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Metal reduction of di- and trisubstituted styrylbenzenes: formation of the highly charged tetra- and hexaanions

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ABSTRACT: The highly charged tetraanion of the unsubstituted *p*-bistyrylbenzene (**1**) and the hexaanion of 1,3,5-tristyrylbenzene (**4**) were generated and studied *in vacuo* at low temperatures. The various reduction steps were followed by UV and several NMR techniques. Extensive folding resulting from quinoid forms, determined to exist in the dianion of *p*-bistyrylbenzene, $\mathbf{1}^{2-}$, are absent in the highly charged tetraanion $\mathbf{1}^{4-}$. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: substituted styrylbenzeres; metal reduction; highly charged tetraanions; highly charged hexaanions

INTRODUCTION

The field of oligo(*p*-phenylenevinylene) (**1**) has been explored extensively in recent years in connection with the design and synthesis of photo- or electrically conducting polymers.[1] The demand for significantly better and improved polymeric systems capable of conducting electricity and still amenable for research sent researchers back to basics. A multitude of anionic and cationic conjugated systems, small enough to be studied, yet still polymer-like in character, have been investigated, only to generate a host of spectroscopic and theoretical conclusions. Conjugative interactions in these anionic systems were found to play a key role in the systems' ability to mobilize their charge. The tendency of the charge density to concentrate at the far ends of a π-segment by means of resonance delocalization was found to increase the charge mobility over the major domain of the system and thus reduce its redox power. Interruption of the resonance mobility by means of placing conjugative insulators, such as *meta*-substituted phenyl groups as in **2**, was found by Müllen *et al.*[2] to affect the redox capability of the system. Traditionally, the increase in the redox ability of **2** was attributed to the absence of interaction between two stilbene units, which may, therefore, be considered as consisting of two distinct polaron segments. For this reason, while **2** is reduced to a tetraanion, **1** with $n = 1$ was found to be reduced to the dianionic stage, exclusively.[3] The puzzling finding that the *o*-distyrylbenzene **3** is capable of accepting four electrons, and thus be reduced to the tetraanion was explained by the cation solvation effect.[4] Owing to their close proximity, the two charge centers of $\mathbf{3}^{4-}$ should be better solvated by the cationic shell, thus allowing a higher redox potential. Another system for which solvation of the counter-ion was found to play an important role is 1,4-diphenylbutadiene.[5] Reduction of the *ap-Z,Z*-diastereomer was found to cause rapid conversion to the more stable *sp-E,E*-diastereomer. In the latter, the increased stabilization imposed by the cation residing near the terminal units of the butadiene segment reduced the destabilization imposed by the electron transfer process.

The charge alternation concept as suggested by Klein and co-workers[6] supplies an additional, more basic, explanation to the above observations. In an alternating carbon framework the formation of a charged center should proceed in such a way as to place a charge on alternating carbons of the same type. Owing to the anionic character of a certain system, one should expect all carbons in the framework to sustain negative charges. Nevertheless, it is the magnitude of the charge that holds alternating qualities. Such alternations originating from coulombic repulsions result in charge distributions of donor–acceptor character and are thus of greater stability. In the described cases, the charge alternation rule predicts that charge distribution in systems such as **3** would be to carbons of similar nature. Therefore, it follows that they can maintain a greater redox power. In systems such as **1** and **2**, in which the alternating tendency places charges on carbons of different sets, the degree of the reduction potential is decreased. This is in complete agreement with the reported observations regarding the polymethylation of *p*-, *m* and *o*-xylenes.[6]

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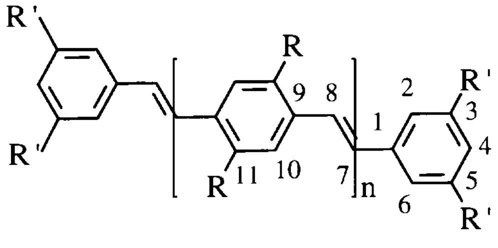
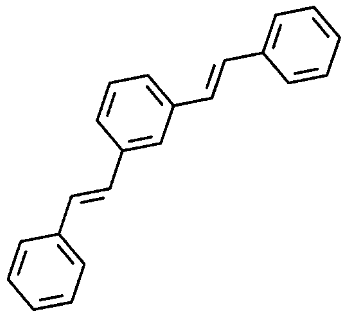


