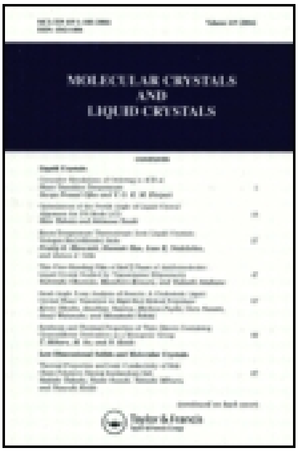

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Novel Oligoradicals and High Spin Formation

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NOVEL OLIGORADICALS AND HIGH SPIN FORMATION

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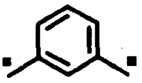
Abstract **Orthogonal alignment and variation of the MO-coefficients at the bridgehead postion has been tested for high spin formation in directly linked arylenes. In 2,2'-bipyrenyl and para-terpyrenyl possessing very small MO-coefficients but also small steric indrance bi- and triradicalanionss are found to be in low spin groundstate, with thermally excited triplet and quartet states 100-1000 calmol^{-1} higher in energy, respectively. For 9,9'-bianthryl biradical formation is well established, such that higher oligomers have been charged resulting in a S = 3/2 for the trimer, a S = 2 for the tetramer and a polyanionradical with descrete S = 1, S = 3/2, and S = 2 states in the polymer, where this highly charged material becomes insoluble. The ground state is again low spin due to increased deviation from orthogonality at low temperatures. The thermally activated higher spin multiplicities are found with ΔE_{ST} = 60 cal/mol (S=1), ΔE_{DQua} = 120 cal/mol (S=3/2), and ΔE_{SQuin} = 180 cal/mol (S=2),**

In another approach diketones have been investigated in depth for their alkaline metal ion bridged ketyl pairs. Thereby, novel high spin states with S = 3/2 and S = 2 multiplicities from intra and inter molecular spin coupled radical centers in meta diketones were evidenced from their zfs-components in the frozen solution EPR spectra. They can only arise from dimerized diketyls.

INTRODUCTION

Organic high spin molecules are a prerequisite for organic based ferromagnets. Several approaches towards high spin molecules are described in the literature.[1,2,3] Most of them are using the 'meta' linkage of radical sites as in 1,3-benzoquinodimethane **1** or the 'disjoint' connection of radical centers both leading to non-Kékule resonance structures.[4,5] High symmetry of aromatic hydrocarbons has also been used, where an additional redox process can transfer the doubly occupied degenerate highest occupied MO's into semioccupied MO's.[6] The latter approach, however, has only succeeded in preparation of biradicals, even if higher symmetries are accessible, as for instance in C_{60}.

In the first approach we wanted to know whether steric hindrance (e.g. orthogonal alignment) combined with variation of the MO coefficient at the bridgehead position of larger aromatic π–units in their radical ion state can also be used for high spin alignment.[7,8] In the second approach possiblities for additional strong intermolecular interactions between high spin molecules were tested. While a large number of stable high spin molecules either with neutral or charged radical centers is known, it has been found in majority that these molecules are rarely suitable for obtaining organic based ferromagnetic materials, since the antiferromagnetic intermolecular interaction compensates the intramolecular spin alignment in the bulk.[1-3] A very promising class of compounds, which are easily accessible but have hitherto not been used in this field, are the ketyl radicals. Since the early work by Hirota and Weissman[9,10] the mono ketyls are known to form strongly coupled biradicals, while for the extended di- and oligoketones no report of higher spin states S>1/2 has been presented so far.[11] Our approach to novel high spin aggregates, therefore, rested upon reexamination of the well known *m*-dibenzoylbenzenes **2a** and **2b**,[12] because they combine two principles towards high spin molecules: i) use of m-phenylene units as spin coupling unit as in **1** and ii) use of metal



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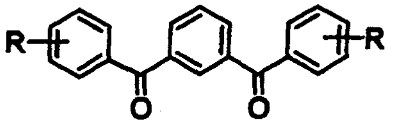
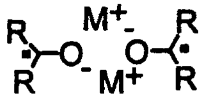


