# Electron Transfer and Conformational Interconversions in 1,*n*-Diphenylpolyenes

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1,4-Diphenylbutadiene (**1**), 1,6-diphenylhexatriene (**2**), and 1,8-diphenyloctatetraene (**3**) are reduced with alkali metals and the resulting paramagnetic monoanions and diamagnetic dianions characterized by ESR and ($^1$H-, $^{13}$C-)NMR spectroscopy, respectively. The stereodynamic behavior of the ions is studied as a function of chain length, charge, and counterion. The reduction of **1**, **2**, and **3** serves as a model experiment for the doping of extended linear polyenes (polyacetylenes).

**Elektronenübertragungen und Konformationsänderungen in 1,*n*-Diphenylpolyenen**

1,4-Diphenylbutadien (**1**), 1,6-Diphenylhexatrien (**2**) und 1,8-Diphenyloctatetraen (**3**) werden mit Alkalimetallen reduziert, und die resultierenden paramagnetischen Monoanionen sowie diamagnetischen Dianionen werden durch ESR- bzw. ($^1$H-, $^{13}$C-)-NMR-Spektroskopie charakterisiert. Das stereodynamische Verhalten der Ionen wird als Funktion der Kettenlänge, der Ladung und des Gegenions untersucht. Die Reduktion von **1**, **2** und **3** dient als Modellexperiment für die Beladung von ausgedehnten linearen Polyenen (Polyacetylenen).

Electron-transfer processes in unsaturated molecules can substantially affect the nuclear geometry. Typical examples are the configurational interconversions in olefins[1], the reduction of bond alternation in annulenes[2], and the flattening of twisted π-systems[3]. Electron-transfer-induced structural changes are particularly relevant in electrically conducting organic systems since the doping of conjugated polymers can increase the conductivity to the near metallic level[4]. If charge transfer alters the geometry and electronic structure of a π-chain[5], the application of rigid band structure models to studies of dopant – polymer interactions[6] is no longer appropriate.

We have recently determined the activation barriers for conformational changes, i.e. for the rotation about single bonds, in various oligophenylene and oligophenylenevinylene species as well as in their corresponding dianions which are formed by two successive electron transfers[7,8]. Ion formation appears to lower the conformational mobility of the hydrocarbons and to decrease the torsional angles about formal single bonds. In some cases we could also detect the radical anions, occurring as primary reduction products, and derive kinetic data for their conformational changes. These studies reveal some significant trends in the series of neutral compound, monanion, and dianion and allow a systematic investigation of structural changes as a function of charge[9].

The oligophenylene compounds are model systems for poly(*p*-phenylenes) in which the conductivity after doping depends upon the interplanar angles between the phenylene units[10]. In a similar fashion one can obtain information concerning the structure of charged polyacetylene chains[5] by making reference to the reduction of simple polyenes. We,

therefore, prepared the radical monoanions and dianions of 1,4-diphenylbutadiene (**1**), 1,6-diphenylhexatriene (**2**), and 1,8-diphenyloctatetraene (**3**) by reduction with alkali metals. ESR and NMR spectroscopic characterization of the charged π systems reveals (i) the mode of charge (spin) density distribution, (ii) the existence of different nonisodynamic conformers, and (iii) the role of the counterions in stabilizing particular isomers. The doubly metallated species were also accessible by twofold deprotonation of suitable dihydro precursors which allowed a comparison with the results from electron-transfer reactions. Only the reductive processes, however, led to a systematic evaluation of charge-induced stereodynamic effects in π systems with intact σ frames.

## 1. Results

Previous NMR measurements of alkali metal salts of doubly charged 1,4-diphenylbutadiene (**1**) have been unsuccessful[11].

**1**, **2**, and **3** were dissolved in dry, degassed ethereal solvents [tetrahydrofuran (THF), dimethoxyethane (DME), and 2-methyltetrahydrofuran (MTHF)] and reduced with highly active lithium or potassium at low temperatures. Spectroscopic monitoring of the reduction allowed the detection of the intermediate radical anions (see below) by ESR and ENDOR spectroscopy and, after the reduction was complete and paramagnetic species were absent, of the dianions by $^1$H- and $^{13}$C-NMR spectroscopy. The NMR (ESR) data of the diamagnetic (paramagnetic) species are reported in Tables 1 and 2.