1 R=R'=H
1a R=Me, R'=H
1b R=H, R'=t-Bu



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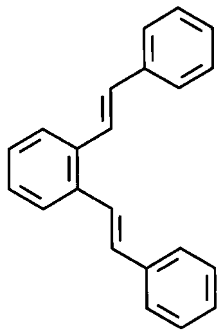

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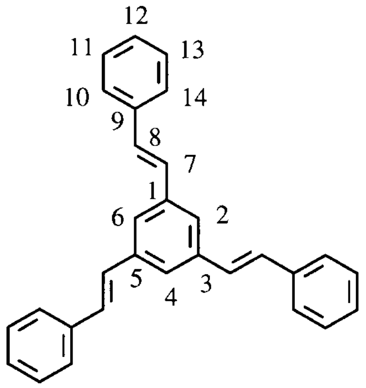

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Here, we describe the reduction of unsubstituted *p*-distyrylbenzene (**1**) and of (*E,E,E*)-1,3,5-tristyrylbenzene (**4**). Compounds **1** and **4** were prepared in 88% and 82% yields from *p*-dibromobenzene and 1,3,5-tribromobenzene, respectively, adopting our published procedures for multiple Heck coupling of oligohaloarenes.[7,8] Semi-empirical studies on both compounds were carried out utilizing the AMPAC 5.0 (1994) program.

EXPERIMENTAL

Chemical reductions of **1** and **4** were carried out in specially constructed 5 mm NMR tubes equipped with a reduction chamber. The alkali metal, either lithium or potassium, was introduced into the reduction chamber as a thin wire (in the case of lithium) or as a mirror of metallic potassium produced by high vacuum distillation. Into the NMR tube containing 4–5 mg of the sample to be reduced and the metal, doubly distilled THF-d_8 was transferred under vacuum and the tube was then flame-sealed. Reduction proceeds when the THF-d_8 solution is brought into contact with the metal by inversion of the NMR tube. All reductions were carried out at dry-ice temperature.

The distinction between the various redox stages was accomplished by the utilization of UV–visible and several NMR techniques. The appearance or disappearance of a paramagnetic radical stage was evident from the appearance or disappearance of the NMR spectrum and the loss of the relevant UV–visible band (see Table 2). All NMR and DNMR spectra were recorded on a Bruker DRX-400 spectrometer at 20 K intervals between 190 and 310 K. The spectral assignments result from a multitude of correlation experiments such as COSY, NOESY, CH-correlation and LRCH-correlation. The π-charge density, Δq_n, on each carbon atom n was estimated from the chemical shift difference observed for that atom prior to and upon doping, $\Delta\delta_n$, and the proportionality constant measured for the specific carbon framework, K_c [Eqn. 1].[9]

$$\Delta\delta_n = K_c \Delta q_n \qquad (1)$$

The identity of the various final reduction stages was confirmed by quenching with D_2O or methyl bromide.

