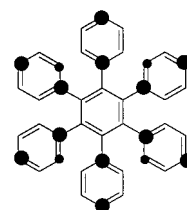

Figure 4. Addition of charge on 2^{6-} compared with 2^{4-}.

served as a model for the chemical shift of a hypothetical hexaphenylbenzene with a nonaromatic central benzene ring.

In the dianion, 1.3 electrons of the charge are located on the central ring, while the remaining 0.7 electron is spread over the six phenyls. This is opposed to standard expectation of separation of the charge to the remote corners of the molecule instead of concentrating the charge in the center of the molecule. However, in the former charge distribution each phenyl loses much of its aromaticity. In contrast, if only the central benzene ring "sacrifices" its aromaticity, while the rest hardly do so, it should behave like a system with three double bonds carrying phenyl groups, (such as the vinyl carbons of styrene) which are known to localize extra charge.[17]

The phenyl substituents exhibit a charge alternation pattern, similar to that of the substituting phenyls in 1^{2-}. The charge alternation is in line with the observation of broader ^1H NMR lines of the *para* and *ortho* protons as compared to that of the *meta* protons.

The central benzene component bears a net charge of two electrons upon reduction of the **2** parent system to a tetraanion; therefore, it is an unprecedented example in which two units of charge reside on a benzene ring in a highly charged system. At the same time, the phenyl substituents maintain the charge alternation pattern, while the six *para* carbons hold one unit of charge and the twelve *ortho* carbons another unit of charge.

According to the ^{13}C NMR analysis, the introduction of two more electrons to the system, thus creating a hexaanion, adds the extra charge (Figure 4) exclusively to the peripheral phenyl rings, while a total of two charges remains on the carbons of the central ring. The charge alternation structure partly collapses, as the *ipso* position receives a significant amount of the additional charge, while the *meta* carbons remain almost neutral.

The DFT calculated charge distribution (derived from Natural Bond Order (NBO)[35] analysis using B3LYP/6-31G*)[36] of the three anions of **2** in their twist boat geometry is presented in Figure 3b.[37] These calculations suggest that most of the net charge resides on the attached phenyl groups and is concentrated mainly on the *para* and *meta* positions without exhibiting a

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(36) A reviewer suggested the use of diffuse functions in these calculations, which are well-known to better mirror the energetic properties of anions by reducing the mutual repulsion between the extra charge and the other electrons (Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301). Due to restrictions of computational sources we could not apply the 6-31+G* basis set (that includes diffuse functions) to all the calculated anions except for 2^{2-}, in which the picture did not change dramatically. We believe, that because the charge in PAH anions is efficiently distributed over the entire π-system rather than localized on specific atoms, no special means need to be taken to reduce the overestimated mutual electron repulsion in this type of anions.
(37) We are aware of the arbitrariness incorporated in the estimation of the partial charges from calculation (since charge distribution is not a quantum mechanical observable). However, we believe that this method of estimation is especially meaningful for PAHs since they contain only carbon in their π-framework, therefore the approximation incorporated in the decision how to split the charge between two neighboring atoms is not harsh due to mutual compensation of the errors.