A chemical structure proof of the dianions $1^{2-}$/2 Me$^+$, $2^{2-}$/2 Me$^+$, and $3^{2-}$/2 Me$^+$ (Me = Li, K) came from
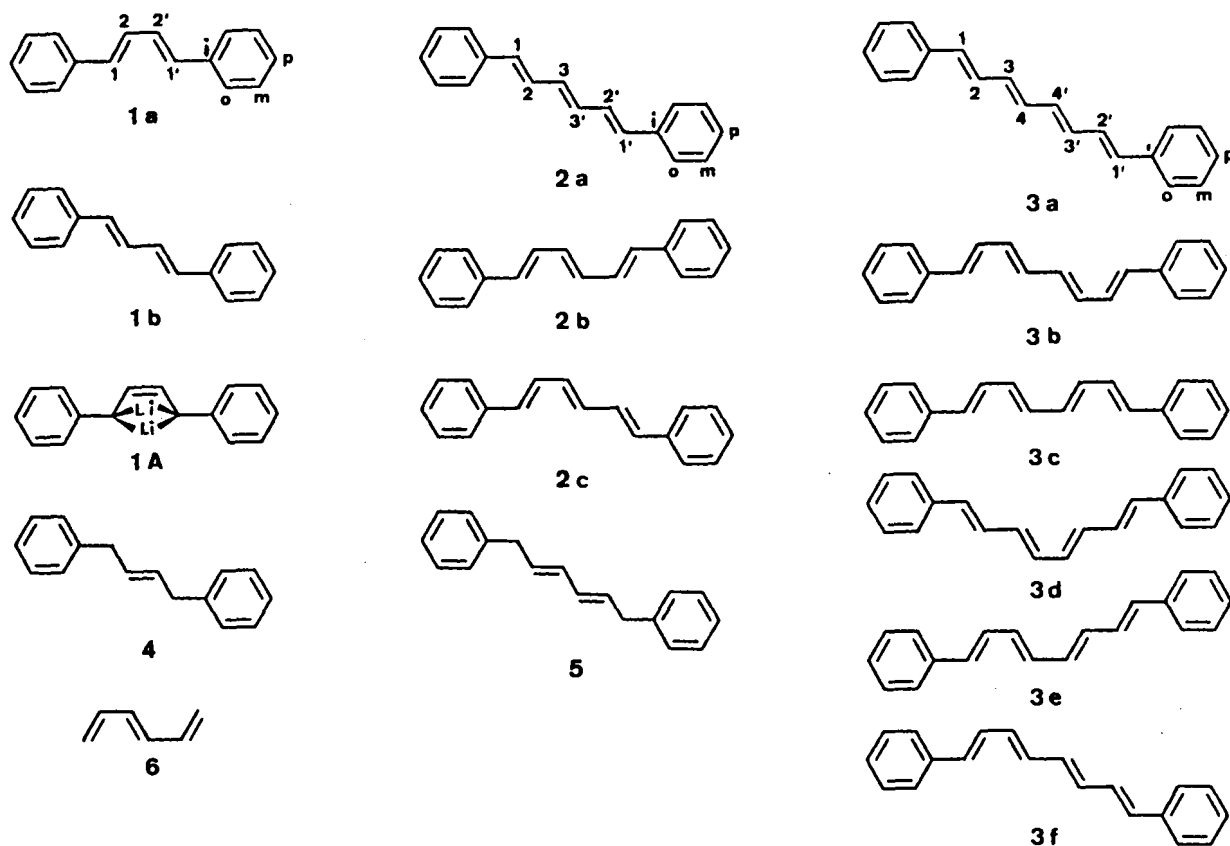
quenching experiments: quenching with dimethyl sulfate gave dimethyl derivatives which were identified by mass spectrometry. Protonation of the dianion salt $1^{2-}/2\,Li^+$ yielded a mixture of 1,4-diphenyl-1-butene and 1,4-diphenyl-2-butene (4), while protonation of $2^{2-}/2\,Li^+$ gave different stereoisomers of 5. This conclusion can be drawn from the number of NMR signals of allylic and olefinic protons. Treatment of 1 and 2 with sodium in dry diethyl ether, followed by the addition of methanol, afforded, on a preparative scale, 4 and 5, respectively. In both cases, mixtures of *cis* and *trans* isomers were obtained after chromatography and crystallization. The dianions could also be obtained by deprotonation of the dihydro precursors 4 and 5 with *n*-butyllithium/tetramethylethylenediamine (TMEDA)[12].

## 2. Discussion

The neutral compound 1 can exist as an *s-cis* (1a) and *s-trans* (1b) conformer, while the higher homologue 2 can form the different conformers 2a − 2c. The possibility of *s-cis/s-trans* isomerism with respect to 3 single bonds in 3 can produce 8 conformers. Since 4 of them are pairwise identical one is left with 6 nonisodynamic conformers from which 2 (3e and 3f) possess a mirror plane identical with the plane of the π system as only symmetry element. In the neutral hydrocarbons 1 − 3 neither the interconversion of the conformers by rotation about the formal single bonds nor the rotation of the phenyl rings could be detected on the NMR time scale.
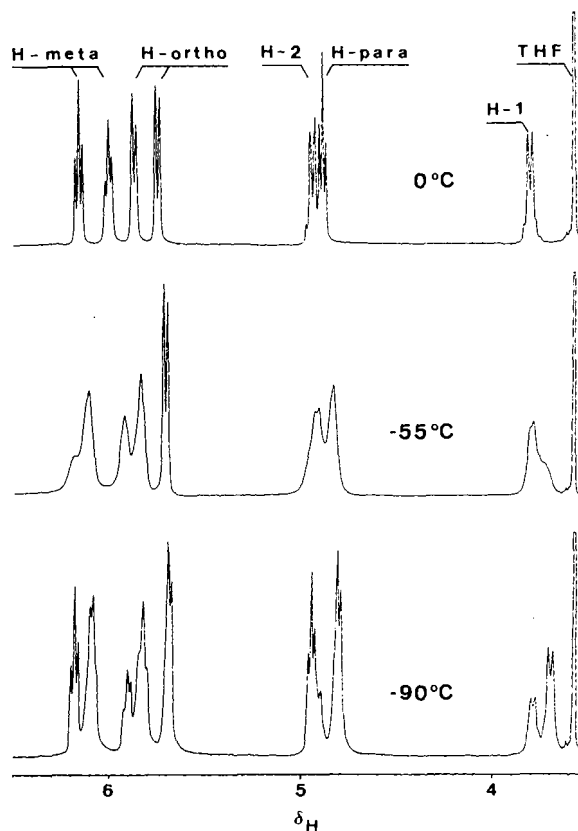
Figure 1. $^1$H-NMR spectra (400 MHz) of $1^{2-}/2\,K^+$ at different temperatures ([D$_8$]THF)

Table 1. $^1$H- ($\delta_H$) and $^{13}$C- ($\delta_C$) NMR chemical shifts and vicinal coupling constants $^3J$ [Hz] of the dianion salts $1^{2-}/2\,Me^+$ and $2^{2-}/2\,Me^+$ (Me = Li, K) ([D$_8$]THF)$^{a)}$

