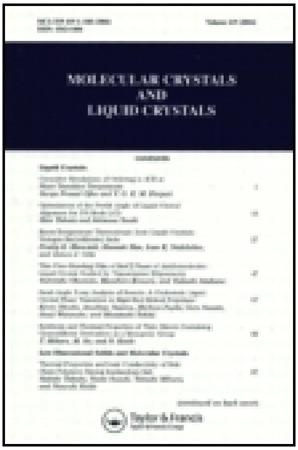

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Martin Baumgartena [a] , Timucin Yüksel [a] , Daniel Caparros [a] & Stoyan Karabunarliev [a] [b]

[a] Max-Planck-Institut für Polymerforschung, D-55128, Mainz, Ackermannweg 10, Germany
[b] Burgas University, 8010, Burgas, Bulgaria

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Novel High Spin Molecules and Intermolecular Aggregates

MARTIN BAUMGARTEN[a], TIMUCIN YÜKSEL[a],
DANIEL CAPARROS[a] and STOYAN KARABUNARLIEV[ab]

[a]*Max-Planck-Institut für Polymerforschung, D-55128 Mainz, Ackermannweg 10, Germany; and* [b]*Burgas University, 8010 Burgas, Bulgaria*

We tried different linkages of radical sites by nearly orthogonal alignment, connection through nodal planes of frontier orbitals, phenylene bridging of π-radical ions, and intermolecular aggregation of radical ions. Thereby we found a new principle for high spin ground states of directly bridged π-radical sites, when they are connected to centers of opposite sign of spin density. Newly synthesized *ortho*-phenylene bridged bisphenothiazines and -phenoxazines and their oxidations are described and extended fuchsons for intermolecular aggregation.

Keywords: organic high spin molecules; radical ions

INTRODUCTION

In the field of organic high spin compounds many efforts went into addressing the question of the nature of intramolecular magnetic exchange induced by a coupling unit between radical sites clarifying its spin exchange coupling nature (see scheme 1).[1] As demonstrated earlier for small coupling units like a single

centers of vanishing MO-coefficients as in 2,7'-oligopyrenylenes[3] so far led only to thermally activated oligoradicals and we earlier assumed to need even stronger steric hindrance to reach high spin ground states.[4] We then tried a new approach by linking aryls through positions of opposite signs of spin density. As theoretical model we therefore have chosen the perinaphthenyl radical[5] which is well established to possess large alternating spin densities in the periphery and AM1 semiempirical calculations together with extended CI to predict singlet triplet splittings of dimeric units. The 1,2'-biperynaphthenyl **1** can thus serve as working model and just possess one single bond with conformational freedom for rotation. For **1** a ferromagnetic exchange coupling CAS[10,10] with a singlet triplet splitting of ΔE_{ST} of 0.3 kcal/mol is predicted.[5]

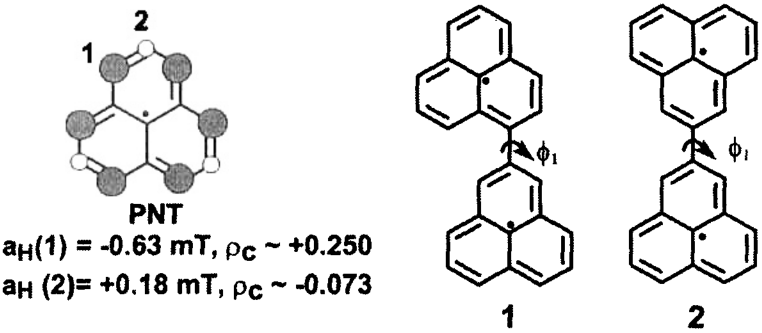
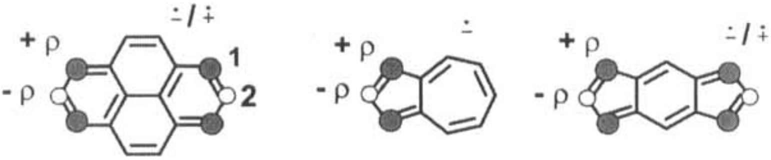
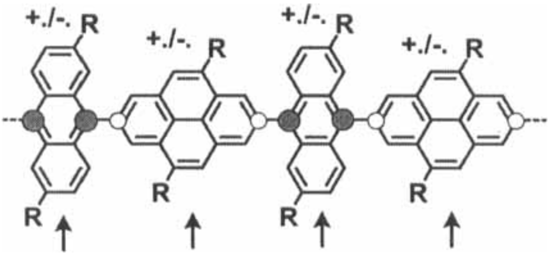