charge alternation pattern. This stands in some distortion to the charge distribution estimated from the ^{13}C NMR shifts. The calculated NMR chemical shifts (calculated by the gauge-including atomic orbitals (GIAO)[38] method on the B3LYP/6-31G* level), which are given in Table 2, in general reflect the same distortion. Despite these differences, there is a reasonable agreement with the experimental data as shown by correlations between the two sets of data ranging from 0.50 to 0.80. Better correlations are obtained when **7** is used as the neutral reference for the experimental elucidation rather than **2**, which lends strength to the finding of loss of aromaticity of the central benzene ring and to the cyclohexa(benzylanion) model (see below). The best correlation is found when the contact ion pair system (CIP) of **2**$^{2-}$/Li$^+$ is calculated in which one Li$^+$ cation is coordinated to two dimethyl ether molecules (as a model for THF) and to the central benzene ring of the dianion, which adopts boat structure. Still, relying on the ^{7}Li NMR chemical shifts, the solvent separated ion system forming the twist-boat conformation is most probably the dominant structure in solution. We believe that the calculations are somewhat limited in predicting charge distribution in a *condensed* phase. Perhaps taking the solvent, the countercations and all solvation states into account would give better correlation to experiment. Such a complex calculation however, is beyond the scope of this work. Since calculations are performed on single points in the conformational hyper-surface, whereas NMR data gives an average picture, it seems that a comparison between the two methods is somewhat problematic. Therefore, we believe that NMR, as far as charge distribution is concerned, gives a more realistic picture that is in line with studies[12,13] on related compounds. The calculations contribute to our understanding of the preferred conformations especially when the NMR shows only an average picture as in the cases of **2**$^{2-}$ and **2**$^{4-}$. We feel that both approaches contribute to our understanding in a complementary way.

The experimental charge distribution of each phenyl ring[39] and the attached central ring carbon resembles very much a benzyl anion.[40] The system may be viewed as a cyclohexa-(benzylanion), that is, a group of six benzyl anions linked to each other in the benzyl positions. Alternatively, it may also be envisioned as two units of *cis*-stilbene separated by two benzyl anions. *cis*-Stilbene and its derivatives are well-known to isomerize to *trans*-stilbene as a result of reduction to dianion even under steric constraints;[41] therefore, the hexaphenylbenzene anions afford a special opportunity to have a glimpse at a fixed form of reduced *cis*-stilbene.

The structural parameters from the DFT calculations strongly support the cyclohexa(benzylanion) model. The bond lengths within the central six-membered ring increase as the charging of the system proceeds. Starting with a bond length of 1.41 Å in the neutral system, they amount to 1.42 (for the four bonds of the same type in the D_2 symmetry) and 1.52 Å (the remaining two bonds of the other type) in the dianion, 1.46 and 1.53 Å in the tetraanion and reach 1.51 and 1.54 Å in the hexaanion. The

Table 4. Calculated (B3LYP/6-31G*) Bond Lengths and Dihedral Angles between the Peripheral Phenyls and the Central Benzene Ring of the Two Species[a]

compound	d C$_{central}$−C$_{ipso}$ (Å)	average dihedral angle (deg)
2	1.50 (1.47−1.53)	64.97 (∼67)
2^{2-}	1.49, 1.45	42.22, 10.54
2^{4-}	1.45, 1.43	24.11, 8.70
2^{6-}	1.42, 1.41	18.58, 7.10

[a] Data from X-ray crystallography[16] are presented in parentheses. The paired values are of the two and four equivalent phenyls of the twist boat structure, respectively. The dihedral angle of the latter was calculated by the average of all possible dihedral angles of the carbons that are adjacent to the central and *ipso* carbon atoms.

latter values are typical values for single carbon−carbon bonds. The C$_{central}$−C$_{ipso}$ bonds have shorter bond lengths and smaller dihedral angles, compared to the neutral parent **2** (Table 4). This is in accordance with the C$_{central}$−C$_{ipso}$ bond lengths that were calculated from the J_{cc} values of the anions of **2**-[13]C$_2$, and in line with what was found for other phenyl-substituted systems.[4,5]

