The Extension of a Polaron (Radical Anion) over Oligophenylenevinylene Chains

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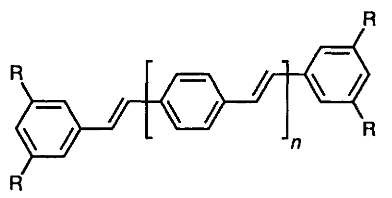
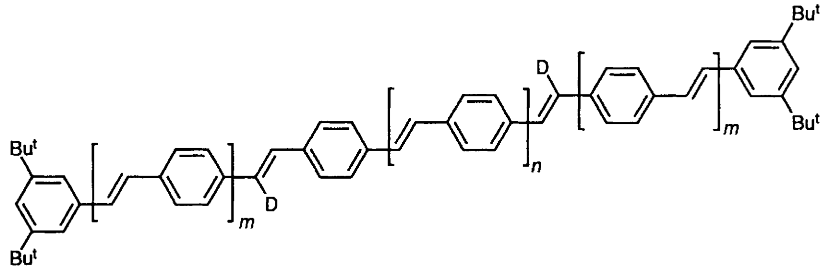
The radical anions obtained from a homologous series of soluble oligophenylenevinylenes have been characterized by ESR and ENDOR spectroscopy in solution; the spin density tends to be localized in a central unit of the chain.

The existence of neutral and charged defects in conjugated polymers is crucial for an understanding of the mechanism of electrical conduction.[1–6] Typical questions for polymers with a non-degenerate ground-state such as polyphenylenevinylenes concern the extension of a polaron (radical ion) over the chain, the degree of the corresponding lattice distortion and the formation of a bipolaron.

Problems with the polydispersity, insolubility and structural inhomogeneity of many polymers prompted us to synthesize a homologous series of well-defined, soluble oligophenylene-



1: $n = 0, R = H$
2: $n = 1, R = H$
3: $n = 2, R = Bu^t$
4: $n = 3, R = Bu^t$
5: $n = 4, R = Bu^t$
6: $n = 5, R = Bu^t$
7: $n = 6, R = Bu^t$



8: $m = 0, n = 2$
9: $m = 1, n = 0$
10: $m = 0, n = 3$
11: $m = 1, n = 1$
12: $m = 1, n = 2$
13: $m = 2, n = 0$

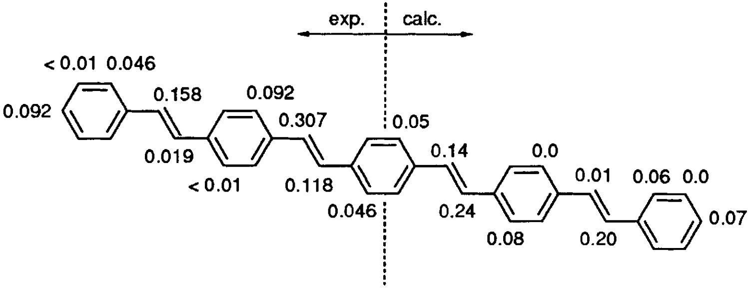


Fig. 1 Hyperfine coupling constants (in mT) for the radical anion $\mathbf{4}^{\bullet -}$

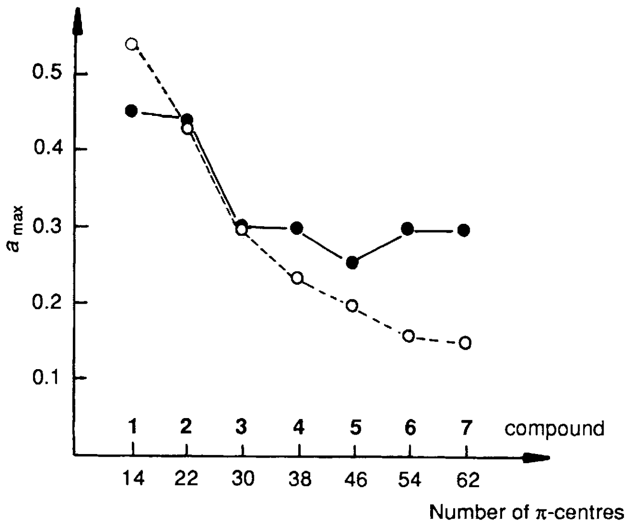


Fig. 2 Calculated (○) and experimental (●) values of a_{max} for the radical anions $\mathbf{1}^{\bullet -}$ to $\mathbf{7}^{\bullet -}$

	a_{max}/mT	
	Calc.	Exp.
1	0.53	0.44
2	0.43	0.44
3	0.30	0.30
4	0.24	0.31
5	0.20	0.25
6	0.16	0.30
7	0.15	0.31

vinylenes **1**–**7**. Their electrochemical reduction and the determination of the corresponding redox potentials as a function of chain-length allowed us to investigate an eventual extra-stabilization of diionic states.[7]