Figure 1: PNT together with spin density [6] and 1,2'- and 2,2'-biperynaphthenyls.

While experimentally a 1,1'-dimerization to a diamagnetic dimer is observed,[6] another symmetric biradical, namely the 2,2'-biperynaphthenyl **2** can be thought, where an antiferromagnetic exchange with $\Delta E_{ST} = -1.7$ kcal/mol is predicted. The reason for this dramatic differences in predicted spin exchange couplings can be rationalized by a pattern of complete alternating spin density wave with large positive and large negativ spin densities for **1** and neighbouring positions of same sign of spin densities at the connecting part of **2** and as in tetramethyleneethane or the aforementioned symmetric biaryl biradical dianions and dications. Thus these predictions should enable new access to a large class of directly linked bi- and oligoradicals and radical ions with ground state high spin multiplicity.



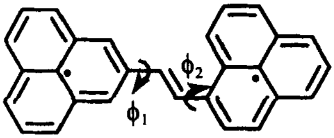
For example we have looked for radical ions possessing alternating spin density in the periphery like pyrene, azulene, and indacene, which could be used by appropriate connection with themselves or other π-units with similar redox potentials. Along this line Gompper[7] has synthesized 1,2'-bipyrenyl and 9-anthryl-2-pyrene where both, dications and dianions should allow ferromagnetic interaction, and we are now focussing on the preparation of oligo-(9,10-anthrylenyl-2,7-pyrenylene)s as suggested high spin compounds upon charging each subunit.



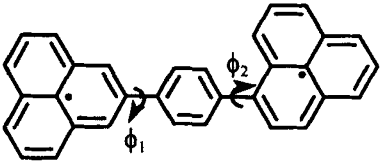
Oligo(9,10-anthrylenyl-2,7-pyrenylene)s

Even more, as shown for direct combination of π-radicals also further extended coupling units reverse their former meaning when positions of opposite sign of spin density are connected to them, e.g. 1,2-ethylene **3** and 1,4-phenylene **4** .

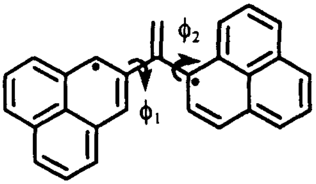
bridging, then favors ferromagnetic exchange while 1,1-ethylene **5** and 1,3-phenylene **6** connection yield antiferromagnetic exchange couplings with 1,2'-biperinaphthenyl (CI = CAS[10,10] as for **1** and **2**).



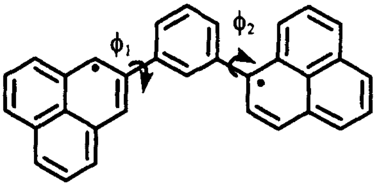
3 FM: ΔE_{ST} = + 2.13 kcal/mol



4 FM: ΔE_{ST} = + 0.81 kcal/mol

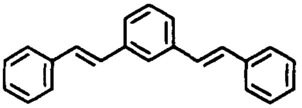


5 AM: ΔE_{ST} = -0.34 kcal/mol



6 AM: ΔE_{ST} = - 2.17 kcal/mol

While many standard bi- and oligoradicals are based on *meta*-phenylene bridging, there are still hidden some further secrets in their general applicability. First I want to mention the distyrylbenzene **7**, where we found earlier[8] that monocharging is combined with a fast charge transfer exchange indicated by a NIR transition at 1800 nm and doubly charging gives a diamagnetic state still exhibiting a strong and broad NIR optical absorption around 1450 nm.