| | 1 | 2 | 3 | o | m | p | ipso | $J_{12}$ | $J_{22'}$ | $J_{23}$ | $J_{33'}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\delta_H$ ($\underline{1a}^{2-}/2Li^+$)$^{b)}$ | 3.60 | 4.91 | | 5.96 | 6.21 | 5.25 | | 11.9$^{c)}$ | 9.6$^{c)}$ | | |
| | | | | | 6.37 | | | | | | |
| $\delta_C$ ($\underline{1a}^{2-}/2Li^+$)$^{d)}$ | covered by THF | 97.5 | | 118.3 | 129.4 | 104.0 | 146.2 | | | | |
| | | | | 110.3 | 128.1 | | | | | | |
| $\delta_H$ ($\underline{1a}^{2-}/2Li^+/(TMEDA)_2$)$^{e)}$ | 3.62 | 4.92 | | 5.88 | 6.14 | 5.15 | | | | | |
| | | | | 5.90 | 6.32 | | | | | | |
| $\delta_H$ ($\underline{1}^{2-}/2K^+$)$^{f)}$ | 3.81 | 4.94 | | 5.74 | 6.00 | 4.89 | | | | | |
| | | | | 5.86 | 6.15 | | | | | | |
| $\delta_C$ ($\underline{1}^{2-}/2K^+$)$^{d)}$ | 74.5 | 102.9$^{g)}$ | | 118.2 | 130.5 | 99.2$^{g)}$ | 143.1 | | | | |
| | | | | 108.3 | 128.7 | | | | | | |
| $\delta_H$ ($\underline{2a}^{2-}/2Li^+$)$^{h)}$ | 3.90 | 5.80 | 5.02 | 5.9 – | 6.5 | 5.22 | | 11.4$^{i)}$ | | 13.9$^{k)}$ | 10.6$^{k)}$ |
| $\delta_C$ ($\underline{2a}^{2-}/2Li^+$)$^{h)}$ | 75.5 | 118.4 | 105.8 | 116.0 | 128.4 | 104.1 | 146.1 | | | | |
| $\delta_H$ ($\underline{2b}^{2-}/2Li^+$)$^{h)}$ | 4.23 | 5.86 | 4.45 | 5.9 – | 6.5 | 5.53 | | 12.8$^{i)}$ | | 9.5$^{k)}$ | 11.5$^{k)}$ |
| $\delta_C$ ($\underline{2b}^{2-}/2Li^+$)$^{h)}$ | 76.9 | 117.8 | 88.2 | 116.0 | 128.4 | 107.7 | 147.0 | | | | |
| $\delta_H$ ($\underline{2c}^{2-}/2Li^+$)$^{h)}$ | 4.05 | 5.35$^{m)}$ | 4.59 | 5.9 – | 6.5 | 5.35 | | 12.3$^{i)}$ | | 9.3$^{l)}$ | 11.1$^{l)}$ |
| | 4.20 | 6.11$^{m)}$ | 4.92 | | | 5.47 | | 12.0$^{i)}$ | | 12.9$^{l)}$ | |
| $\delta_C$ ($\underline{2c}^{2-}/2Li^+$)$^{h)}$ | 71.7 | 110.1$^{g)}$ | 99.5 | 116.0 | 128.4 | 105.6$^{g)}$ | 146.8 | | | | |
| | 81.3 | 125.9 | 93.5 | | | 107.1 | 146.4 | | | | |
| $\delta_H$ ($\underline{2b}^{2-}/2K^+$)$^{m)}$ | 4.22 | 5.88 | 4.39 | 5.9 – | 6.5 | 5.44 | | 12.9 | | | |
| $\delta_C$ ($\underline{2b}^{2-}/2K^+$)$^{m)}$ | 79.0 | 118.7$^{g)}$ | 92.0 | 119.4$^{g)}$ | 128.3 | 105.8 | 146.3 | | | | |
| | | | | 111.3 | 129.1 | | | | | | |
| $\delta_H$ ($\underline{2c}^{2-}/2K^+$)$^{m)}$ | 4.03 | 5.20 | 4.67 | 5.9 – | 6.5 | 5.13 | | 12.3 | | | |
| | 4.37 | 5.90 | 4.70 | | | 5.40 | | 12.6 | | | |

a) NMR spectra were recorded at 400 MHz ($^1$H) and 100 MHz ($^{13}$C), respectively on a Bruker AM 400 spectrometer.–b) 200 MHz, $T$ = 0 °C.–c) These values result from computer analysis of the AA'BB' spin systems.–d) $T$ = 0 °C –e) $T$ = –80 °C.–f) $T$ = 0 °C, at $_2$–80 °C two distinct doublets ($\delta$ = 3.70 and $\delta$ = 3.79) are observed and assigned to H-1 of two stereo-isomers of $\underline{1}^{2-}/2K^+$. The other resonances overlap and cannot be analyzed. –g) These carbon signals cannot be clearly connected to the carbon positions since the $^1$H-NMR resonances of the attached protons overlap.–h) $T$ = 20 °C.–i) The protons H-1 give first order signals (doublets).–k) These values result from a computer analysis of the AA'BB' spin system of H-2 and H-3 obtained upon decoupling of the H-1 protons.–l) These values result from the first order signals of the H-2 and H-3 protons, which are obtained by successive decoupling of the H-3 and H-2 protons.–m) $T$ = –40 °C.

Table 2. ESR hyperfine coupling constants $a_H$ [mT] of the radical anion $1^{-\cdot}$

| counterion/ solvent system | temperature range [°C] | $a_H$ | structure type |
|---|---|---|---|
| DME/K | –80 – –10 | 0.492,0.324,0.248,0.191,0.167,0.071,0.049 | A |
| THF/Li | –110 – –10 | 0.491,0.324,0.248,0.191,0.167,0.071,0.049 | A |
| MTHF/Li | – 90 – –20 | 0.490,0.322,0.248,0.190,0.168,0.073,0.049 | A |
| THF/K | –110 – –40 | 0.514,0.324,0.248,0.190,0.168,0.073,0.048 | A |
| MTHF/K | –90 – –20 | 0.519,0.319,0.248,0.195,0.159,0.074,0.052 | A |
| | | 0.562,0.288,0.230,0.203,0.181,0.074,0.052 | B |

However, the stereodynamic situation is markedly different in the corresponding ionic species. There is no doubt from the number of $^1$H- and $^{13}$C-NMR signals of the dianion $1^{2-}$ that its dilithium salt exists as a single stereoisomer. Moreover, its chemical shifts are strikingly similar to the dilithio species which is prepared by deprotonation of 4 with n-butyllithium/TMEDA and obtained as crystalline material $1^{2-}/2\,Li^+/(TMEDA)_2$ and subsequently dissolved in THF$^{12)}$. Note, that this formula describes the elemental composition, but, for the moment, has no structural significance. The $^1$H- and $^{13}$C-NMR spectra of the latter species remain unaffected with temperature variation between –80 °C and +20 °C. In contrast, when the dianion $1^{2-}$ was formed by reduction with potassium we observed a mixture of two stereoisomers (2:1 ratio, –90 °C) (see Figure 1).

