

## Radical ion building blocks for organic magnetic materials

(computational and experimental approaches)

Martin Baumgarten,

Max-Planck-Institut für Polymerforschung, Postfach 3148, 55021 Mainz, Germany

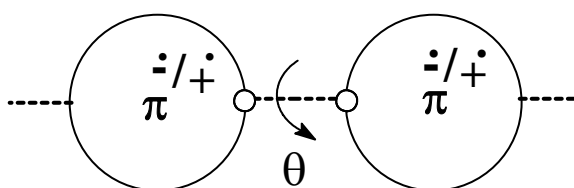
### I. Introduction

In recent years we have combined synthetic, spectroscopic and theoretical approaches in order to obtain deeper insight into mechanisms of electron spin spin interactions focussing mainly on radical ions of organic  $\pi$ -systems and their possible use for new high spin molecules.<sup>1-3</sup> We tried to test different approaches like direct linkage with close to orthogonal alignment, linkage through nodal planes of frontier orbitals, phenylene bridging of  $\pi$ -radical ions, and intermolecular aggregation of radical ions.

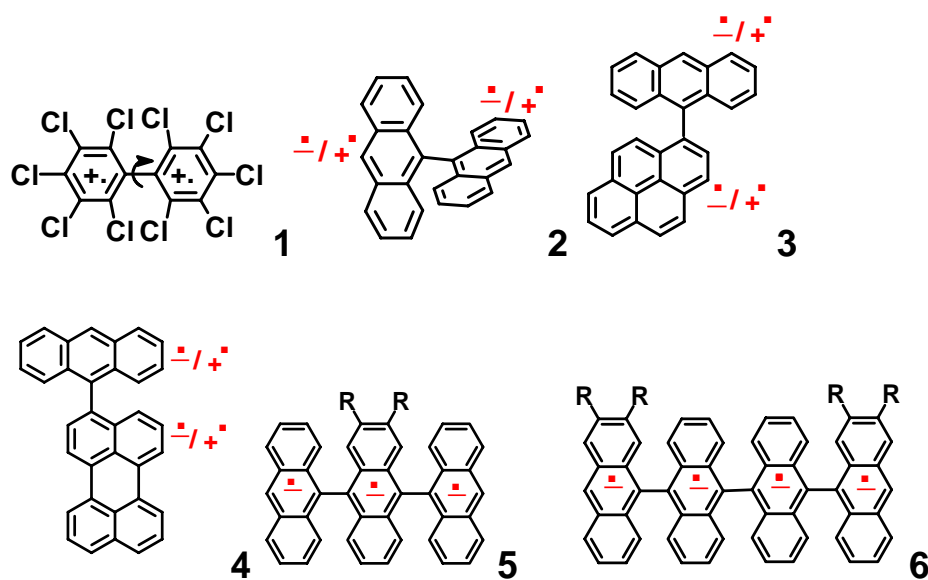
### II. Directly linked bi- and oligoradical ions

The conjugative interaction in bi- and oligoarylenes strongly depends on the topology and geometry of linkage. The linkage can lead either to fully extended conjugated polymers like polyparaphenylene or to systems of almost independent redox active subunits like poly(9,10-anthrylene)s. While for the former class charged excitations extend over several repeat units, the latter class allows the formation of radical ions on each separate subunit.

Scheme 1: schematic presentation of directly linked  $\pi$ -radical ions.



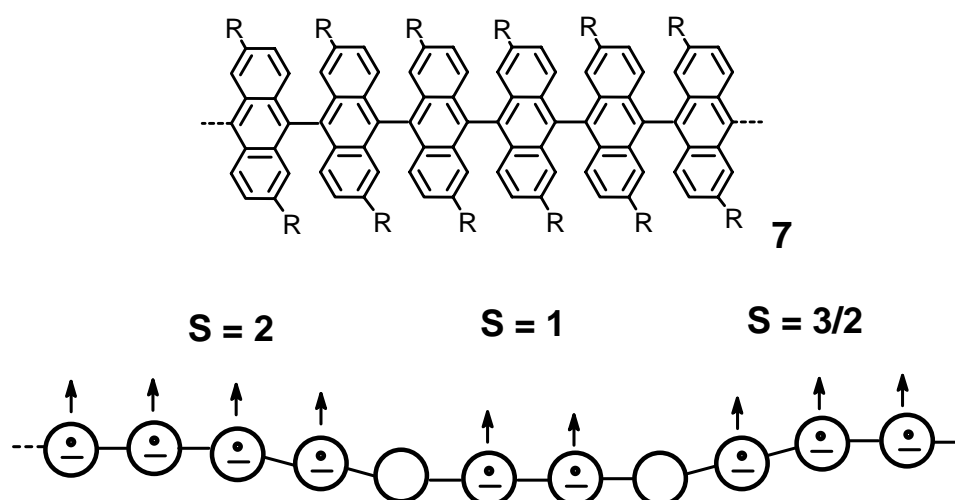
An early example of a conjugation separated biradical was given by Veciana et al.<sup>4</sup> with the perchlorobiphenyl dication **1**, where the large chloro-substituents lead to a strong twisting of the biphenyl unit and also decrease the oxidation potential. For exploring whether pure hydrocarbons can also be used for oligoradical formation upon charging, we started to study other congested bi- and oligoarylenes based on the anthracene unit **2-7**.<sup>5-8</sup>