2a, **R** = *p-tert*-butyl
2b, **R** = 2,4,6-trimethyl



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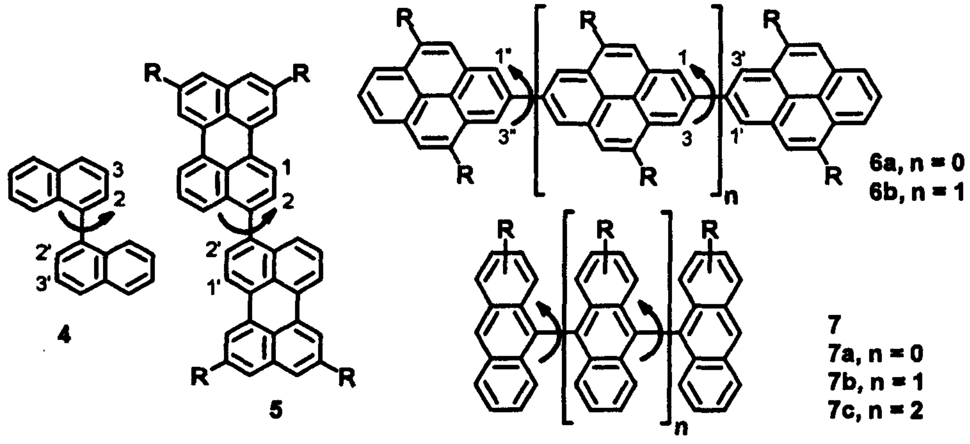
ketyls **3** as spin carrying centers to allow for intra and inter molecular couplings.[3,9-12]

RESULTS

Bi- and Oligoarylenes may either be viewed as extended π-systems or as directly linked redox active units. This classification depends on the π–interaction between the arylenes which is determined by the steric hindrance and the MO-coefficient at the bridgehead position. For 1,1'-binaphthylene (**4**) the chromophores are nearly independent and an angle of torsion of 78° is given from x-ray structural analysis.[13] Upon charging a completly delocalized monoanion of $4^{\cdot-}$ with partially flattened subunits with θ = 50° is revealed from EPR/ENDOR spectroscopy and higher charging results in a diamagnetic dianion. In 3,3'-biperylene **5**, where the MO-coefficient at the bridgehead position is reduced from 0.229 (**4**) to 0.153 (**5**), similar steric demands as in **4** are prevailing, and only a vanishingly small bathochromic shift (6 nm) is observed when compared to perylene itself. These conditions result in a bistable state, enabling a switch of the mono radical anion from a stage of complete delocalization at high temperatures to a localized form at low temperatures within the timescale of the EPR experiment ($10^{-7}s^{-1}$),[14] but the dianion is still spin paired.



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5

6a, n = 0
6b, n = 1

7
7a, n = 0
7b, n = 1
7c, n = 2

Very small MO-coefficients at the bridgehead position (ρ = -0.054) are found when coupling pyrenyls (**6**) through position 2, placed on the nodal plane of the HOMO and LUMO. Although the steric situation in **6** is close to the one in biphenyl the small MO-coefficient leads to an effective uncoupling of the electrophores, allowing nearly independent charging of the subunits.[15] Therefore bi- and triradicalanions are found for the dimer **6a** and trimer **6b** with axial (E = 0) zero field splittings (zfs) of D_{bi} = 7.90 mT and D_{tri} = 5.53 mT, respectively, but the temperature dependent measurements revealed groundstate singlets and doublets. For $\mathbf{6a}^{2\cdot-}$ and $\mathbf{6b}^{2\cdot-}$ the maximum of EPR signal intensity is found at 40 K, while for the trimer $\mathbf{6b}^{3\cdot-}$ it lies above 100 K, corresponding to triplet-singlet and quartet-doublet excitations of roughly 100-1000 cal/mol.