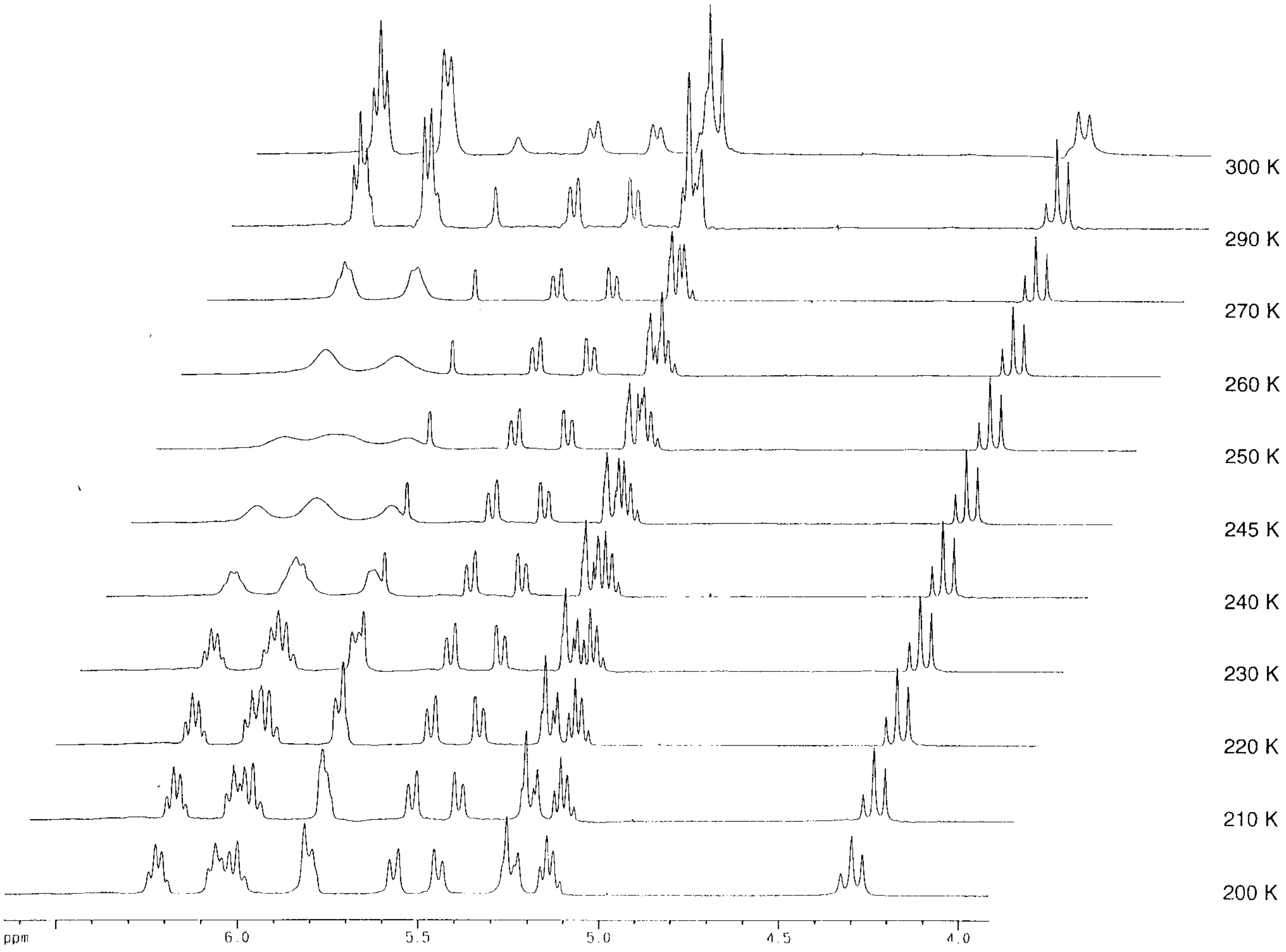
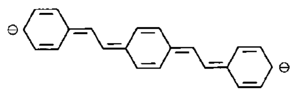


Figure 1. Variable temperature ^1H NMR of dianion $\mathbf{1}^{2-}/2Li^+$

Quenching with O_2 was also employed in order to show that rearrangements and inter- or intramolecular reactions did not take place. In no case were skeletal modifications observed.