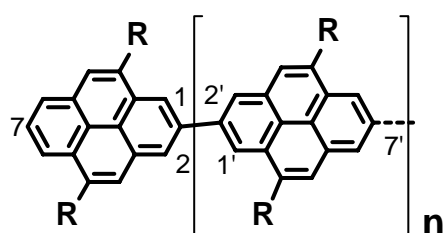
Bianthryl can be oxidized with  $\text{SbCl}_5$  to the biradical dication (zero field splitting  $D$ ,  $D = 21.0$  mT) or reduced with alkali metal to the biradical dianion ( $D = 16.5$  mT) and therefore higher oligomers were synthesized. Temperature dependent studies of the zero field splittings (zfs) in the frozen solution EPR (electron spin resonance or electron paramagnetic resonance) spectra, revealed that the multiple charged oligo(9,10'-anthrylene)s **2,5,6** exhibit thermally excited high spin multiplicities with the maxima of signal intensities 20, 40, and 60 K for the bi-, tri- and tetraradicals, respectively, corresponding to 60, 120, and 180 cal/mol.<sup>7</sup> The low temperature measurements of the bianthryl dianion additionally revealed that the average orthogonal alignment in liquid solution is lost, with a clear orthorhombicity of the zero field splitting parameters  $D$  (17 mT) and  $E$  (0.9 mT) at 20 K which correlate to an angle  $\theta$  of roughly  $80^\circ$  when judging from the two extremes  $E=0$  ( $\theta = 90^\circ$ ) and  $E_{\text{max}} = D/3$  ( $\theta = 0^\circ$ ) assuming a cos function. Also the dianions and dications of **3** and **4** form thermally activated biradicals,<sup>8</sup>

leading to the conclusion that weakly coupled biaryls **2-4** with strong intramolecular twisting (orthogonal approach) enable biradical formation in either redox process (oxidation, reduction). In the polymer **7**, charging led to discrete higher spin states of  $S=1$ ,  $S=3/2$ ,  $S=2$  (see Scheme 2) comparable to those in the small oligomers, but then precipitation occurred and the spin states are either separated through a neutral anthrylene unit or a doubly charged one.

Scheme 2: Poly(2,6-Di-tert.-butyl-9,10-anthrylene) anions with separated parts of oligoradicals



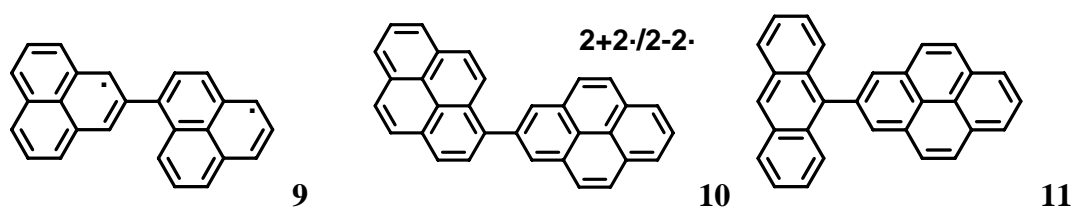
Also the bridging through a so called nodal plane of the frontier orbitals as in the bipyrenyl **8a** and terpyrenyl **8b** enables bi- and triradical formation upon multiple charging.<sup>9</sup> But again these spin states were found to be thermally activated with maximum EPR signal intensity for the triplet and quartet state at 40 and ca. 100 K corresponding to ca. 120 and several hundred cal/mol of thermal activation of the higher spin states. For the stabilization of the low spin state in these systems, spin polarization is responsible.



**8 a,b ; n = 1,2**

Due to spin polarization, small but nonnegligible spin densities propagate to the nodal  $\pi$ -sites, including the bridging 2 position. The direct overlap between the  $\pi$ -spin densities of the same sign in the 2 and 2' positions destabilizes the triplet.<sup>9,10</sup> The antiferromagnetic spin exchange between the bridging sites may only be avoided when the conjugative interaction is completely broken in an exact orthogonal alignment. Thus stronger steric hindrance would certainly be needed for the promotion of ferromagnetic coupling in the bi- and oligoradicals **2-8**, a task which seems still difficult to achieve synthetically.