9,9'-bianthryl **7a** is known to be aligned nearly orthogonal such that the chromophores are uncoupled, allowing biradical formation when charged twice.[8] We therefore studied also higher oligomers like trimer **7b**, and tetramer **7c**. During the reduction process several spin states could be identified through changes in their zero field splitting components, also establishing tri- (S = 3/2) and tetraradicalanion (S=2) formation, for $\mathbf{7b}^{3\cdot-}$ (see Fig. 1) and $\mathbf{7c}^{4\cdot-}$, respectively.[8,16] Additional to the identification of each spin state by measuring the transition states, further evidence for the highest possible spin states relies on the computer simulation[17] of the experimental EPR spectra and the detection of $\Delta m_s = 3$ transitions at $B_{res}/3$, which is just one of the very rare cases where a $\Delta m_s = 3$ transition could be measured at X-band frequency.[16,18] The corresponding zfs-components are given in Table 1. The stability of these higher charged states is proven by the detection of high field shifted ^{1}H-NMR-resonances for all protons of the hexaanion $7c^{6-}$, whose assignment to individual molecular positions is secured by cross correlation in the 2D spectrum.

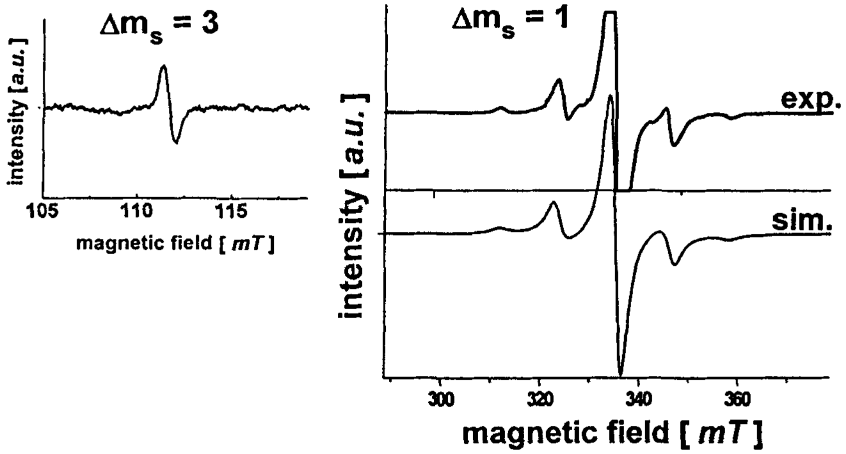
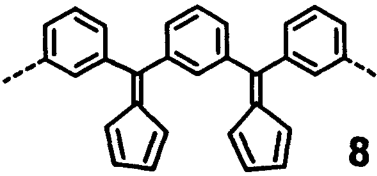


FIGURE 1 EPR spectra of triradical $7b^{3\cdot-}$ together with computer simulation.

Since the reduction to higher spin states worked out fine, we proceeded to preparation of polymeric anthrylene compounds 7 which became available by coupling reaction of bisanthrone with the 9,9'-dilithio derivative of trimer **7b**. Even in the polymer, containing 20 repeat units in average, polyanion formation is accompanied by detetion of triplet, quartet, and quintet states. The highly charged material becomes insoluble, however, and it is not found out yet, whether higher spin states are excluded by non charged or doubly charged anthrylenes in between.

Temperature dependent studies of the signal intensity have been performed in order to identify the ground state multiplicities, revealing two important features for the bianthrylene $7a^{2\cdot-}$: i) the triplet state is thermally activated by 60 cal/mol and ii) the symmetry is lowered upon decrease of temperature. The increase of signal separation of the x and y zfs components is in agreement with x-ray structural results of the neutral trimer **7b**, where an angle θ of torsion between the anthracenes of 75^o has been measured.[19] Despite the hope for larger stability of the higher spin states the temperature dependency of their fine structure resulted in low spin ground states, with $\Delta E_{DQua} = 120$ *cal/mol (S=3/2) and* $\Delta E_{SQuin} = 180$ *cal mol (S=2), respectively. Thus* even stronger limitations of the rotational freedom between the anthracenes are still necessary for orthogonal alignment with high spin groundstate in the charged species.

Bridging of radical centers through a *m*-phenylene unit is well established for high spin formation,[2] and we started from the ketones **2** and their derivatives. Ketones are important intermediates in organic syntheses being easily derivatized and, as outlined in the introduction, possess interesting properties upon charging. The preparation of the corresponding fulvenes **8** has been accomplished by Oda (Osaka, Japan)[20] and we were able to demonstrate their high spin character upon charging. Even more, it was possible to differentiate between strong intra and weaker inter molecular couplings, where the latter are already found in frozen solution spectra of the monoanion.