RESULTS AND DISCUSSION

Treatment of **1** with alkali metal (Li, K) in THF-d_8 yielded a fluorescent blue solution, which exhibited UV bands at 566 and 630 nm and no NMR spectrum, and was thus characterized as the radical anion stage. Longer exposure to the metal (95 min with potassium and *ca* 3 days with lithium at −40 °C) resulted in the formation of the dianion as a deep matt-blue solution. In both the ^1H NMR and ^{13}C NMR spectra of $\mathbf{1}^{2-}/2Li^+$ the existence of a dynamic process (Fig. 1) is evident. At 200 K, two sets of ^1H and ^{13}C signals are present, in a 7:3 ratio, possibly corresponding to the two conformers of $\mathbf{1}^{2-}$ labeled here as **A** and **B**. As the temperature is raised (265 K) the barrier to rotation about the formal single bonds C-1—C-7 is overcome, resulting in the complete broadening of the phenyl-proton signals. This results in the signal unification corresponding to the *ortho* and *meta* protons. Protons H-10 and H-11 remain a pair of dissimilar doublets even at higher temperatures suggesting that rotation around the formal single bonds C-8—C-9 is not overcome. The potassium salt of $\mathbf{1}^{2-}$ exhibits a dynamic process in which the rotational barrier around the C-1—C-7 bond is overcome at approximately 250 K. A complete coalescence was not achieved and therefore barrier energies are not reported.



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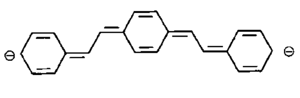

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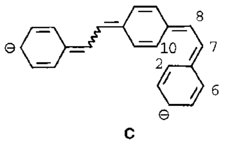


C

Close inspection of the NOESY spectrum reveals strong NOE interactions between H-10–H-2 and H-10–

Table 1. ^{1}H and ^{13}C NMR chemical shifts for the Li and K salts of **1**$^{2-}$ and **1**$^{4-a}$

Compound	Parameter	1	2	3	4	5	6	7	8	9	10	11
1 (300 K)	δ_H	—	7.59 (6.28)	7.34	7.23	7.34	7.59	7.26	7.26 (12.5)	—	7.59	7.59
	δ_C	138.2	127.0	128.8	128.0	128.8	127.0	128.5	129.1	137.4	127.3	127.3
1^{2-}/2Li^{+} (200 K)	δ_H	—	6.08 (8.96)	6.27	5.22	6.11	5.87	5.47 (9.06)	5.61 (9.36)	—	4.30 (12.5)	5.28 (12.7)
Conformer I	δ_C	143.1	111.9	129.1	104.9	127.6	120.7	114.4	128.4	116.6	84.7	112.2
1^{2-}/2Li^{+} (200 K)	δ_H	—	6.06 (8.09)	6.26	5.21	6.10	5.86	5.47 (9.06)	5.61 (9.06)	—	4.32 (12.0)	5.29 (12.7)
Conformer II	δ_C	143.0	111.7	129.1	104.7	127.6	120.5	114.4	128.4	116.1	84.3	112.3
	$\Delta\delta_H$	—	1.51	1.07	2.01	1.23	1.72	1.79	4.65	—	3.29	2.31
	$\Delta\delta_C$	−4.9	15.1	−0.3	23.1	1.2	6.3	14.1	0.7	20.8	42.6	15.1
1^{2-}/2Li^{+} (300 K)	δ_H	—	6.11 (7.55)	6.29	5.37	6.29	6.11	5.53 (9.06)	5.70 (9.06)	—	4.33 (12.1)	5.36 (13.1)
	δ_C	143.9	116.3	128.2	106.5	128.2	116.3	114.1	128.7	116.0	82.7	111.5
1^{2-}/2K^{+} (200 K)	δ_H	—	6.21	6.36	5.38	6.21	5.98	5.37	5.70	—	4.30	5.38
Average	δ_C	143.1	111.7	129.2	107.7	127.6	120.5	114.3	128.4	116.6	84.6	112.2
1^{2-}/2K^{+} (300 K)	δ_H	—	6.19	6.40	5.40	6.40	6.19	5.40	5.71	—	4.37	5.40
1^{4-}/4K^{+} (230 K)	δ_H	—	4.59	5.87	4.10	5.87	4.54	3.15	3.02	—	5.37	5.54
	$\Delta\delta_H$	—	3.00	1.47	3.13	1.47	3.05	4.11	4.24	—	2.22	2.05
1^{4-}/4K^{+} (300 K)	δ_H	—	4.61	5.93	4.15	5.93	4.52	3.18	3.07	—	5.55	5.55

[a] Chemical shifts given in δ, ppm (coupling constants, Hz).