Recently we have proposed a novel approach toward stabilization of high spin states in directly linked biaryl radicals. Conjugated monoradicals combine large positive and small negative p-site spin densities in an alternating fashion. The nominally antiferromagnetic interaction between adjacent  $\pi$ -sites could lead to parallel spin alignment in a biradical when the two monoradicals are linked through  $\pi$ -sites of opposite spin densities. A typical example of such a ferrimagnetic  $\pi$ -spin system is 1,2'-biperinaphthenyl **9**. Semiempirical calculations with configuration interaction to account for spin polarization suggest stabilization of the triplet state relative to the singlet, whereas for the 2,2' bridged perinaphthenyls the predicted ground state is singlet. The conceptual idea proposed here can be extended to a large class of biaryls where the triplet state should be a stable ground state entity.



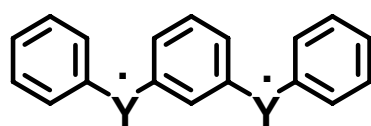
The general prerequisite for a molecule to serve as a building block in a high spin bi- or polyradical structure is the presence of alternating spin density in the neutral or charged monoradical form. Such candidates are azulene, s-indacene, pyrene, other molecules whose frontier  $\pi$ -orbitals possess a nodal plane, and some nonalternant aromatic hydrocarbons. Along

this line Gompper<sup>12</sup> synthesized 1,2'-bipyrenyl **10** and 2(9-anthryl)-pyrene **11**. The latter molecules are predicted triplet biradicals in their dication and dianion (2+ and 2-) forms. They are already characterized as persistent biradical and currently we study the temperature dependence of their zero field splittings to establish the singlet-triplet energy difference.

Since this direct combination should allow ferromagnetic electron spin-spin interaction, it follows that also 1,2-ethylene or 1,4-phenylene (*para*) bridging should result in triplet state molecules,<sup>11</sup> while *meta*-phenylene bridging should destabilize the triplet state, compared to the symmetrical substitution. And this important prediction will be further tested and leads us to the next chapter, where the phenylene bridging of radical ions is considered.

## 2. Phenylene bridging of radical ion sites, Kekulé vs. non-Kekulé structures

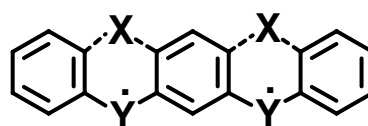
After it was shown that the degree of rotation between the conjugation planes of two bridged monoradicals plays an important role for the effective spin-spin coupling, we studied this problem in more depth starting calculations of ground state multiplicities of typical neutral or charged biradicals **12-18a**.<sup>13</sup> Thereby additional fixation to ladder type structures of the Schlenk hydrocarbon derivatives as in **12-18 b-f** was included. The results clearly indicate that the triplet state of the Schlenk hydrocarbon should be stabilized upon planarization of the backbone through a saturated methylene (-CH<sub>2</sub>-) bridge, with the extra phenyl substituents being twisted out of conjugation. This effect certainly enhances the spin density on the radical centers and in the bridging *meta*-phenylene unit.



**12a-18a**

Y = CH (**12a**), CPh(**13a**), CCH<sub>3</sub>(**14a**)

<sup>+</sup>NPh(**15a**), <sup>+</sup>NH(**16a**), N(**17a**) NO(**18a**)



**12-18 b-e**

X = CH<sub>2</sub> (**b**), CO (**c**), O (**d**), S(**e**), NH (**f**)

Y = **12 - 18**

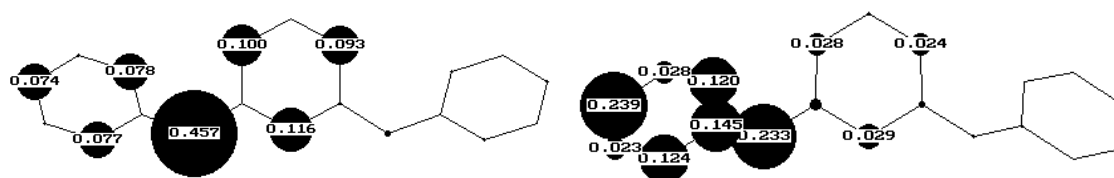


Figure 1: The POLO density distributions of singly linked biradicals **12a** and **17a**.

If , on the other hand, the neutral carbon radicals are exchanged by nitrogen the situation changes completely. Cationic nitrogen centers lead to a large increase of the twisting angle  $\theta$  to the *meta*-phenylene coupling unit and results in a strong/dramatic destabilization of the triplet state (Fig. 1, Table 1).

Table 1: Semiempirical calculated (AM1) singlet triplet ( $\Delta E_{ST}$  /eV) splittings of **12-18 a-e**.