This is obvious from the two doublet signals of 1-H at high field. Upon increasing the temperature, two effects can be seen: Firstly, the proportion of the minor component (at low temperature) gradually increases with temperature; and secondly, line broadening due to a dynamic exchange between the two forms occurs. Coalescence takes place at about –55 °C; at 0 °C the sharp resonances of the rapid-exchange spectrum are observed, although it cannot be strictly ruled out that only one isomer is present. For both

$1^{2-}/2\,Li^+$ and $1^{2-}/2\,K^+$ the *ortho* (*meta*) carbons of the phenyl groups are nonequivalent even at room temperature indicating that phenyl rotation is slow on the NMR time scale.

How can one explain the different stereochemistry of the organolithium and organopotassium species? In their pioneering work on carbanion structures, Schleyer[12,13] and Streitwieser[14,15] provided evidence for the unique ability of lithium nuclei to form "non-classical" bridged structures. A typical example is 2,2′-dilithiobiphenyl in which the *ortho* carbons C-2 and C-2′ are bridged by two lithium nuclei above and below the plane of the π systems[16]. The species $1^{2-}/2\,Li^+/(TMEDA)_2$ constitutes a related case since it adopts a crystal structure in which the terminal centers C-1/C-1′ are bridged by two Li nuclei, and the central C-2/C-2′ bond possesses a *cis* arrangement[12]. Ignoring the TMEDA units, structure **1A** appears to be an adequate description. This outcome and the above NMR results indicate that $1^{2-}/2\,Li^+$ and $1^{2-}/2\,Li^+/(TMEDA)_2$ adopt solution structures similar to that one of the latter in the solid state. However, the strong preference for a *cis* arrangement of the C-2/C-2′ bond is brought about only by the small and strongly polarizing lithium counterions; for the dipotassium analogue we observe two isomers which most probably differ in the *cis* and *trans* arrangement of the C-2/C-2′ bond.

In principle, one could also expect stereoisomerism with respect to the C-1/C-2 bond of $1^{2-}/2\,Me^+$. However, a comparison of the vicinal coupling constants $^3J$(1-H, 2-H) of $1^{2-}/2\,Me^+$ (see Table 1) with those of related oligophenylene-vinylene compounds[7] points toward a *trans* arrangement at the C-1/C-2 bond. The coupling constants of $1^{2-}/2\,Li^+$ re-

sult from an iterative computer analysis of the AA′BB′ spin system. The *trans* arrangement is conform with the crystal structures of $1^{2-}/2\,Li^+/(TMEDA)_2$[12] and $6^{2-}/2\,Li^+/(TMEDA)_2$[17]. Further support comes from the fact that mono- and dianions derived from (*cis*- and *trans*-)stilbene possess a *trans* configuration of the olefinic bond[1,18,19].

The $^1H$- and $^{13}C$-NMR spectra of $2^{2-}$ (Li and K salts) are more complicated (see Figure 2). It appears that any olefinic carbon (hydrogen) of $2^{2-}/2\,Li^+$ at room temperature gives rise to 4 signals. The $^1H$-doublet signals at highest field can readily be assigned to the terminal hydrogen nuclei 1-H. Irradiation at the particular doublet signals allows for an identification of the resonances of 2-H, a related procedure leading to an identification of the absorptions of 3-H. The signals of the aromatic *para* protons are assigned on the basis of their splitting patterns. The assignments of the corresponding carbons are achieved by selective $^{13}C\{^1H\}$ decoupling and by an H,C-COSY experiment (see Figure 2)[20].

The homo- and heteronuclear decoupling experiments and the knowledge of the number and relative intensities of the NMR signals allow for an identification of *three* different stereoisomers; only two of these species, the most and least abundant one, can possess a $C_2$ axis through the central bond C-3/C-3′ and perpendicular to the molecular plane.

It is straightforward from symmetry arguments to describe the carbon framework of these isomers by structures similar to **2a** and **2b**, while the third isomer must be assigned to **2c**.

An attempt has been made to detect a possible conformational interconversion by ]D-NMR exchange spectroscopy (based on a NOESY sequence)[21]. However, up to $+40\,°C$ no exchange cross peaks have been detected (mixing time up to 2 s).

The observation of different stereoisomers in solutions of both $2^{2-}/2\,Li^+$ *and* $2^{2-}/2\,K^+$ must be contrasted with results provided by Bates et al. for hexatriene (**6**) and its dilithio derivative[17]. They found that $6^{2-}/2\,Li^+/(TMEDA)_2$ possesses a crystal structure with a *cis* arrangement of both the C-2/C-3 and C-2′/C-3′ bond.

Two findings are obvious from the comparison of the solution structures of $1^{2-}/2\,Li^+$ and its homologue $2^{2-}/2\,Li^+$: the strong preference for a charged $C_4$ structure with a *cis* arrangement of the C-2/C-2′ (**1**) and C-2/C-3 (**2**) bond is a specific property of (i) the lower homologue **1** and (ii) the *dilithio* derivative. A "Z,Z" structure similar to **2b** (with a *cis* arrangement both at the C-2/C-3 and C-2′/C-3′ bond) is no more preferred in the homologous "hexatriene" dianion with a more extensive π-charge delocalization. Consequently, the lithium and potassium species behave similarly. In both cases, the phenyl rotation is slow below $-30\,°C$.