Cyclization of 2^{2-} and Formation of Dihydro-9,18-diphenyl-phenanthro[9,10-*b*]triphenylene dianion (3^{2-}). After few weeks of storage at below −15 °C of both the lithium and sodium salts, a new species appeared in coexistence with the anions of **2**, having a typical phenyl pattern (ABB′CC′) and an ABCD pattern in the ratio of 1:2 (Table 5). We were inclined to conclude that this is a product of a dehydrogenation cyclization reaction, which is well-known for other dianionic systems.[29,42−44] Two pairs of the periphery phenyls undergo dehydrogenation cyclization to phenantrecene units and two phenyls remain nonreacted. The two remaining phenyls must be *para* to each other, otherwise the phenantrecene units would have lost symmetry and would have exhibited two different ABCD patterns. This NMR pattern is in line with the formation of a reduced species of **3**. Treatment with oxygen yielded **3**.[45] The ^{1}H NMR spectrum is shifted upfield to that of what was reported for **3**,[45] implying that it belongs to an anion. The ^{13}C NMR is shifted upfield typically to a dianion ($\Sigma\delta_C$ = 270 ppm). The conclusion that the reduction state is of a dianion, was strengthened after Bock et al. reported the crystallization from dimethoxyethane (DME) of [**3**$^{2-}$/Li$^+$(DME)$_2$]$^-$Li$^+$ as the reaction product of **2** with lithium powder.[9]

The mechanism's pathway should go through the tetrahydro intermediate similarly to what was suggested for the dehydrogenation cyclization of *ortho* terphenyl dianion and of 2,3-diphenylquinoxaline dianion[42,43] and found for [5]-helicene dianion.[29] Such a mechanism is also suggested and supported by semiempirical calculations performed by Bock et al.[9] Their suggested mechanism starts from the boat conformation of [**2**$^{2-}$Li$^+$(DME)$_2$]$^-$, which is reported as a minimum structure. The lithium atom which is considered as forming a contact ion pair is coordinated to two carbon atoms at the tips of the central ring as well as to either oxygen atom of two solvent molecules (DME). The second lithium cation necessary for overall

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Table 5. NMR Chemical Shifts of for the Li and Na Salts of 3^{2-}

compound		1	2	3	4	4a	8a	8b	9	*ortho*	*meta*	*para*	*ipso*
3	δ_H	7.19	6.90	7.34	8.40	-	-	-	-	7.39	7.34	7.38	-
(298 K)	δ_C	130.8	125.9	127.2	124.2	133.0	131.6	131.3	135.0	134.3	130.4	128.5	144.5
$3^{2-}/2Li^+$	δ_H	8.16	7.21	7.11	8.45	-	-	-	-	6.28	6.39	5.56	-
(270 K)	δ_C	130.2	124.0	121.2	122.7	129.6	133.7	136.4	86.5	114.9	127.2	106.1	140.7
$3^{2-}/2Na^+$	δ_H	8.10	7.26	7.16	8.52	-	-	-	-	6.09	6.30	5.40	-
(270 K)	δ_C	130.3	124.5	121.4	122.7	129.3	133.4	136.6	87.4	111.9	128.4	104.3	139.6
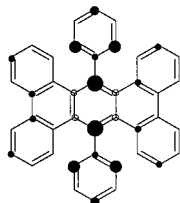
Figure 5. Experimental (^{13}C NMR) charge distribution in 3^{2-}.

neutrality is considered as being solvent-separated and was therefore omitted.

In our calculations, we confirm that the (imperfect) boat conformation of $[2^{2-}Li^+(CH_3-O-CH_3)_2]^-$ refers in fact to a minimum structure. However, according to the experimental ^{7}Li NMR findings, there is only one type of lithium atom exhibiting a resonance in the solvent separated ion pair (SSIP) region of -1.08 ppm.[46] In light of this circumstance, one could propose an alternative mechanism for the formation of 3^{2-}, starting from the twist-boat conformation of 2^{2-}. Otherwise, the SSIP system with the 2^{2-} having a twist boat conformation may be the dominant species in solution while the species which yields the cyclization product is the less common CIP $2^{2-}/Li^+$ with the boat conformation. We also find it intriguing to find out whether the dehydrogenation occurs simultaneously in both sides or consecutively, and whether the sp^3 hybridized hydrogens are syn or anti to each other.