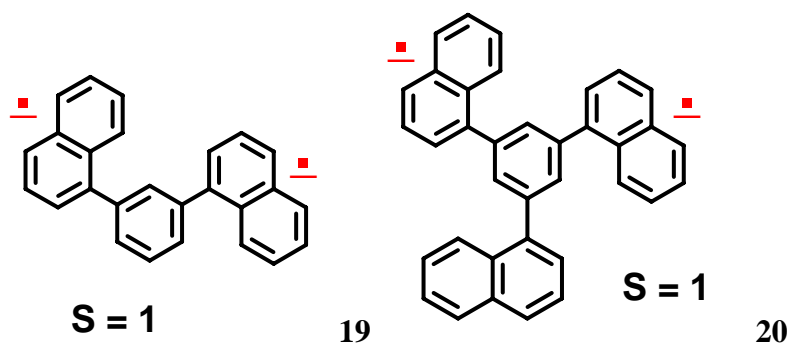
$\cdot Y \setminus X$	- (a)	CH <sub>2</sub> (b)	C=O (c)	O (d)	S (e)	NH (f)	S=O (g)	SO <sub>2</sub> (h)
$\cdot\text{CH}$ ( <b>12</b> )	0.45	0.40	0.28	0.14	0.14	-0.20	0.003	0.18
$\cdot\text{CPh}$ ( <b>13</b> )	0.20 <sub>ex1</sub>	0.36 <sub>ex2</sub>	0.24	0.14	0.14	-0.18	0.003	0.11
$\cdot\text{CCH}_3$ ( <b>14</b> )	0.48	0.32	0.23	0.10	0.12	-0.18	0.003	0.16
$\cdot\text{+NPh}$ ( <b>15</b> )	0.02	0.05	0.07	-0.12	-0.21	-0.37	0.002	0.04
$\cdot\text{+NH}$ ( <b>16</b> )	0.03	0.03	0.08	-0.15	-0.20 <sub>ex3</sub>	-0.44	0.001	0.04
$\cdot\text{N}$ ( <b>17</b> )	0.86	0.53	0.31	0.16	0.06 <sub>ex3</sub>	-0.30	0.003	0.13
NO $\cdot$ ( <b>18</b> )	0.22	0.19	0.15	0.16	0.22	0.10	0.01	0.09

ex = experimentally verified: ex1 [14], ex2 derivative of **13b** [15], ex3 derivatives of **16e** and **17e** [16]

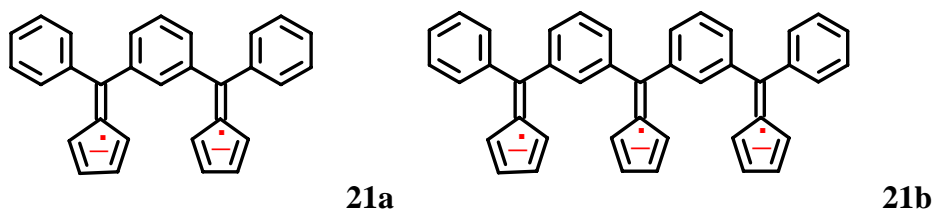
## 2.1. Radical anions

In 1992/1993 we started to study different phenylene bridged redox centers **19-24** given below, since not many charged  $\pi$  radical sites had been used before. The 1,3,5-(tris-1-naphthyl)benzene **20**, however, could be reduced with K in THF only to the biradical dianion, with very similar properties as the di-naphthyl-benzene **19** reported by Tukada<sup>17</sup> (Na/THF), indicating that the

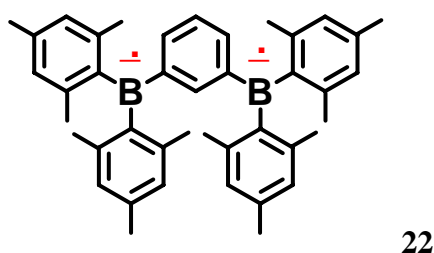
third naphthyl unit does not contribute much to the spin density delocalization in the doubly charged state.



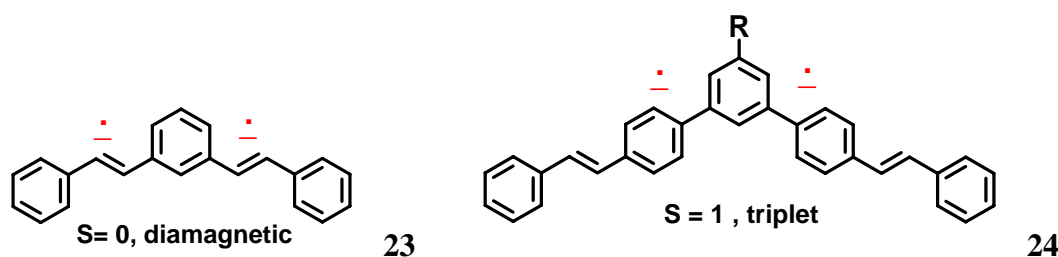
The fulvenes **21a,b** and the diboride **22** were studied in collaboration with Profs. M. Oda and K. Okada (Osaka, Jp) <sup>18</sup> and for **21**<sup>2,2-</sup>, for our first time, we found a linear behavior of EPR signal intensity versus reciprocal temperature (Fig.2) indicating a triplet ground state of the dianion.