H-6. Other NOEs determined between H-10–H-8, H-10–H-2, H-11–H-7, H-11–H-2 and H-11–H-6. Such a correlation, more specifically the NOE between H-10–H-2 and the absence of NOE interaction between H-8–H-2 or H-8–H-6, rules out both **A** and **B**. It is reasonable, however, to predict that such NOE interactions would arise from a conformer such as **C** resulting from the quinoid form. Interaction between the anionic centers at C-7 and C-10 with the cationic species, as expected to exist in the s-*cis* conformer **C**, should reduce the energy involved with the dianion and stabilize the system. Such stabilization which is clearly temperature dependent would place H-10 and H-2 close enough to produce such NOE interactions. The duality of ^{1}H and ^{13}C signals are thus attributed to the existence of s-*cis*/s-*cis* and s-*cis*/s-*trans* species. In **1a**$^{2-}$ and **1b**$^{2-}$ such folding is obviously minimized as a result of steric interaction. In fact, in **1a**$^{2-}$/2Li^{+} folding does not exist at all.[10] Compound **1b**$^{2-}$/2K^{+} exhibits a dynamic process involving species similar to **A** and **B**, exclusively.[11] The chemical shifts assigned to H-10 in both **1a**$^{2-}$/2Li^{+} and **1b**$^{2-}$/2K^{+} is at 5.77 and 5.35 ppm, respectively, whereas the resonance observed for that same proton in **1**$^{2-}$ (in both the potassium and lithium salts) is 4.30 ppm. This higher field resonance along with the downfield resonance of H-2 hints at the variations in the electronic effects imposed on the central benzene ring as a consequence of substitution, as with **1a**$^{2-}$, and more importantly they point to the presence of a coulombic compression between H-10 and H-2 of the folded charged phenyl ring, now lying side by side to the central ring. Further support for the existence of *trans–cis* interchange comes from the decrease in coupling constants of the formal olefinic bonds. Whereas upon reduction both **1a**$^{2-}$ and **1b**$^{2-}$ clearly exhibit no change in the vicinal coupling constants, a reduction of *ca* 3 Hz is observed in **1**$^{2-}$ as compared with **1** (Table 1). However, owing to the complete overlap of the olefinic signals of both s-*cis*/s-*cis* and s-*cis*/s-*trans* species alternations in the $^{2}J_{\text{vic}}$ could not be measured.

Two distinctive observations can be made upon comparing the lithium and the potassium salts of **1**$^{2-}$: the increased resolution and temperature sensitivity observed for the ^{1}H NMR spectrum of the potassium salt of **1**$^{2-}$ versus its lithium salt. These are consistent with the presence of a strongly held ion pair in both the potassium and lithium salts, yet with a strongly polarized K^{+} system. The polarization effect of the potassium cation compared with that of the lithium counterion is clearly exhibited in the nicely resolved proton spectrum of the salt. This is further supported on grounds of the lowered rotational barrier observed for the potassium salt, as illustrated by the phenyl ring barriers. A bathochromic shift in the UV spectrum of the lithium salt of **1**$^{2-}$ compared with that of the potassium salt (Table 2) leads to the conclusion that the lithium salt is less compact and thus tends to exhibit the behavior of a solvent-separated ion pair (SSIP).[13] This rationalizes a higher rotational barrier of the phenyl rings in the lithium salt. The polarization effect has been shown to be smaller for potassium salts than for the smaller lithium and sodium cations and thus contradicts the observations made here.[13] However, these effects should not be dismissed on the grounds of cation size arguments only. Here, the polarization observed for the potassium salt stems from strong contact ion-pair (CIP) interactions which are