Also of interest is the π-bond order and thus the double bond character of the "formal" double and single bonds in the dianionic species. Indeed, within a simple π-MO model one predicts the π-bond orders of the formal double (single) bonds to decrease (increase) upon ion formation. It is in accordance with this expectation that, in contrast to the neutral compounds, the phenyl rotation in both $1^{2-}/2\,Me^+$
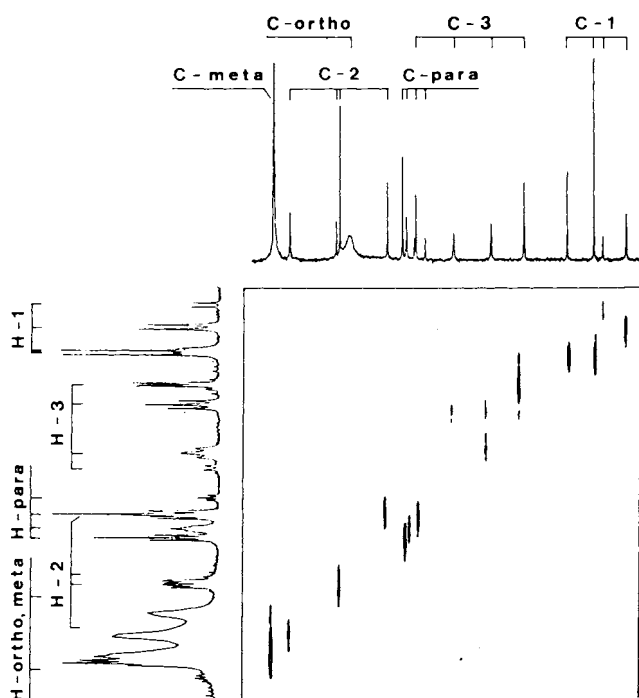


Figure 2. H,C-COSY NMR spectrum ($^1H$: 200 MHz, $^{13}C$: 50 MHz) of $2^{2-}/2\,Li^+$ in $[D_8]THF$ at room temperature

and $2^{2-}/2\,Me^+$ is slow on the NMR time scale. Also anticipated is the fact that the barrier for phenyl rotation is lower for the higher homologue in which the excess charge is more extensively delocalized.

The bond lengths determined for $1^{2-}/2\,Li^+(TMEDA)_2$ [C-2/C-2′: 1.423 Å, C-1/C-2: 1.498 Å] support a "1,4-dilithio-2-butene" structure with a formal C-2/C-2′-double bond according to formula 1A[12]. It appears, however, that in the crystal each lithium interacts with only three of the four butadiene carbons so that an "ideal" doubly 1,4-bridged structure is not adpoted. The situation is even less clear in the crystal of $6^{2-}/2\,Li^+/(TMEDA)_2$ where the C-1/C-2 and C-2/C-3 bonds are about equally long and significantly shorter than the central bond C-3/C-3′[17]. This led the authors to approximate the structure as that of two allyl moieties attached by a single bond. The experimental result is consistent with an ab initio MO calculation for lithium-doped polyacetylene. In the elemental composition, $(C_6H_6Li_2)_x$, which corresponds approximatly to the maximum doping level for $(CH)_x$, each lithium nucleus is equidistant from 3 adjacent carbon atoms[5]. An interpretation of the vicinal H,H-coupling constants $^3J$ determined for solutions of $1^{2-}/2\,Li^+$ and $2^{2-}/2\,Li^+$ (see Table 1) is not straightforward since the $^3J$ values are known to reflect both the $\pi$-bond order of the corresponding CC bond and the dihedral angel $\varphi$ of the HCCH unit[22]. It is characteristic, however, that in $1^{2-}/2\,Li^+$ the coupling constant $^3J$(1-H, 2-H) = 11.9 Hz (C-1/C-2 trans) is significantly larger than $^3J$(2-H, 2′-H) = 9.6 Hz (C-2/C-2′ cis). It should be noted in this context that while the identification of $2c^{2-}/2\,Li^+$ follows from symmetry reasons, the differentiation of $2a^{2-}/$

$2\,Li^+$ and $2b^{2-}/2\,Li^+$ (see Table 1) is based on the vicinal H,H-coupling constants. Particularly significant, therefore, is the large value of $^3J$(2-H, 3-H) in $2a^{2-}/2\,Li^+$. The coupling constants have been obtained by computer analysis of the AA′BB′ signal pattern of 2-H and 3-H, resulting from decoupling of 1-H.

Taking, as is generally accepted, the $^{13}$C-NMR chemical shifts $\delta_C$ of $\pi$-charge-delocalized ions to be a measure of the local $\pi$-charge densities $q_\pi$,[2,23,24], the observed sequence of $q_\pi$(C-1) > $q_\pi$(C-3) > $q_\pi$(C-2) and the high $\pi$-charge at the para phenyl carbons of $2^{2-}/2\,Me^+$ (Me = Li, K), are in accord with the prediction of a $\pi$-MO model. The relative $^1$H- and $^{13}$C-NMR chemical shifts and, in particular, the high-field resonance of 1-H and C-1 in $1^{2-}/2\,Me^+$ can be rationalized both within a $\pi$-MO approach and by reference to structure 1A which implies sp$^3$ hybridization of C-1 and C-4. Clearly, a distinction between "more ionic or more covalent" solution structures is not meaningful in view of the available experimental evidence. It is significant, however, that the stronger $\pi$-charge delocalization in the (more ionic) higher homologue finds its counterpart in the prevailing stereochemistry: the ability of the metal counterions to control the stereochemistry of the charged hydrocarbon framework is obvious only for the diene with two metal atoms per $C_4$ unit and with a high charge at the terminal centers.

The highly complex $^1$H- and $^{13}$C-NMR spectra of $3^{2-}/2\,Li^+$ (see Figure 3) are conform with the expectation that the number of stereoisomers of dianions is an increasing function of the chain length. It has been mentioned above that 3 can give rise to 6 non-isodynamic conformers, 4 of which possess a $C_2$ axis (3a and 3b) or mirror plane (3c and 3d) through the central C-4/C-4′ bond. Consequently, a maximum of 8 distinct signals for each olefinic proton (carbon) may be observed in the NMR spectra of the dianion.

Analogous to the cases of $1^{2-}$ and $2^{2-}$, and consistent with HMO coefficients, the NMR resonances of 1-H (and C-1) are the most upfield olefinic resonances. From the $^1$H-NMR spectrum, 6 distinct doublets (1-H, spacing ca. 12 Hz) could be observed. It is impossible to perform assignments of the other olefinic signals since they are completely overlapped. One would not expect a complete analysis of the complex stereodynamic situation.