The diboride **22**, on the other hand, showed only a very small zero field splitting of approximately 3.7 mT (0.0034 cm<sup>-1</sup>) when reduced with K in THF and we hesitated to publish this result, while a year later Rajca <sup>19</sup> showed a relatively strong zero field splitting of  $D_{\max} = 0.022 \text{ cm}^{-1}$  for this same compound, which differs strongly with the counter ion conditions in mixtures of MTHF/THF. Whether also intermolecular coupled aggregates are formed and responsible for these dramatic differences, as in the case of ketyl radical anions discussed in the next chapter has not been established so far.

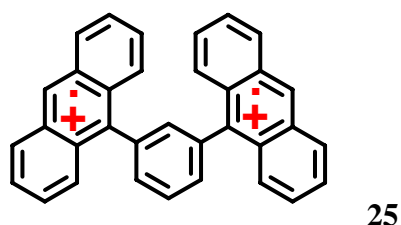


The *meta*-distyrylbenzene **23** showed a striking behavior upon charging. In the monocharged form a strong CT absorption in the NIR region ( $\lambda_{\text{max}} = 1700$  nm) occurs, suggesting that the monoradical species is localized on a single stilbene unit with charge transfer to a neutral styryl part. The dianion also absorbs at long wavelength ( $\lambda_{\text{max}} = 1400$  nm) but turns out to be diamagnetic instead of yielding a biradical with the *meta*-phenylene as a ferromagnetic coupler.<sup>20</sup> This result puts some question mark to the generalization of the Fukutome's model,<sup>21</sup> also intensively studied by Dougherty and his group.<sup>22,23</sup> The bis-stilbenylbenzene **24**, on the other hand, can be doubly charged to the biradical state and semiempirical calculations also suggest a triplet ground state for this molecule.<sup>24</sup>

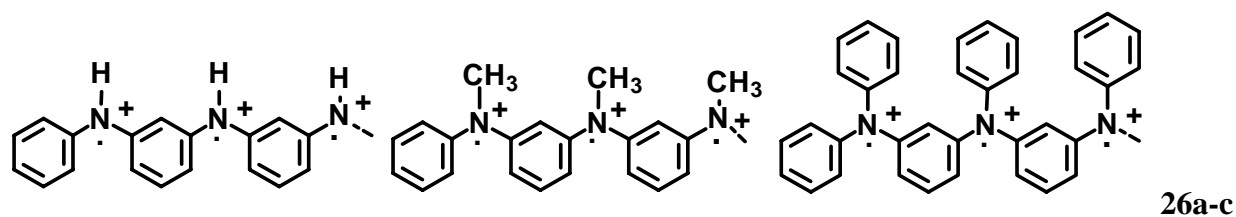


## 2.2. Radical cations

There are not many dications of aromatic hydrocarbons in the literature. One example was given by Tukada<sup>17</sup> for the 1,3 bis-(9-anthryl)benzene **25**, which according to their results should possess a ground state triplet multiplicity.

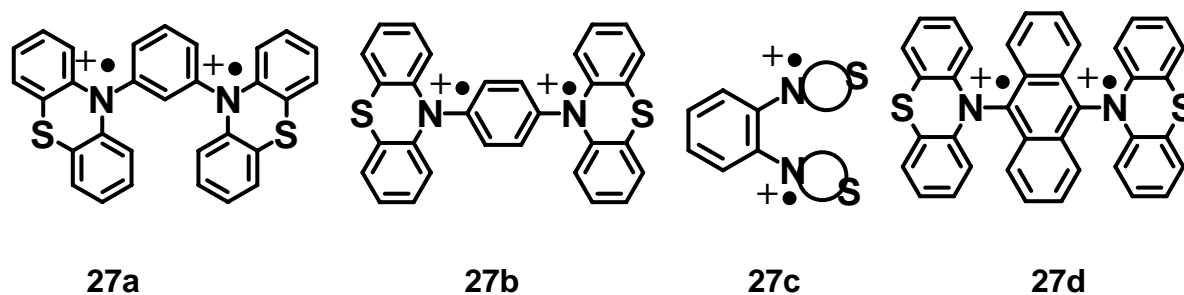






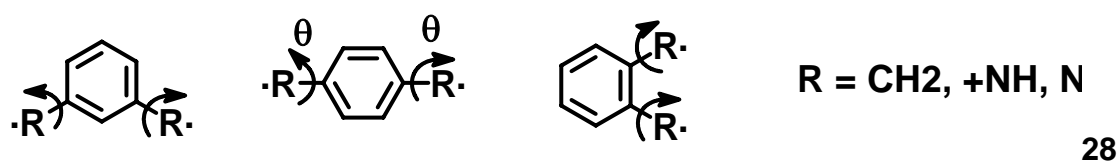
For polymeric amino cation radicals **26 a-c** and different derivatives, we predicted ferromagnetic coupling between the spin centers<sup>25,26</sup> and further bandstructure considerations will be outlined by Tyutyulkov and Dietz in this volume. But care should be taken by comparing small subunits as presented earlier like **15** and **16**,<sup>13</sup> since very different spin density distribution can occur and depending on the substituents the ground state multiplicity can be changed. Similar findings have been reported by Blackstock et al.<sup>27</sup> and Takui et al.<sup>28</sup> and will be discussed in an extended part in this volume. Instead of phenylene also 1,3-substituted triazines<sup>29</sup> can be used, where the triplet state for diamino dications is stabilized compared to the former.