Table 2. UV–visible bands measured in THF at 298 K

Compound	λ (nm)
Stilbene	295[a]
(Stilbene)$^-$	492, 699
(Stilbene)$^{2-}$	504
1	316
$\mathbf{1}^-/\mathrm{Li}^+$	566, 630
$\mathbf{1}^{2-}/2\mathrm{K}^+$	799
$\mathbf{1}^{2-}/2\mathrm{Li}^+$	810
$\mathbf{1}^{3-}/3\mathrm{K}^+$	480
$\mathbf{1}^{4-}/4\mathrm{K}^+$	504
4	436
$\mathbf{4}^-/\mathrm{Li}^+$	608, 753
$\mathbf{4}^{2-}/2\mathrm{Li}^+$	497, 634
$\mathbf{4}^{3-}/3\mathrm{Li}^+$	643
$\mathbf{4}^{4-}/4\mathrm{Li}^+$	477, 618
$\mathbf{4}^{5-}/5\mathrm{Li}^+$	360, 486, 595
$\mathbf{4}^{6-}/6\mathrm{Li}^+$	478

[a] Ref. 12.

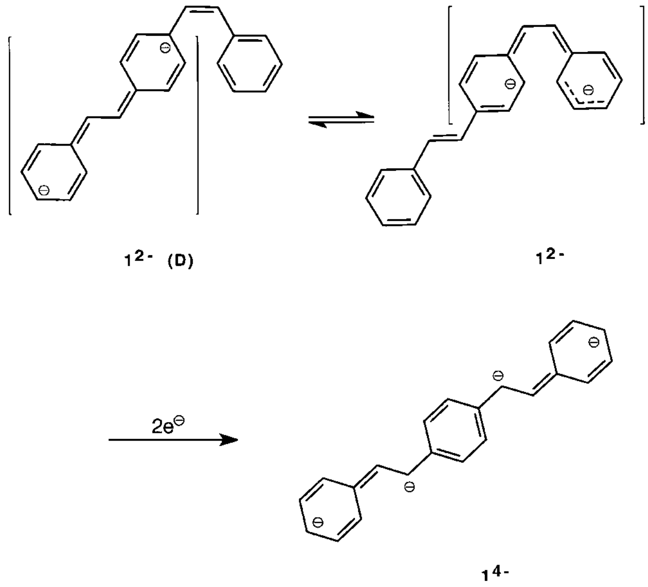


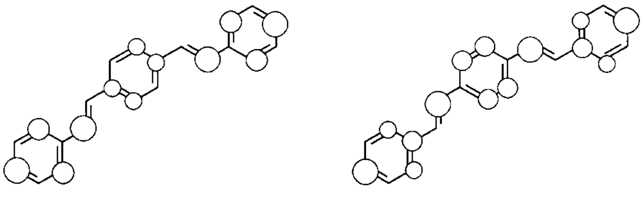
Figure 2. Reduction of a p-distyrylbenzene polaron to a tetraanion

smaller in the less compact lithium salt. The overall chemical shift resemblance of the ^{1}H NMR spectrum of $\mathbf{1}^{2-}/2\mathrm{Li}^+$ at 300 K to the corresponding potassium salt at 200 K may serve as additional evidence for the SSIP character of the lithium salt. This resemblance is temperature dependent and results from the destruction of the solvation shell and the formation of a tighter ion pair. As the temperature is reduced to 200 K the solvent shell is regenerated and delocalization increases. A diminutive yet consistent upfield shift of all protons in $\mathbf{1}^{2-}/2\mathrm{Li}^+$ accompanies such variation in the delocalization and results in a more homogeneous and a more paratropic system.

Quenching of the dianion solution with molecular oxygen under anhydrous conditions resulted in the retrieval of the parent compound **1** having a molecular ion in the mass spectrum at *m/z* 282 and exhibiting a ^{1}H NMR spectrum consistent with the structure of **1.** Quenching with liquid methyl bromide under similar conditions resulted in the isolation of the dimethylated product **1**-Me$_2$ showing a molecular ion at *m/z* 312.