Charge Distribution in 3^{2-}. The elucidation of the charge distribution from the ^{13}C NMR[47] shows that the phenanthrecene units, which are fused to the central benzene ring, carry only a very small amount of charge while most of it (0.35 e$^-$) is localized on the 9,10-benzylic positions (Figure 5). The rest of the charge is held by the phenyls in a charge alternation fashion, where the charge is mainly located on the *ortho* and *para* positions. These results are in excellent agreement to the calculated charge distribution except for the lower calculated charge density at the *ortho* position.[9] The agreement between experiment and calculations shows that the use of the ^{13}C chemical shifts of the neutral axially twisted 3 for extracting the charge distribution is legitimate despite the conformational differences of 3^{2-}, which was found to have a boat conformation held by a Li$^+$ "glue" in the solid phase.[9] The same conformation is also likely to exist in solution due to the high charge density at the benzylic position, which is found by NMR.

Isolation of 3. The synthesis of 3 by Pascal et al.[45] was carried out by the heating phenyclone and 9-bromophenanthrene at 340 °C in a yield of 4%, whereas in our NMR investigations we obtained a pure solution of 3^{2-} in THF-d_8. We therefore checked whether the alkali reduction of 2 would give higher yields.

Following the process of the reaction in a NMR tube showed that heating the brown anionic mixture in contact with the metal pushes the reaction toward the formation of the 2^{6-} and this inhibits the dehydrogenation reaction. The concentration of 3^{2-} raises only when the solution is kept without the metal and is accompanied by the appearance of small gray particles. This supports the suggested mechanism in which 3^{2-} originates from 2^{2-} (here regenerated from 2^{6-}).[9] Therefore, we synthesized 3 from 2 by treatment of 2 in THF solution with lithium wire and immediately after reaching a brown color, the solution was detached from the metal and was warmed at 65 °C for 24 h. The solution was then quenched with O$_2$ and the product was purified by solid-phase chromatography from the remaining 2, giving 3 in 27% yield (see Experimental Section).

Conclusions

Reduction of 1 and 2 was achieved by their reaction with lithium or with sodium in THF-d_8 under high vacuum and was monitored by NMR. While 1 gave only one charged product, tetraphenylbenzene dianion (1^{2-}), 2 offered three charged diamagnetic species of 2 in addition to a charged cyclization product, namely the dianion of dihydro-9,18-diphenylphenanthro[9,10-*b*]triphenylene (3^{2-}). In addition to the experimental determination of the charge distribution of 3^{2-} by NMR, we described a stepwise reduction of 2 showing that 2^{2-} is not only a synthon of 3^{2-} but is also the precursor of highly charged loaded π-systems—the tetraanion and hexaanion of 2. Utilizing the metal reduction of 2 as described here offers an accessible method to prepare 3.

Outlook

The remarkable ability of fullerenes as well as of polycyclic aromatic hydrocarbons (PAHs) to reversibly store electrons has stimulated interest in their use as new charge storage materials. The cyclohexa(benzylanion) revealed in this work carries six units of charge over seven carbon rings and has a better capability for electron storage, that is, six electrons on 42 carbons a 1:7 ratio as opposed to C$_{60}$ which can carry six electrons[48] with a 1:10 ratio. 2 joins other PAH systems, which we have recently shown to be highly charged with excellent charge-to-carbon ratios.[49,50] Therefore, in addition to their theoretical importance,[17] the highly charged PAHs may thereby be even more attractive than fullerenes as molecular batteries.

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Experimental Section

All quantum chemical DFT calculations described herein were performed on (B3LYP/6-31G*) level by utilizing Gaussian 98.[51] The charge distribution was calculated with NBO by using the NBO 4.0[52] subprogram in the Jaguar 4.0[53] program. The 1D and 2D NMR spectra were recorded on a Bruker DRX-400 pulsed FT spectrometer operating at 400.13, 100.62, and 155.51 MHz for ^{1}H, ^{13}C, and ^{7}Li NMR, respectively. Chemical shifts were measured relative to a solvent peak, which was calibrated according to the temperature.[54] Charge distribution in the π system was calculated out of the differences between the ^{13}C NMR spectra of the neutral and the charged species using the following equation: $Q_i = (\delta_{Ni} - \delta_{Ci})/K_C$, where Q_i is the partial charge, δ_{Ni} is the ^{13}C chemical shift in the neutral system and δ_{Ci} is the ^{13}C chemical shift in the charged system of carbon i.[26]