In the $^{13}$C-NMR spectrum of $3^{2-}/2\,Li^+$, a broad resonance at $\delta = 116-120$ is observed for the ortho carbons, due to dynamic exchange caused by the rotation of the phenyl group, as was found to be the case in the spectrum of $2^{2-}/2\,Li^+$. The meta carbons give sharp signals at $\delta = 130-131$ and the resonances of the ipso carbons at $\delta = 149-150$. The remaining 37 signals, due to the para carbons and the olefinic carbons, were not separated in groups and thus could not be assigned to specific centers. This is consistent with a more uniform distribution of charge over the olefinic carbons in the progression to chains of longer chain length. The total of 37 resonances for the 5 carbon positions represents an "average" of 7.4 signals for each aromatic and olefinic carbon. This finding is only consistent with the presence of all 6 conformers for which 40 signals would be
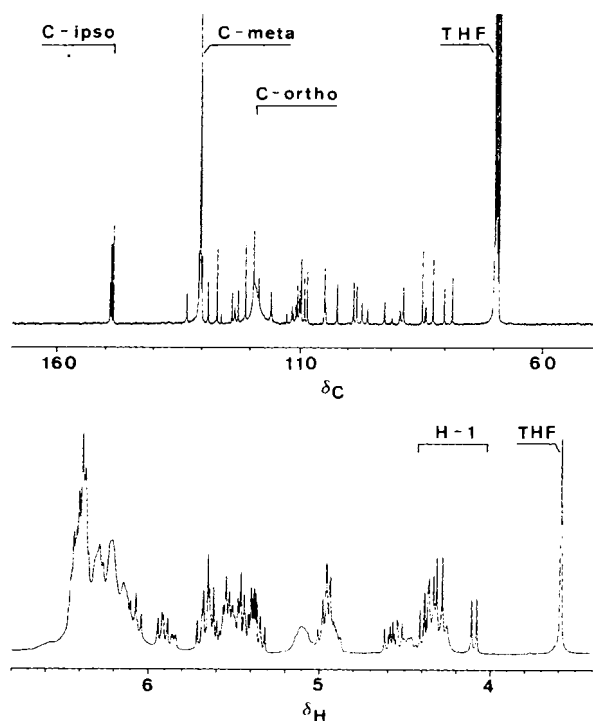


Figure 3. $^1$H- (400 MHz) and $^{13}$C- (100 MHz) NMR spectra of $3^{2-}/2\,Li^+$ at room temperature ([$D_8$]THF)

expected. The missing 3 signals could not be observed, because they are covered by other resonances.

The remarkable stereochemical behavior of the dianionic systems requires a comparison with the corresponding radical monoanions. The radical anion of **1** has been prepared and described as a single species with *s-trans* conformation[25]. In experiments devoted to detect stereoisomerism in radical anions of 1,*n*-diphenylpolyenes we varied the solvent (THF, MTHF, DME), the counterion (Li, K), and the temperature ($-110$ to $-10\,°$C). The resulting radical anions were characterized by ESR and ENDOR spectroscopy (see Figure 4).
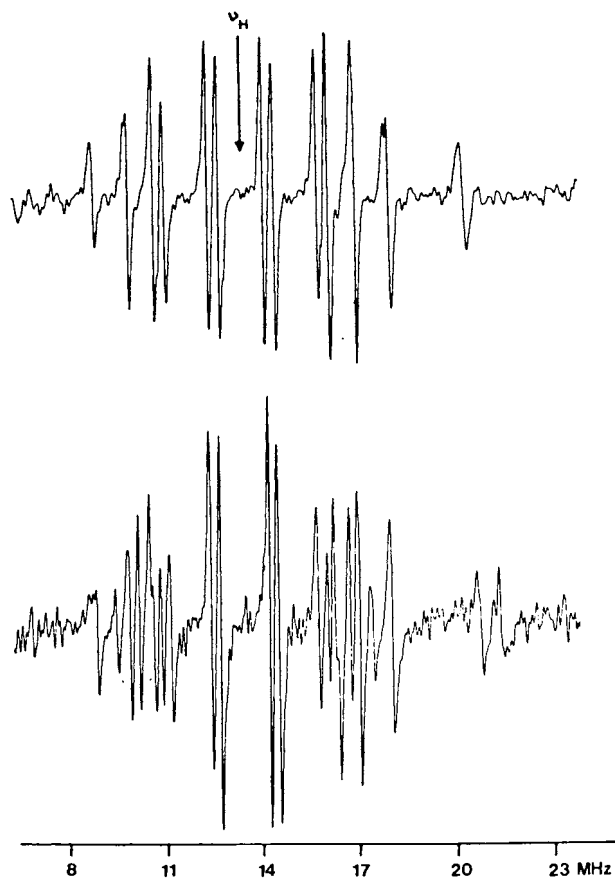


Figure 4. ENDOR spectra of the radical anion **1**⁻·/K⁺. Top: dimethoxyethane, $-80\,°$C; bottom: 2-methyltetrahydrofuran, $-80\,°$C

The experimental conditions applied and the ¹H-hyperfine coupling constants are reported in Table 2 (see Scheme 1, top). The crucial outcome is that, depending on the solvent/counterion system, two different species, **A** and **B**, can be observed for the radical anion **1**⁻·. Not surprisingly, in cases where a mixture of both **A** and **B** occurs, the particular radical anions can only be detected by ENDOR spectroscopy since the corresponding ESR spectra arise from a superposition of absorptions of **A** and **B**. The experimental conditions DME/K, THF/Li, and MTHF/Li only yield a single radical **A** with virtually no detectable temperature dependence of the hyperfine coupling constants. In contrast, while the system THF/K only gives rise to a single species

**A** at low temperature ($-100\,°$C), increasing the temperature to about $-40\,°$C produces a mixture between **A** and a second radical anion **B**. This effect is reversible since lowering of the temperature brings about the disappearance of **B**. Still another situation is observed in MTHF/K: even at low temperature the spectra indicate the presence of **A** *and* **B**; an increase of the temperature neither influences the hyperfine coupling constants nor affects the relative concentration of **A** and **B**.

In cases where mixtures of both radical anions **A** and **B** occur, the assignment of coupling constants of either **A** and **B** has been achieved from a comparison with the spectra of the pure radical **A** and by triple-resonance experiments[26]. In the latter case, irradiation of a single line affects only the signals of the same spin system.