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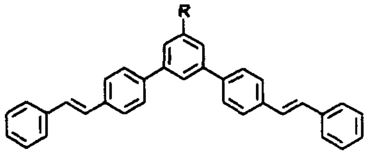

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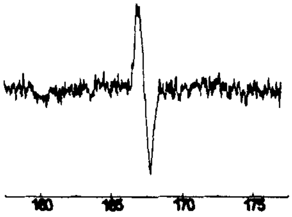
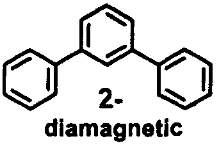


Figure 2: Δms=2 signal for the triplet dianion of **8**.

For the extended distilbenylbenzene **8**, on the other hand, a single charge is localized on one phenylstilbene branch and doubly charging yields a triplet biradical, indicated by their zero field splittings also with a transition in the Δm_s=2 region, and no hint for a thermal activation (4-100 K).

These facts/findings may also be considered in the context of polaronic ferromagnets (Fukutome model).[9] i) If the chargeable unit becomes too small and charge transfer between the two branches occur no high spin molecule will result. ii) If one extends the oligomeric series to the next higher oligomer (e.g. four phenyl units) no FC coupler exists. Most easily this can be shown for *meta*-terphenyl and *meta*-quaterphenyl but holds also for the oligo- *meta*-phenylenevinylenes. In *meta*-terphenyl **9** the dicharged forms are diamagnetic and in *meta*-quaterphenyl **10** two biphenyl units will be charged with an antiferromagnetic exchange coupling between 3 and 3' position.



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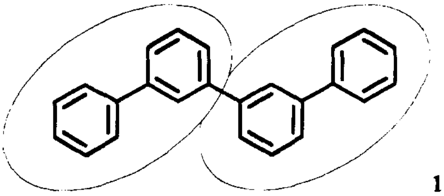

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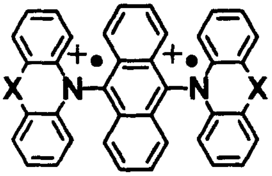
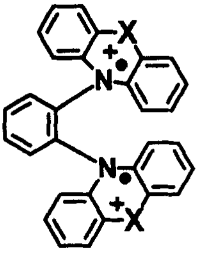
After we had studied biradical dications of *meta*- and *para*-phenylene bridged bisphenothiazines and bisphenoxazines together with K. Okada [10] we prepared also the 9,10-anthrylene **11a,b** and *ortho*-phenylene **12a,b** bridged derivatives.



X = S, O



11a,b **a**: X = S, **b**: X = O **12a,b**

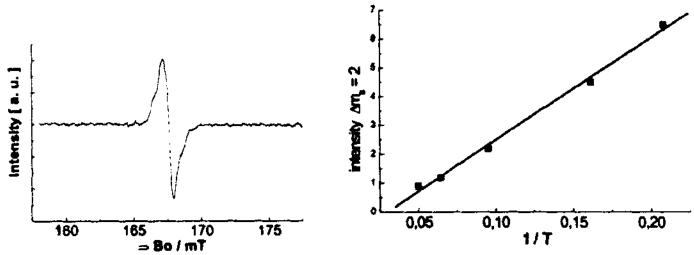


Figure 3: EPR Δm_s=2 signal of **11a**$^{2+}$ (H_2SO_4) and plot of signal intensity vs. 1/T.