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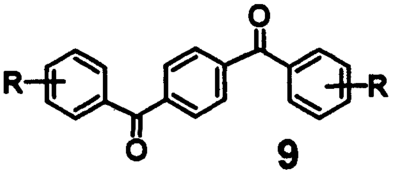

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The early EPR measurements of the ketyl radicals themselves,[9,10] on the other hand, revealed that they exhibit complex spectroscopic behavior: they can exist not only in the forms of free ions and ion pairs but may aggregate to dia- and paramagnetic dimers.[9,12] Upon reduction of the *tert*-butyl-diketone **2a** the well known characteristics

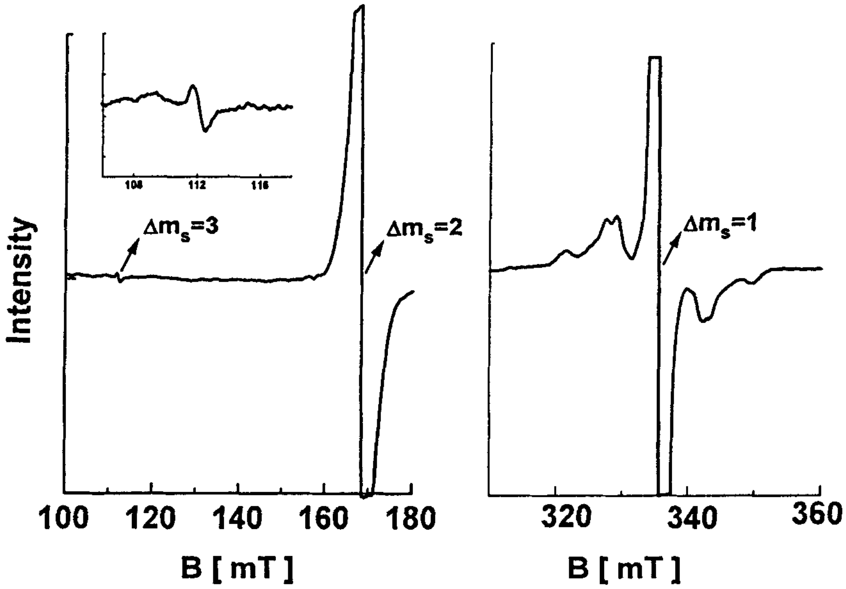

FIGURE 2 Fozen solution EPR spectrum of $(\mathbf{2b})_2^{3\cdot-}$ in THF/K.

of the monoanion have been found (λ_{max} = 401, 514 nm),[12] but some further reduction immediately led to a frozen solution EPR spectrum consisting of large zfs components with 11.3 and 20.0 mT, by far exceeding the anisotropic components of the monoradicals. These zfs are comparable to those reported for the benzophenone (**BP**) radical anion.[10] Slightly further reduction to the dianionic state is combined with increase of optical absorptions at 340 and 682 nm for the dianion and leads to a well defined new EPR spectrum from a different spin state which should stem from an S = 3/2 state (Fig. 2, Tab.1). The computer simulation of this quartet state with zfs values D = 7.125 mT and E = 0.25 mT produce good agreement between simulated and experimental spectrum, not only for the signal spacings, but also for their relative intensities. The quartet state is even evidenced by detection of a $\Delta m_S = 3$ transition at