Herein we characterize the radical anions derived from **1**–**7** (with up to 8 phenyl units) and of their deuteriated derivatives **8**–**13** by means of their solution ESR and ENDOR spectra. The detailed analysis of the prevailing spin density distribution constitutes an unprecedented approach for describing the extension of a 'charged defect' over the chain.

The radical anions $\mathbf{1}^{\bullet -}$ to $\mathbf{13}^{\bullet -}$ have been prepared in dimethoxyethane (DME) by reduction of the neutral compounds with potassium; the monocharged species are stable below $T = 270$ K and exhibit intense ESR and ENDOR spectra. The former are resolved only in the case of $\mathbf{1}^{\bullet -}$, $\mathbf{2}^{\bullet -}$ and $\mathbf{3}^{\bullet -}$. The larger systems exhibit S-shaped ESR spectra without any hyperfine resolution. For all radical anions the determination of the hyperfine coupling constants is based on the ENDOR experiment (200 K).

For a typical example, *i.e.* radical anion $\mathbf{4}^{\bullet -}$, the whole set of hyperfine coupling constants is given in Fig. 1. The assignment is based on a HMO–McLachlan calculation.[8,9]† The assignment of the two largest coupling constants of $\mathbf{4}^{\bullet -}$ and its higher homologues is also based on experimental evidence since we

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† The ENDOR signal corresponding to a_{max} of $\mathbf{3}^{\bullet -}/K^+$ exhibits a small (temperature independent) splitting of 0.02 mT. This finding might indicate the presence of two non-isodynamic conformers differing by the angle of torsion about the formal single bonds close to the central benzene ring. The conformers, however, do not differ significantly in the mode of spin density distribution. Conformational isomerism[9] can also be deduced from the NMR spectra of the dianion salt $\mathbf{3}^{2-}$–$2K^+$.

have available the series of deuteriated derivatives **8–13**. For systems with an odd number of benzene units (**2**$^{\cdot -}$, **4**$^{\cdot -}$ and **6**$^{\cdot -}$) the protons with the largest coupling constants are localized at the two double bonds directly connected with the central ring; for the systems with an even number of benzene units (**1**$^{\cdot -}$, **3**$^{\cdot -}$, **5**$^{\cdot -}$ and **7**$^{\cdot -}$), these coupling constants (a_{max}) belong to protons localized at the two double bonds connected to the central stilbene moiety. The only exception from this rule is the stilbene radical anion[10] itself in which one finds the proton with the largest coupling constant at the central π-bond.

From a MO theoretical point of view one would expect that the increasing size of the π-systems leads to an increasing distribution of spin density which is reflected mainly by the largest hyperfine coupling constant a_{max}. Fig. 2 provides a schematic comparison of calculated [HMO–McLachlan procedure[8] ($\lambda = 1.2$) and McConnell[11] equation ($Q = 2.5$ mT)]‡ and experimental values of a_{max} for the radical anions **1**$^{\cdot -}$ to **7**$^{\cdot -}$. Obviously, for **1**$^{\cdot -}$ to **3**$^{\cdot -}$ there is a good correspondence between calculated and experimental coupling constants. With increasing size of the systems (**4**$^{\cdot -}$ to **7**$^{\cdot -}$) the experimental value of a_{max} is stabilized around 0.3 mT, whereas the calculated value drops to 0.15 mT. Obviously, the assumed distribution of spin density is not confirmed by the experiment. Instead, the experimental values for a_{max} are indicative of a localization of spin density in central parts of the molecules.

The energy gain associated with an extended spin delocalization over the chain depends on a tendency towards uniform π-bond orders of formal double and single bonds and, thus, also on the angle of torsion about the latter. Accordingly, the observed tendency towards spin localization may result from the fact that the delocalization energy per single bond decreases with increasing chain length. Another relevant factor is the polarizing effect of the counter-ion. In dealing with the relative importance of both influences a comparison of the radical anion structure in solution and in the solid-state should be revealing. Such studies are under way.[12]

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‡ Of course, within this simple approach the Q-value of the McConnell equation is kept constant for the homologous series.