Recent reports showed that *meta*-phenylene does not always act as ferromagnetic coupling unit, especially when due to strong steric hindrance the conjugation planes of the radical centers are twisted close to perpendicular to the phenylene unit. Such examples are reported for bisnitroxides by Rassat et al.<sup>30</sup> (see also Rassat in this volume) and Iwamura et al.<sup>31</sup> and confirmed and explained in *ab initio* calculations by Borden.<sup>32</sup> We studied and compared in cooperation with K. Okada (Osaka, Jp) some extremely hindered cases namely the *meta*-, *para*-, *ortho*-phenylene, and the 9,10-anthrylene bridged bisphenothiazines **27a-d**, and bisphenoxazines (S = O) as well as 1,3,5-trisubstituted benzenes.<sup>33-35</sup>



The phenothiazine and phenoxazine units can easily be oxidized with sulfuric acid to their corresponding cation radicals. All the compounds yielded biradicals with typical zero field

splittings in the  $\Delta m_s = 1$  region closely reflecting the size of spin density on nitrogen and the averaged distance between the radical centers. In addition strong  $\Delta m_s = 2$  signals have been measured which are further split due to  $^{14}\text{N}$  ( $I=1$ ) hyperfine coupling corresponding to the one found also in liquid solution of the monoradical cations. For elucidating the ground state spin multiplicity temperature dependent studies of the signal intensities were performed and to our surprise the *para*-phenylene bridged biradicals **27b** behaved Curie like with linear dependence, while *meta*-phenylene connected **27a** yielded a maximum around 10-15 K, clearly demonstrating thermal activation (28 cal/mol) of the triplet state. To our knowledge this is the first clear cut experiments demonstrating that *para*-phenylene connected biradicals might be more stable triplet than *meta*-phenylene connected ones.<sup>36</sup> These examples also demonstrate that one should not combine the orthogonal approach together with *meta*-phenylene bridging. Even the *ortho*-phenylene bridged bisphenothiazinyl, which is somewhat more difficult to synthesize due to the strong steric hindrance, has now been shown to form biradicals in sulfuric acid, but not upon electrochemical oxidation.<sup>37</sup> For a better understanding of the role of bridging unit for twisted biradicals we used AM1-CI calculations on the triplet stabilities for model benzoquinodimethane (xylylene) type biradicals **28**.<sup>38</sup>

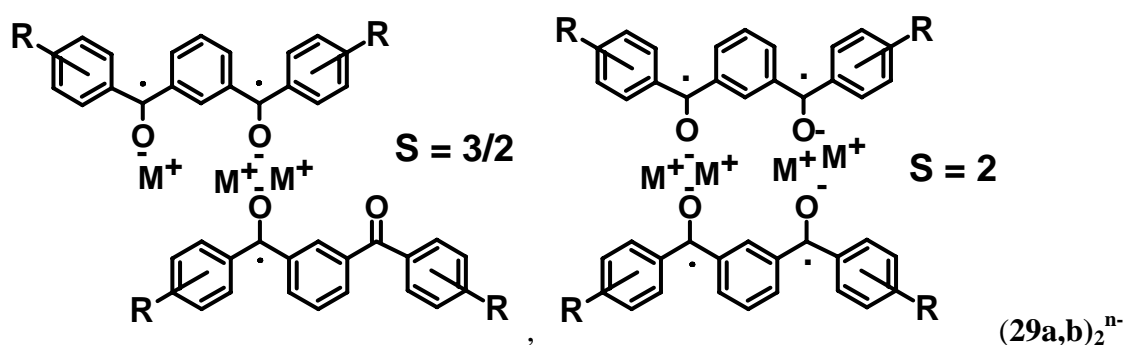


For  $\theta$  between 60 and 90° it is shown that *para*- and *ortho*-phenylene coupled biradicals may be more stable triplet than the *meta*-isomers, which even may yield singlet. Preliminary ab-initio calculations<sup>39</sup> support these findings.

### 3. Intermolecular aggregation

High spin molecules have been considerable valuable building blocks for organic magnetic materials as far as they can be coupled ferromagnetically in three dimensions.<sup>40,41</sup> Three principles for intermolecular spin exchange have been considered so far: i) metal bridging,<sup>42</sup> ii)

hydrogen bonding,<sup>43,44</sup> and iii) stack type alignment.<sup>45,46</sup> In this vein we reconsidered some basic principles, starting with the bridging of ketyl radicals by their counteranions. The carbonyl function thereby seemed very promising since already in the 60's Hirota and Weissman<sup>47,48</sup> demonstrated that benzophenone forms strongly intermolecular coupled biradicals upon alkali metal reduction. This principle, on the other hand, has not further been used for obtaining higher spin states. We thus used the easily accessible *meta*-dibenzoylbenzenes **29a** (R = 4-tert.-butyl) and **29b** (R = 2,4,6-trimethyl),<sup>2,49</sup> for testing our prediction. Like in benzophenone the monoanions of **29a**<sup>-</sup> exhibit strongly coupled radical pairs, where the large zfs components (11.3 and 20.0 mT) by far exceed the anisotropic hyperfine couplings.