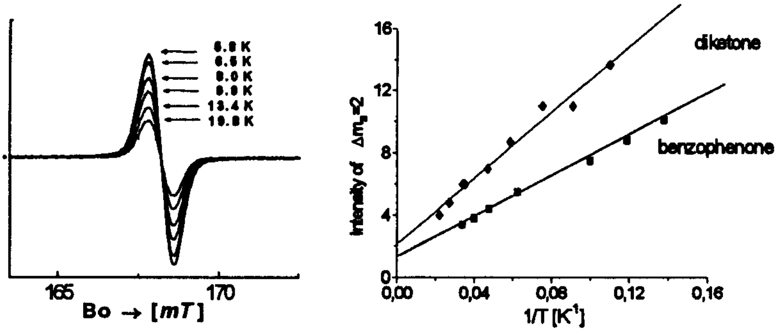

FIGURE 3 EPR signal intensity of $(\mathbf{2a})_2^{3\cdot-}$ $\Delta m_S = 2$ and plot vs. 1/T

very low temperatures (10 K, Fig. 2 left and insert). Since intermolecular coupled radical centers are often aligned antiferromagnetically, the temperature dependence of the EPR signal intensity ($\Delta m_S = 2$) was measured for $(\mathbf{2a})_2^{3\cdot-}$ and we included also benzophenone $(\mathbf{BP})_2^{2\cdot-}$ for comparison (Fig. 3). In both cases the plot of EPR signal intensity versus 1/T yielded straight lines down to 10 K, typically for high spin ground state multiplicity. Continued reduction of **2a** led to changes of the EPR characteristics again, while in the optical absorption spectra nearly no contributions from the monoanion could be detected (λ_{max}: 680, 340 nm). The EPR spectrum exhibited even larger spin-spin couplings with maximum splittings of 40.1, and 35.0 mT, which can be well simulated under the assumption of an S = 2 state (total splitting 6D and 3(D + 3E)).

In the mesitylene derivative **2b** a similar species is found upon prolonged reduction with zfs components of 45.0 and 38.0 mT with K^+ as counterion (Tab. 1). The EPR spectra closely resemble those obtained by Dougherty et al. for a quintet state with large rhombic components.[21] The smaller zfs components in the case of $(\mathbf{2b})_2^{4\cdot-}$ compared to $(\mathbf{2a})_2^{4\cdot-}$ can easily be understood in view of enhanced steric hindrance and some donating effects of the methyl groups in **2b**, increasing the charge and spin density in the central part of the molecule.

Although being less interesting, even higher reduction states are accessible and characterized by different zfs components. In the case of **2b**, a trianion radical (S=3/2) presumably from a dimer like $(\mathbf{2b}^{2\cdot-})(\mathbf{2b}^{3\cdot-})$ has been found (D = 6.4 mT). For **2a** the reduction to the trianion shifts the absorption bands hypsochrome to 600 nm, while the former fine structure vanishs and only a weak biradical with D = 5.2 mT remains detectable in frozen solution. In these highly reduced states often protonation as a side reaction is observed.

TABLE 1: zfs parameters of the different spin states in frozen solution.

compound	Spin	D	E
benzophenone **BP**$^{\cdot-}$	1	10.2-10.3	0 - 0.1
(2a)$_2^{3\cdot-}$	3/2	7.125	0.25
(2a)$_2^{4\cdot-}$	2	6.68	1.66
(2b)$_2^{4\cdot-}$ (K)	2	7.5	1.72
(2b)$_2^{4\cdot-}$ (Li)	2	7.33	1.25
6a$^{2\cdot-}$	1	7.90	0-0.1
6b$^{3\cdot-}$	3/2	5.53	0-0.1
7a$^{2\cdot-}$	1	16.5	0-0.5
7b$^{3\cdot-}$	3/2	11.9	0-0.5
7c$^{4\cdot-}$	2	9.0	0-0.5

It is interesting to note that large zfs components exceeding those reported for benzophenone can also be observed in para-diketones **9**, which are normally be thought to undergo spin pairing in the diradical state. Thus the strong intermolecular spin coupling through counter metal ions prevents spin pairing even in para conjugated π-systems without strong steric hindrance.

CONCLUSION

The oligoarylenes can be tuned to form oligoradicalanions but the steric demands are still not sufficient for stable high spin formation even in the case of strong counter ion conditions (contact ion pairs, MTHF-K) as obtained for the anthrylenes, since at low temperatures a deviation from orthogonal alignment occurs.

The high spin ketyl molecules and aggregates once formed are thermally extraordinary stable and can be stored at room temperature without change of the spin state. This principle of combination of inter- and intermolecular spin coupling hopefully opens the way to new organic based ferromagnetic materials.

ACKNOWLEDGMENT

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