Preparation of the Reduction Samples. 2 (20 mg) was added to a 5 mm NMR glass tubes with an 8-mm extension. The alkali metal (kept in paraffin oil, cleaned from the oxidized layer and rinsed in petroleum ether 40−60 °C) was introduced under argon to the extension as a lithium wire or a piece of sodium. The extended tube was then placed under high vacuum and dried by flame. In the case of sodium, the metal was sublimed several times, creating a sodium mirror on the 8-mm extension. Approximately 1 mL of anhydrous THF-d_8 (dried over a sodium/potassium alloy under high vacuum) was vacuum transferred to the NMR tube and was degassed several times. Finally the extended tube was flame-sealed under high vacuum.

Controlled Reduction Process. The reduction takes place when the THF-d_8 solution is brought into contact with the metal by inversion of the sample and is stopped by returning the sample to the upright position separating the metal from the solution.

Quench reactions. Quenching with oxygen was performed under a nitrogen funnel. The sample was broken, and the 8 mm extension containing the metal was removed. A mild stream of oxygen gas was bubbled through a syringe into the cooled solution until the color disappeared. Reaction with D$_2$O was performed by braking the sample in a glovebag and pouring the solution into a vial containing 5 mL of D$_2$O. The product was then extracted with dichloromethane and dried over magnesium sulfate, and finally the solvent was evaporated.

Synthesis. Tetraphenylbenzene (1). The compound was prepared according to the known procedure:[15a] mp 266 °C (lit. 267−268 °C,[15a] 268−269 °C[15b]). Mass spectrum m/z (relative intensities): 384(5) 383(32) 382(M$^+$ 100) 305(10) 191(3) 183(8) (lit.[15a] 384(4) 382(100) 305(11) 191(7) 183(28)). ^{1}H NMR δ_H (THF-d_8, rt) 7.24−7.32 (m, 20H), 7.85 (s, 2H) ppm. ^{1}C NMR δ_C (THF-d_8, rt) 141.6, 140.3, 133.7, 130.6, 128.6, 127.3 ppm.

Dibenzylketone-^{13}C$_2$. The synthesis is a modification of the literature procedure.[55] α-Phenylacetic acid-^{13}C (99.6 atom % ^{13}C, 1 gr, 7.3 mmol) and iron powder (150 mg) were added to a round-bottomed flask attached to a distillation apparatus. The thermometer was in contact with the reagents mixture, which was warmed to 320 °C. Afterward, the thermometer was positioned over the distilled mixture. The yellowish-brown mixture was then fractionally distilled. The fraction boiling between 200 and 300 °C was collected to afford dibenzylketone-

^{13}C$_2$ (540 mg, 73%). The product was used as a starting material for preparing tetraphenylcyclopentadienone-^{13}C$_2$ without further purification.

Tetraphenylcyclopentadienone (Tetracyclone)-^{13}C$_2$. The synthesis is a modification of the literature procedure.[55] The above ^{13}C–labeled dibenzylketone (540 mg, 2.5 mmol), benzil (540 mg, 2.6 mmol) and 2.6 mL triethylene glycol were added to a round-bottomed flask, and gently warmed to 100 °C until the benzyl melted. 0.25 mL of trimethyl ammonium hydroxide benzyl (40% in methanol) was added, and the mixture was heated for 5 min. After the mixture was cooled to room temperature, 3 mL of methanol was added, and the mixture was filtered to give deep purple crystals, which were washed several times with methanol until the filtrate turned purple-orange (350 mg, 35%): mp 207 °C (lit. 213−220 °C).[55]