Another question concerns the assignment of the hyperfine coupling constants $a_H$ to the individual protons. We have calculated the $a_H$ values by means of the McLachlan[27] procedure and the McConnell[28] equation. The satisfactory agreement between experimental and calculated values which is obvious from Scheme 1 provides strong evidence for the given assignment. Moreover, the hyperfine coupling constants of **A** and **B** are rather similar. Guided by experience accumulated in the study of the dianions, we identify the species **A** and **B** as stereoisomers of the 1,4-diphenylbutadiene radical anion **1**⁻·.

How can the counterion/solvent system control the stereochemistry of the ion pair **1**⁻·/Me⁺? Paramagnetic or diamagnetic carbanions are known from extensive evidence to exist as equilibria of contact ion pairs and solvent-separated ion pairs[15,29,30]. The latter are generally favored by smaller counterions (with better eigensolvation), lower temperatures, larger organic ions, and by strongly cation-solvating (e.g. chelating) solvents[31]. The stabilization of an *s-cis* arrangement of the central C-2/C-2′ bond in **1**⁻· is expected to be most pronounced in an pair with a tight interaction of the counterion and the butadiene π system. This interaction is known from the dianion **1**²⁻ to include a bridging of the carbons C-1 and C-4. Species **B** is, indeed, only observed under those experimental conditions which favor a tight ion pair. Consequently, we determine that the radical anions **A** and **B** exist in an *s-trans* and *s-cis* conformation, respectively. It should be emphasized that the cation/anion interaction is much more important for the stereochemistry of the doubly charged anions than of their singly charged analogues.

After reduction of **2** with potassium in DME at $-90\,°$C we observed the ESR and ENDOR signals of a single radical anion (species **C**). Among the experimental coupling constants $a_H$ [mT], six (0.492, 0.265, 0.252, 0.205, 0.171, 0.067) are due to 2 protons, while one coupling constant (0.051) must be assigned to 4 protons. The assignment of these coupling constants to the individual positions (see Scheme 1, center) follows, again, from a correlation of experimental and calculated data. As expected, the largest coupling constant is due to the terminal centers of the triene chain. When **2** was reduced with potassium in MTHF, the resulting radical anion gave rise to different ESR and ENDOR spectra.

Scheme 1. Experimental and theoretical ESR hyperfine coupling constants $a_H$ [mT] of the radical anions $1^{-\cdot}$ (top), $2^{-\cdot}$ (center), and $3^{-\cdot}$ (bottom). The calculated data are given in parentheses. The experimental values have been determined under the following conditions; $1^{-\cdot}$: 2-methyltetrahydrofuran with $K^+$ as counterion, the upper values are due to species **A**, the lower ones to species **B**; $2^{-\cdot}$: dimethoxyethane with $K^+$ as counterion (species **C**), the data of a second species **D** are discussed in the text; $3^{-\cdot}$: dimethoxyethane with $K^+$ as counterion. In all cases the assignment of the nonequivalent *ortho* and *meta* phenyl protons is tentative.
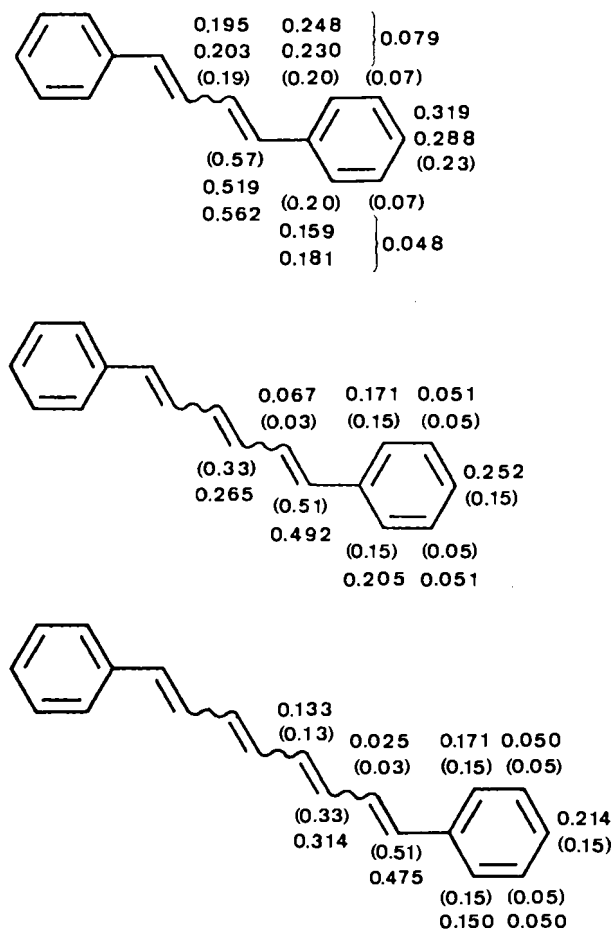


From the ENDOR resonances we obtained the following coupling constants: 0.562, 0.518, 0.501, 0.367, 0.259, 0.205, 0.174, 0.154, 0.009, 0.056, 0.029 mT. The number of coupling constants leaves no doubt that more than one stereoisomer is present. However, the overlapping of the complex signals does not allow a detailed analysis. It is characteristics that there are *three* large coupling constants with a value of about 0.5 mT. According to the behavior of the pure stereoisomer **C** (see Scheme 1, center), these $a_H$ values must be assigned to 1-H. It cannot be decided from the data how many different stereoisomers are actually present. What is clear beyond doubt, however, is that experimental situations favoring tight ion pairs, again, give rise to more than one stereoisomeric form of the radical anion $2^{-\cdot}$.

The ESR-hyperfine coupling constants of $3^{-\cdot}/K^+$ are also given in Scheme 1 (bottom). Since in the ENDOR spectrum of $3^{-\cdot}/K^+$ the largest coupling (due to 1-H) only gives rise to a single line a conclusion as to stereoisomers cannot be drawn.

## 3. Conclusion

Compounds **1** − **3** provide the first examples of linear conjugated polyenes in which the structural effects of electron-transfer processes, namely, the formation of different stereoisomers upon doping, can be systematically monitored for both mono and doubly charged species. It appears that knowledge of the crystal structure of $1^{2-}/2Li^+/(TMEDA)_2$ contributes to an understanding of the solution structures of the dianionic species. Care must be taken, however, when extending such discussions to higher homologues with longer $\pi$ systems and to organometal systems with counterions other than lithium. The model character of **1** − **3** for polyacetylene would demand an inclusion of 1,n-diphenyl-polyenes with extended $\pi$ chains. Studies directed toward doping of the latter are under way.