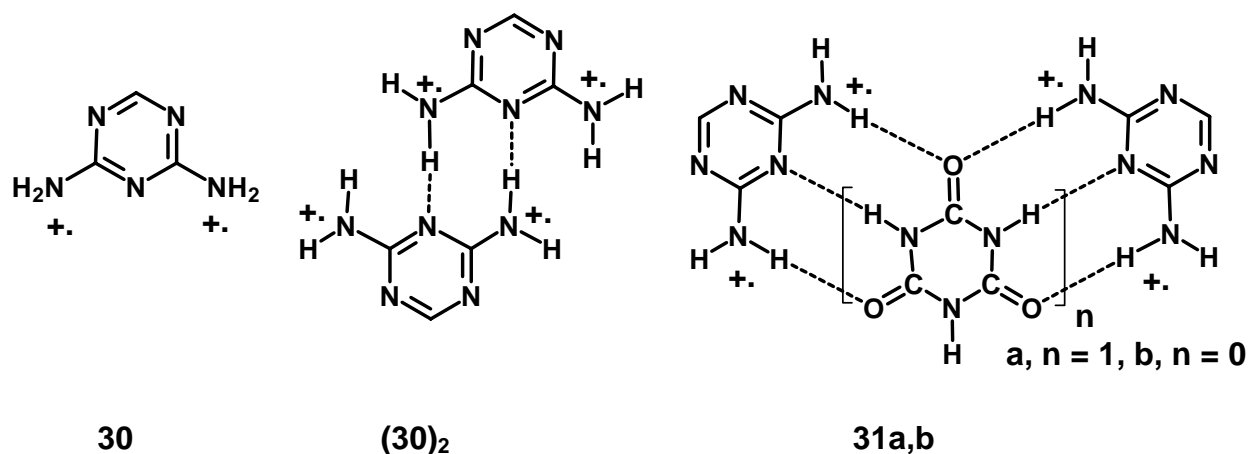


In the mixture of mono- and dianionic states, indicated also by raise of optical absorptions at 340 and 682 nm, the EPR spectrum changes dramatically due to formation of the next higher spin state with  $S = 3/2$ , which can only arise upon formation of dimeric diketones (**29a**)<sub>2</sub><sup>3,3-</sup>. The identification of this spin state is evidenced by detection of a  $\Delta m_S = 3$  transition at one third of the typical resonance field, measurable only at very low temperatures, and can be reproduced by computer simulations with zfs values  $D = 7.125$  mT and  $E = 0.25$  mT. Since intermolecular coupled radical centers are often aligned antiferromagnetically, the temperature dependence of the EPR signal intensity was controlled yielding typical Curie behavior down to 10 K supporting strongly the high spin ground state multiplicity.<sup>2,49</sup> Continued reduction even allowed the detection of the quintet state  $S = 2$  with maximum splittings of 40.1, and 35.0 mT.

In the charged mesitylene derivative **29b**, the quintet state from dimeric dianions with zfs components of 45.0 and 38.0 mT seems to be favored over the quartet state. The smaller zfs

components in the case of  $(29a)_2^{4\cdot-}$  compared to  $(29b)_2^{4\cdot-}$  can easily be understood in view of enhanced steric hindrance and larger donating effects of the methyl groups in **29b**, increasing the charge and spin density in the central part of the molecule. Up to now, however, we did not succeed to obtain even higher spin states in extended phenylketone oligomers.

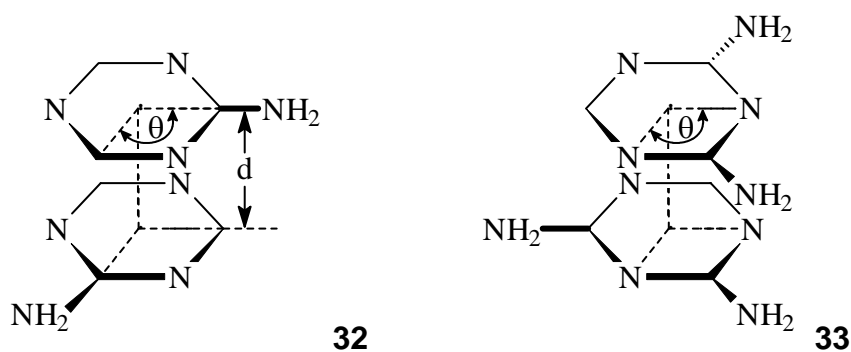
Recently some stable radicals have been bridged through hydrogen bonds<sup>43,44</sup> but it was not made clear if hydrogen bonds in these cases just fix the spin centers in stack type arrangement which, according to McConnell's model, should allow ferrimagnetic interaction or whether the interactions are possible through hydrogen bonds. Starting first with semiempirical calculations on the spin-spin interaction of many different hydrogen bridged radicals we then depicted the diaminotriazine dication **30** as basic unit, after we found an even stronger triplet stabilization in **30** than in the corresponding diaminophenylene dication.<sup>27,50</sup> Diaminotriazine can be hydrogen bridged to itself  $(30)_2$  or to neutral cyanuric acid **31a** where the charging should yield the tetraradicals.<sup>27</sup>