1,4-Hexaphenylbenzene-^{13}C$_2$ (2-^{13}C$_2$). The synthesis is a modification of the literature procedure.[56] The above ^{13}C-labeled tetraphenyl-cyclopentadienone (350 mg, 0.9 mmol), diphenylacetylene (320 mg, 1.8 mmol), and benzophenone (1.7 g) were added to a round-bottomed flask attached to an air condenser. The mixture was warmed over a flame for 45 min and the solution turned orange-brown. Diphenyl ether (1 mL) was added, and the solution was refluxed until all the solids were dissolved. The product solidified upon cooling. The crystals were washed with benzene, then filtered, and finally dried in a vacuum at 50 °C (412 mg, 89%): mp 454 °C (lit. 454−455 °C).[56] Mass spectrum major fragment at m/z (relative intensities): 537 (6), 536 (M$^+$, 12), 382 (36), 335 (23), 285 (26), 169 (100), 119 (62), 69 (91). ^{1}H NMR (THF-d_8, rt): 6.89 m. ^{13}C NMR (THF-d_8, rt): 141.7, 141.8, 132.6, 127.6, 126.2 ppm.

9,18-Diphenyltetrabenz[a,c,h,j]anthracene (3). The reaction apparatus was prepared in a manner similar to that of the reduction systems described above except for the following: A 20 mm glass tube replaced the NMR tube, the 8 mm extension had two narrowed necks (the lithium wire was put in the upper part), and hexaphenylbenzene (100 mg, 0.2 mmol) was dissolved in 4 mL of anhydrous THF (dried over a sodium/potassium alloy under high vacuum). The solution was brought in contact with the metal for 36−48 h and turned brown. The lithium wire was removed by sealing the lower narrowed neck, and the solution was heated at 65 °C for 24 h. The green solution was cooled in an ice bath and oxidized with a moderate stream of oxygen gas under an argon funnel to give a yellow solution. The solution was extracted with dichloromethane, which was rinsed with water, and dried. The product was purified using a preparative thin-layer chromatography plate (silica; hexanes/toluene 1:1). The product layer (rf = 0.85) was extracted with dichloromethane. A yellow powder of 9,18-diphenyltetrabenz[a,c,h,j]-anthracene was obtained (26 mg, 27%): mp 370 °C dec UV (324, 350, 390, 413 nm) and high-resolution mass spectrometry were compatible with the literature.[45]

NMR Data. 2^{2-}/2Li$^+$: δ_H (THF-d_8, 220 K) 6.42 (d, 12H, $J = 8.3$ Hz, *ortho*), 6.55 (dd, 12H, $J = 8.3$, 5.3 Hz, *meta*), 6.18 (t, 6H, $J = 5.3$ Hz, *para*) ppm. δ_C (THF-d_8, 220 K) 128.4 (*ortho*), 127.2 (*meta*), 116.4 (*para*), 144.9 (*ipso*), 117.1 (*central*) ppm. δ_{Li} (THF-d_8, 200 K) −1.08 ppm.

2^{2-}/2Na$^+$: δ_H (THF-d_8, 220 K) 6.34 (d, 12H, $J = 7.8$ Hz, *ortho*), 6.55 (dd, 12H, $J = 7.8$, 7.0 Hz, *meta*), 6.16 (t, 6H, $J = 7.0$ Hz, *para*) ppm. δ_C (THF-d_8, 220 K) 128.3 (*ortho*), 127.4 (*meta*), 115.8 (*para*), 143.8 (*ipso*), 117.5 (*central*) ppm.

2^{4-}/4Li$^+$: δ_H (THF-d_8, 220 K) 5.56 (d, 12H, $J = 5.0$ Hz, *ortho*), 6.25 (dd, 12H, $J = 5.0$, 4.1 Hz, *meta*), 5.37 (t, 6H, $J = 4.1$ Hz, *para*) ppm. δ_C (THF-d_8, 220 K) 121.7 (*ortho*), 127.3 (*meta*), 103.4 (*para*), 140.4 (*ipso*), 99.5 (*central*) ppm. δ_{Li} (THF-d_8, 200 K) −1.45 ppm.