The charge distribution on $\mathbf{1}^{2-}/2\mathrm{M}^+$ as calculated from the corresponding ^{1}H NMR spectrum shows that 59% of the total charge resides on the central benzene ring, 29% on the two phenyl rings and only 12% on the double bonds. Both alkylation and protonation reactions, nevertheless, occur on the double bonds, exclusively. The large charge distribution at the central benzene ring is due to a resonance form of type **D** as shown in Fig. 2. The possibility of a further reduction to the tetraanion is therefore striking. A 16 h continuous exposure with the metallic potassium mirror resulted in the disappearance of the characteristic blue color of $\mathbf{1}^{2-}/2\mathrm{K}^+$ and the appearance of a dirty-red colored solution. The disappearance of the dianionic species was followed by UV–visible spectroscopy that showed a gradual increase in the 480 nm band corresponding to the $\mathbf{1}^{3-}$ radical-anion species and a decrease in the dianion bands at 740 and 799 nm. An even longer exposure time to the metallic surface (for an additional 20 h) resulted in a purple solution exhibiting a UV–visible band at 504 nm and a well resolved ^{1}H NMR spectrum at 240 K, characterizing the highly charged and unexpected tetraanion $\mathbf{1}^{4-}$. The appearance of the tetraanion was proved by quenching with D_2O under inert conditions. This resulted in a tetradeutero species ($C_{22}H_{18}D_4$) having a molecular mass of 290. Slow admission of oxygen under cold (5 °C), anhydrous conditions proved the reversibility of the reduction process. All attempts at acquiring ^{13}C NMR data proved futile. Such behavior had been observed previously in our laboratory in connection with numerous annelated corrannulenes (M. Rabinovitz, E. Shabtai and A. Weitz, unpublished results). Exposure of **1** to lithium metal under identical reduction conditions resulted in no color change beyond the dianionic stage or in the disappearance of the dianionic species.

The ^{1}H NMR spectrum observed exhibits high-field shifts for all protons with the exception of H-10 and H-11, as compared with $\mathbf{1}^{2-}$. This expected tendency results from the reduction in negative-charge magnitudes in the tetraanion at these carbon centers. In fact, the largest charges in $\mathbf{1}^{4-}$ are hosted on carbon atoms C-1, C-4, C-8 and C-10 (Fig. 3). Electron transfer to the *s-trans* segment which remains almost neutral (structure **D**) results in the alternation of the charge at positions C-8 and C-1 and the positioning of an identical charge, in both sign and magnitude, on C-10 and C-11. The polarization of the two segments, results in the doubling of the charge residing at the *para* position of either of the two phenyl rings as compared with the charges found on C-10 and C-11. The charge delocalization of the tetraanion may,



1^{2-} 1^{4-}

Figure 3. Calculated charge distribution in $\mathbf{1}^{2-}$ and $\mathbf{1}^{4-}$

therefore, be described as fully quinoidal in character, while that of the preceding dianion exhibits some degree of charge partitioning.

The reduction of compound **4** with lithium metal resulted in a brownish solution, exhibiting no NMR spectrum. A reddish-brown solution was obtained after a prolonged exposure to the metal. Both the ^{1}H and ^{13}C NMR spectra clearly suggest the formation of the hexaanion $\mathbf{4}^{6-}$ ($K_c = 143$) with a total proton shift of $\Sigma\Delta\delta_H = 74.85$ and a total carbon shift of $\Sigma\Delta\delta_C = 857.10$ ppm (Table 3). When **4** is reduced with potassium, a faster, yet more defined, reduction process is observed. After an initial fine-tuned exposure to the metal, monitored exposures yield a full spectrum of colors: light blue ($\mathbf{4}^{-}$), navy ($\mathbf{4}^{2-}$), deep brown ($\mathbf{4}^{3-}$), green ($\mathbf{4}^{4-}$), brown ($\mathbf{4}^{5-}$) and red–brown ($\mathbf{4}^{6-}$). In their UV–visible spectra mixed stages (where two species are present at one time) are observed. The NMR spectra of neither the dianion nor the tetraanion were obtained at various temperatures. Semiempirical computations point to the fact that a two-electron transfer to the neutral molecule reduces one of the stilbene units, creating a dianionic polaron segment attached to two nearly neutral phenylene arms. With the dianion triplet state lying only 0.035 eV higher than the singlet state, the system exits in a triplet–singlet equilibrium with an overall paramagnetic character. Introduction of two electrons to the dianion results in triplet state species, having a stilbene dianion and two phenylene arms each charged with a single electron. There is no spin pairing at this stage and the tetraanion also remains paramagnetic. These paramagnetic systems do not yield high-resolution NMR spectra and it is only at the very final stage (*i.e.* $\mathbf{4}^{6-}$) when spin pairing occurs that an NMR spectrum is observed (evidence for the hexaanionic stage was given by quenching with D_2O, resulting in the hexadeuturo **4**-d_6 having a molecular ion peak in the mass spectrum of *m/z* 396).