For the dication of **11a** virtually no differences in the zero field splittings (D= 4.7 mT) compared to the *para*-phenylene bridged biradical occurred and again a Curie like behavior of the EPR biradical signal intensities was found. Also for the *ortho*-phenylene bridged biradicals **12a,b**, we could identify biradical dications upon oxidation in sulfuric acid (H_2SO_4 or D_2SO_4) with D = 21.3 mT for the bisphenothiazines **12a** and D = 24.0 mT for the bisphenoxazines **12b**. But using electrochemical oxidation ($N^+R_4PF_6^-$,CH_2Cl_2) in a newly designed cell for EPR/ENDOR and optical absorption measurements,[11] only monoradicals of *ortho*-bisphenothiazinyl- benzene **12a** were accessible showing a strong exchange interaction in liq. solution (5 line EPR spectrum, hfc with two nitrogen nuclei), and further oxidation led to loss of EPR signal intensity.

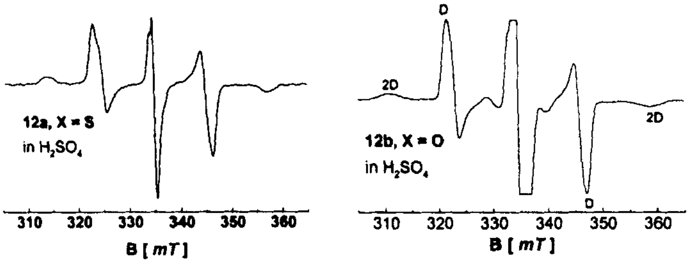
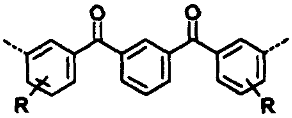


Figure 4: The frozen solution EPR spectra of **12a** and **12b** in sulfuric acid.

Thus we will further test for counter ion influences on the biradical dication formation.

Finally we looked into aggregation phenomena of high spin molecules by metal bridging. After our first reports on high spin states in dibenzoylbenzenes **13**,[4,12] this field has further emerged.[13,14] While we could identify S=3/2 and S=2 states upon double reduction (K/THF) of dibenzoylbenzene, only explainable by dimerization effects through -O^--K^+-O^--bridges as in benzophenone, higher oligo-benzoyls did not allow formation of even higher spin states. It is assumed here that charge is stabilized on different benzophenone type subunits with extreme high potential barrier for additional charging of a ketyl unit in between.



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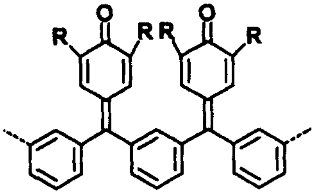

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Therefore the synthesis of the corresponding fuchson derivatives **14** was endavored, where the oligobenzoyls **13** are used as precursors. We also succeeded now in preparation of the corresponding 1,3,5-trisubstituted benzene derivatives, which are even more promising for network formation.

CONCLUSION

As we demonstrated in the first part, even direct linkage of π-radicals and π-radical ions can be used for ground high spin state formation when combining positions of opposite sign of spin density. This approach can also be used for oligomers and polymers and when applied to larger bridging units like ethylene and phenylene the classification of antiferromagnetic and ferromagnetic coupling units reverse their usual meaning.

Other examples of carefull consideration of *meta*-phenylene as ferromagnetic coupling unit were demonstrated for the oligo-*meta*-phenylenes and -phenylenevinylenes. Also for the bridged bisphenothiazines and bisphenoxazines, where *para*-phenylene and 9,10-anthrylene bridging yield stable triplet biradicals, the usual meanings of coupling units are reversed since the charged *meta*-phenylene and 1,3,5-trisubstituted benzene derivatives are thermally activated. The *ortho*-phenylene bridging surprisingly shows dramatic different results, depending on the oxidant used.

Finally, the approach to stabilize reduced states in ketyl radical anions by extending the π-system has been outlined, and should clearly be differentiated from the oligofuchsons reported by Dougherty[15] (with one phenyl ring more between the spin carrying units), where the intramolecular spin spin interaction becomes extremely weak.

ACKNOWLEDGMENT

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