2^{4-}/4Na$^+$: δ_H (THF-d_8, 220 K) 5.35 (d, 12H, broad, *ortho*), 6.30 (t, 12H, broad, *meta*), 5.13 (t, 6H, broad, *para*) ppm.

2^{6-}/6Li$^+$: δ_H (THF-d_8, 180 K) 3.78 (d, 4H, $J = 4.9$ Hz, *ortho*), 4.64 (d, 4H, $J = 4.8$ Hz, *ortho*), 4.79 (d, 4H, $J = 5.7$ Hz, *ortho*), 6.28 (dd, 4H, $J = 4.9$, 4.5 Hz, *meta*), 6.35 (dd, 4H, $J = 4.8$, 4.4 Hz, *meta*), 6.00 (dd, 4H, $J = 5.7$, 4.4 Hz, *meta*), 4.49 (t, 2H, $J = 4.5$ Hz, *para*) 4.55 (t, 4H, $J = 4.4$ Hz, *para*) ppm. δ_{Li} (THF-d_8, 200 K) −2.54 ppm.

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2⁶⁻/6Na⁺: δ_H (THF-d_8, 180 K) 3.47 (d, 4H, $J = 8.1$ Hz, *ortho*), 4.55 (d, 4H, $J = 8.6$ Hz, *ortho*), 4.81 (d, 4H, $J = 8.3$ Hz, *ortho*), 6.19 (dd, 4H, $J = 8.1, 6.2$ Hz, *meta*), 6.36 (dd, 4H, $J = 8.6, 5.4$ Hz, *meta*), 5.96 (dd, 4H, $J = 8.3, 5.4$ Hz, *meta*), 4.27 (t, 2H, $J = 6.2$ Hz, *para*) 4.35 (t, 4H, $J = 5.4$ Hz, *para*) ppm.

3²⁻/2Li⁺: δ_H (THF-d_8, 270 K) 8.16 (d, 4H, $J = 8.1$ Hz, H1), 7.21 (t, 4H, $J = 7.3$ Hz, H2), 7.11 (t, 4H, $J = 7.3$ Hz, H3) 8.45 (d, 4H, $J = 8.0$ Hz, H4), 6.28 (d, 4H, $J = 8.2$ Hz, *ortho*), 6.39 (dd, 4H, $J = 8.2, 6.7$ Hz, *meta*), 5.56 (t, 2H, $J = 6.7$ Hz, *para*) ppm. δ_C (THF-d_8, 220 K) 130.2 (C1), 124.0 (C2), 121.2 (C3), 122.7 (C4) 129.6 (C4a), 133.7 (C8a), 136.4 (C8b), 86.5 (C9), 114.9 (*ortho*), 127.2 (*meta*), 106.1 (*para*), ppm. δ_{Li} (THF-d_8, 200 K) several lines, center of gravity: 1.45 ppm.

3²⁻/2Na⁺: δ_H (THF-d_8, 270 K) 8.10 (d, 4H, $J = 8.1$ Hz, H1), 7.26 (dd, 4H, $J = 8.0$ Hz, H2), 7.16 (t, 4H, $J = 8.0$ Hz, H3) 8.52 (d, 4H, $J = 8.0$ Hz, H4), 6.09 (d, 4H, $J = 8.2$ Hz, *ortho*), 6.30 (dd, 4H, $J = $ 8.2, 6.7 Hz, *meta*), 5.40 (t, 2H, $J = 6.7$ Hz, *para*) ppm. δ_C (THF-d_8, 220 K) 130.3 (C1), 124.5 (C2), 121.4 (C3), 122.7 (C4) 129.3 (C4a), 133.4 (C8a), 136.6 (C8b), 87.4 (C9), 111.9 (*ortho*), 128.4 (*meta*), 104.3 (*para*), ppm.