## Experimental

**1** − **3** are commercially available and were purified by recrystallization from methanol. The techniques applied for the preparation of the anions have been extensively described by us elsewhere[32].

*Quenching Studies.* − 1) *Dimethyl Sulfate:* The sealed NMR tube was opened under argon and the dianion solution was added dropwise to a solution of dimethyl sulfate in dry, degassed THF. The reaction mixture was stirred for a few minutes, extracted with aqueous ammonia and water in order to remove the dimethyl sulfate; the organic layer was then dried with sodium sulfate and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel (Merck Kieselgel 60, 70−230 mesh ASTM) with chloroform as eluent. The first fraction was found to contain a dimethyl derivative as characterized by mass spectrometry. Mass calculated and found for $C_{18}H_{20}$, $m/z$ = 236.1, and $C_{20}H_{22}$: $m/z$ = 262.1.

2) *Methanol:* The sealed NMR tube was opened under argon and a few drops of methanol were added to the dianion solution. The color of the solution ($1^{2-}/2Li^+$: red, $2^{2-}/2Li^+$: blue) disappeared immediately. The solvent was evaporated under reduced pressure and the residue purified by chromatography (experimental conditions see above). In the case of the quenching of $1^{2-}/2Li^+$, the product was shown by $^1$H-NMR spectroscopy to be a 1:2 mixture of 1,4-diphenyl-1-butene [identified by multiplets at δ = 2.55 (2H), 2.8 (2H), 6.2−6.5 (2H), 7.1−7.5 (10H)] and 1,4-diphenyl-2-butene (4) [identified by multiplets at δ = 3.53 (4H), 5.73 (2H), 7.1−7.5 (10H)]. In the case of quenching of $2^{2-}/2Li$, the $^1$H-NMR spectrum of the product **5** shows a multiplet at δ = 3.4−3.6 (4H) which was assigned to be the allylic and benzylic resonances of a mixture of 3 stereoisomers. The other multiplets are δ = 5.4−6.6 (4H, olefinic) and δ = 7.1−7.4 (10H, aromatic).

*1,4-Diphenyl-2-butene* (**4**) *and 1,6-Diphenyl-2,4-hexadiene* (**5**): **4**[33] und **5**[34] were prepared on a preparative scale by reduction with sodium in dry diethyl ether and final addition of methanol[35]. The products were purified by chromatography on silica gel (Merck Kieselgel 60, 70−230 mesh ASTM) with hexane (for **4**) or tetrachloromethane (for **5**) as eluent, followed by three recrystallizations from methanol. In both cases, a mixture of stereoisomers was obtained as apparent from the $^1$H-NMR spectra. − $^1$H NMR (CDCl$_3$, 200 MHz): **4**: Mixture of 2 stereoisomers in a ratio of 3:1; δ = 3.37 (m, major isomer, 4H) and δ = 3.54 (d, $^3J$ = 6 Hz, minor isomer,

4H), δ = 5.64 – 5.72 (2H, olefinic), 7.15 – 7.30 (10H, aromatic). **5**: Mixture of 2 stereoisomers in a ratio of 3:2; δ = 3.4 (d, $^3J$ = 6 Hz, major isomer, 4H) and δ = 3.6 (d, $J$ = 7.5 Hz, minor isomer, 4H), δ = 5.7 – 6.6 (4H, olefinic), 7.1 – 7.35 (10H, aromatic).

*[μ-(1,4-Diphenyl-2-butene-1,4-diyl)]bis(N,N,N',N'-tetramethyl-1,2-ethanediamine-N,N')dilithium* [**1A**(TMEDA)$_2$]: **1A**/(TMEDA)$_2$ was prepared according to the literature[12]. The purple crystals were placed at the bottom of an NMR tube under an argon atmosphere, dissolved in [D$_8$]THF (distilled in from storage vessel) at −100°C and characterized by NMR spectroscopy immediately.

*Equipment:* The ESR and ENDOR spectra of the paramagnetic derivatives of **1**$^{-\cdot}$ – **3**$^{-\cdot}$ were measured with a Bruker ESP 300 spectrometer. The $^1$H- and $^{13}$C-NMR spectra of the diamagnetic ions were recorded with a Bruker AM 200 and a Bruker AM 400 spectrometer. The products of the quenching reactions were identified by mass spectra taken with a Varian MAT CH7A instrument. The simulation of the AA'BB'-spin systems were performed with the Bruker program PANIC, Version 85051.

CAS Registry Numbers

(*E,E*)-**1**: 538-81-8 / (*E,E*)-**1**$^{\cdot-}$ · K$^+$: 116003-62-4 / (*E,E*)-**1**$^{\cdot-}$ · Li$^+$: 116003-61-3 / **1A**(TMEDA)$_2$: 97128-18-2 / (*E,E,E*)-**2**: 17329-15-6 / (*E,E,E*)-**2**$^{\cdot-}$ · K$^+$: 116048-79-4 / (*all-E*)-**3**: 22828-29-1 / (*all-E*)-**3**$^{\cdot-}$ · K$^+$: 116048-80-7 / (*E*)-**4**: 1142-22-9 / (*Z*)-**4**: 1142-21-8 / (*E,E*)-**5**: 105230-99-7 / (*E,Z*)-**5**: 105230-98-6 / (*Z,Z*)-**5**: 115943-82-3 / PhCHLiCH=CHCHLiPh: 96548-38-8 / PhCHKCH=CHCHKPh: 111865-01-1 / PhCHLi(CH=CH)$_2$CHLiPh: 115943-77-6 / PhCHK(CH=CH)$_2$CHKPh: 115943-78-7 / PhCHLi(CH=CH)$_3$CHLiPh: 115943-79-8 / PhCHMeCH=CHCHMePh: 115943-80-1 / PhCHMe(CH=CH)$_2$CHMePh: 115943-81-2 / (*E*)-PhCH=CH(CH$_2$)$_2$Ph: 27066-35-9

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