Similarly to the charge profile observed for $\mathbf{1}^{4-}$, the charge distribution in $\mathbf{4}^{6-}$ is concentrated at the internal ends of the olefinic bonds. As estimated from the ^{13}C NMR spectrum, 44% of the total charge residing in $\mathbf{4}^{6-}$ is found at the olefinic bond, with 35% of the charge distributed over the phenyl rings and 21% on the central benzene ring. As with alkylation of $\mathbf{1}^{4-}$, alkylations and protonations of the hexaanion $\mathbf{4}^{6-}$ proceed exclusively to the olefinic positions.

CONCLUSIONS

The unexpected, highly charged systems described here are unprecedented. The high electron-per-carbon values of 0.36 and 0.4 in $\mathbf{1}^{4-}$ and $\mathbf{4}^{6-}$, respectively are clearly the highest of their type. Although a value of 0.36 e^{-} per carbon atom was also calculated for the *m*- and *o*-distyrylbenzenes, a value of only 0.18e^{-} per carbon was measured for the substituted *p*-distyrylbenzenes $\mathbf{1a}^{2-}$ and $\mathbf{1b}^{2-}$ described above. With an increasing number of styryl segments fused to substituents of the central benzene ring, the charge per carbon atom decreases as the system is capable of distributing the charge over a larger carbon skeleton (see, for example, ref. 11: compound **5** 0.28 e^{-} per carbon, compound **2b** 0.26 e^{-} per carbon, compound **3** 0.28 e^{-} per carbon). The accommodation of charge with a predetermined capacity of two electrons per styryl branch is a resultant of charge distribution over a system where conjugative insulators are present. Substitutions on the styryl branches should assist in the distribution of the charge in a way similar to that observed with the *para*-, *ortho*- and *meta*-topologies. The absence of substitution on the inner and terminal benzene rings of **1** contributes to the increased redox power of the system by allowing extensive folding in the dianionic stage. This results in a highly localized stilbene moiety and a nearly neutral styryl group to which a second pair of electrons may be transferred. The higher redox activity of

Table 3. ^{1}H and ^{13}C NMR data and charge densities of the lithium salt of 4^{6-a}

Compound	Parameter	1, 3, 5	2, 4, 6	7	8	9	10	11	12	13	14
4(240 K)	δ_H	—	7.76	7.32 (16.6)	7.40 (16.7)	—	7.62	7.38	7.26	7.38	7.62
	δ_C	138.7	124.5	128.6	129.4	138.0	127.1	129.2	128.2	129.2	128.2
$\mathbf{4}^{6-}$ (240 K)	δ_H	—	3.57	2.42 (10.6)	3.59 (10.6)	—	4.82	5.89 δ	4.22	5.31	4.97
	δ_C	130.0	70.7	57.6	75.0	128.6	99.4	128.9	85.0	124.2	116.0
Measured	Δq_c	−0.06	−0.37	−0.50	−0.38	−0.07	−0.19	−0.0	−0.30	−0.04	−0.08
Calculated	Δq_c	+0.11	−0.34	−0.45	−0.32	−0.02	−0.21	−0.10	−0.61	−0.14	−0.14

[a] Chemical shifts are given in δ, ppm (coupling constants, Hz).

the potassium metal as compared with lithium assists in the final stage of reduction. Owing to the reduced CIP character of the lithium salt, no reduction beyond the dianionic stage, $\mathbf{1}^{2-}$, was observed when lithium was employed.

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