Thereby it was found that when combining two biradicals hydrogen bonded through a neutral cyanuric acid molecule **31a** the quintet is strongly stabilized ( $\Delta E_{QT} = 0.04$  eV) in difference to the self aggregate  $(30^{2\cdot 2+})_2$  and the spaced dimer without the cyanuric acid (**31b**<sup>4.4+</sup>), where no stabilization is found ( $\Delta E_{QT} < 0.001$  eV). The former motif clearly resembles the one of covalently linked biradicals through a *meta*-phenylene unit, since the biradicals span an angle of

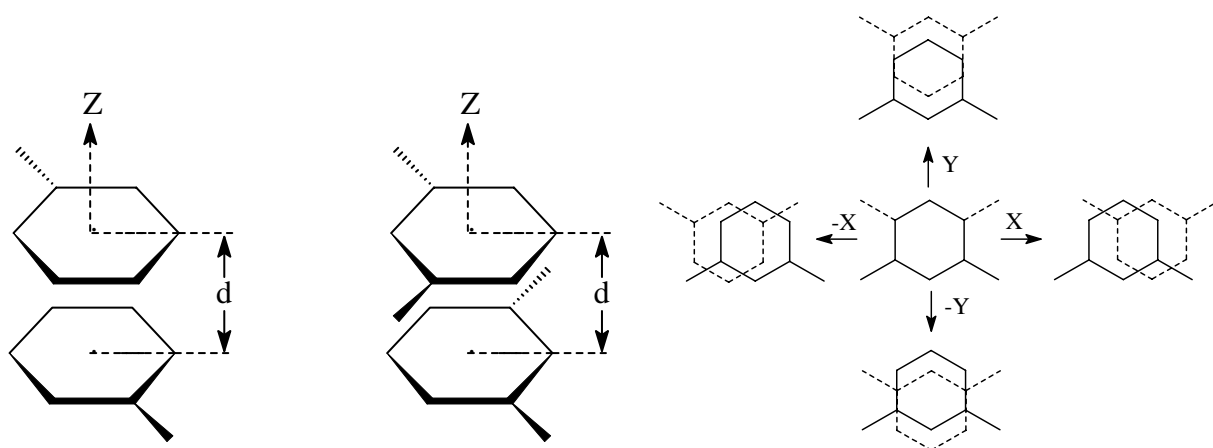
120 degrees and there is an odd number of centers between the spin carrying unit. Further synthetic efforts are now directed towards this issue.

In a recent paper, stack type alignment of aminotriazine cations **32** and diaminotriazine dication **33** was calculated and the high spin stabilization compared to results for the hydrogen bonded structures mentioned before.<sup>51</sup>



Thereby it was shown that the ferromagnetic coupling through space strongly depends on the distance ( $d$ , calculated for 0.1 Å steps from 2.5-4.0 Å along  $z$ ) and alignment (rotational angles  $\theta$  for every 10° from 0-180° and movement along  $x$  and  $y$  calculated in 0.5 Å steps) of the radicals as predicted earlier.<sup>45</sup>

Scheme 3: Considered movements of mono- (**32**)<sup>2,2+</sup> and dication radicals (**32**)<sup>4,4+</sup>



Usually the stack type interaction is stronger than a through hydrogen bond interaction, and only for distances  $d > 4.0$  Å these interactions become of comparable size.

#### **4. Conclusion**

In this review it is shown that radical ions of organic  $\pi$ -systems can be used for the synthesis of novel high spin molecules either by direct linkage or connection through organic spacers like phenylene. Thereby some rules are given and some exceptions where the simple predictions are not followed. The high spin molecules, which should be created to maximum extent, may than be considered as building blocks for new intermolecular aggregates, and some possibilities for such spin alignment in larger entities are discussed in the final section.

#### **5. Acknowledgment**

I wish to thank all the contributors who helped to achieve these results and are cited in the text and references, especially Prof. Dr. Stoyan Karabunarliev (Burgas University, BG), Dipl.-Ing. Lileta Gherghel, Profs. Nikolaj Tyutyulkov together with Fritz Dietz who also helped with reading corrections and Prof. Keiji Okada. Financial support by the Volkswagenstiftung, the Deutsche Forschungsgemeinschaft and the Fond der chemischen Industrie is gratefully acknowledged.

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