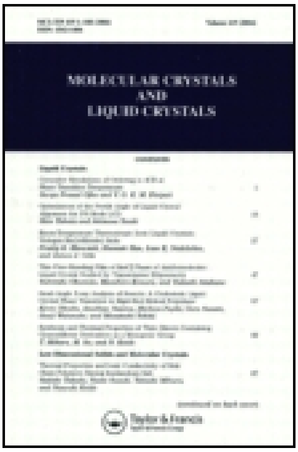

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Martin Baumgarten, Daniel Caparros, Kimihiro Yoshimura & Stoyan Karabunarliev (2002): Aspects of High Spin Formation in Organic π-Systems, Molecular Crystals and Liquid Crystals, 376:1, 525-534

To link to this article: http://dx.doi.org/10.1080/10587250210761

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 525-534
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1058-725X/02 $12.00 + .00

Aspects of High Spin Formation in Organic π-Systems

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Abstract Since highly condensed symmetric hydrocarbons like corannulene, hexabenzocoronene, [60]fullerene etc. tend to undergo symmetry reduction upon charging by Jahn-Teller distortion, we tested to use bridged triphenylenes to obtain higher spin states. In another approach a new access towards directly connected delocalized radicals and radical ions was predicted as basis towards high spin ground states. Towards easier reducable π-units extended oligo-semiquinone-methides have been prepared enabling charging to high spin ground states.

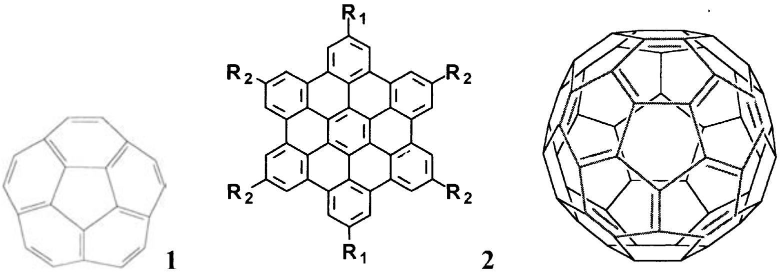
Keywords: organic high spin molecules; radical ions; triplet states

INTRODUCTION

In the field of organic high spin molecules large progress has been made over the last ten years and even the first purely organic ferromagnets were reported.[1-3] While ferromagnetic materials persistent to room temperature became available from mixed organic/inorganic hybrid solids, [4,5] for organic materials up to now only very low transition temperatures to the ferromagnetic regime were reported and the search towards new building blocks and extended high spin aggregates is still increasing.[1,2,6]

RESULTS AND DISCUSSION

Looking into antiaromatic annulenes with high symmetries (≥ C_3) stable triplet ground states are found for twofold charged molecules having threefold symmetry as 1,3,5-triphenylbenzene (2-,2+), triphenylene (2-) and donor substituted derivatives (2+), while coronene undergoes strong Jahn-Teller distortion leading to singlet ground state danion and dication. [7,8] Our efforts in fused polycycles so far focussed on corannulene, hexabenzocoronene and fullerenes (SCHEME 1).



SCHEME 1: corannulene (**1**), hexabenzocoronene (**2**), [60]fullerene(**C_{60}**)

In cooperation with Rabinovitz and Scott [9] we found that the doubly charging of corannulene is combined with loss of EPR signal intensity and color change, but ^{1}H-NMR could only be evidenced at low temperatures ($T < 200$ K), leaving the question of some thermally acivated triplet states at high field and room temperatures.

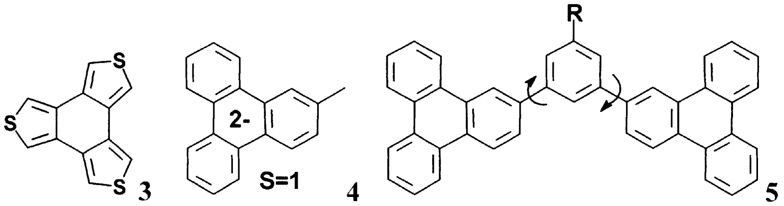
The hexabenzocoronene (hbc), made soluble by use of different alkyl groups (R_1,R_2) as one example of the fused polycycles from Müllen et al., [10] showed different proton hyperfine couplings for the monoanions but for varying substitution patterns $R_1 = R_2$ and $R_1 \neq R_2$, all the dianions possess identical D-values, indicating loss of symmetry by Jahn-Teller distortion. This could also be predicted from AM1-CI calculations where the D_{6h} triplet minimum lies above the C_{2h} absolute singlet state minimum. Thus only thermally excited dianionic biradicals, trianionic triradicals and tetraanionic biradicals were evidenced,[10] however with a dramatic increase of triplet stabilization compared to coronone dianion.[7]

[60]fullerenes have gained immense interest over the last ten years and in 1992 we already started studying their charging behavior.[11,12] While different thermally excited zero field splitting components could be found for the dianions (λ_{max} = 947 nm), all of them were lost upon trianion formation, although the LUMOs of C_{60} are triply degenerate. In order to prove independence of counter ion conditions we also repeated the charging process up to the trianion electrochemically by EPR and parallel optical absorption control.[13] Thereby identical absorption spectra as upon potassium or lithium reduction were found, and after a single sharp EPR line detection for the monoanion in solution and frozen state, zfs components in the frozen state EPR could only be found upon increase of dianion concentration,

while all of them were lost upon trianion formation, combained with raise of a new NIR transition at 1372 nm, indentifying a doublet state trianion (S=1/2).

This was requested by Shohoji et al. who claimed a novel triradical trianion and even higher spin states but without any other control of the charged state.[14] Quickly afterwards Fässler et al. reported on single crystal identification of doublet state (S=1/2) trianions supporting our results.[15]

We thus looked towards other threefold symmetric systems and prepared a benzotrithiophene (**3**) for charging,[16] but found no accessible dications since the monocations immediately started to polymerize. We then thought about higher spin states upon bridging of triphenylenes, where each unit could be charged to a dianion. Earlier, persistent triplet state dianion of methyl substituted triphenylene (**4**) was reported.[17] The bridging of the boronic acid derivatives of triphenylenes via Suzuki coupling with an alkylated-dibromo-phenylene coupling unit was straightforward resulting in **5**.[18]



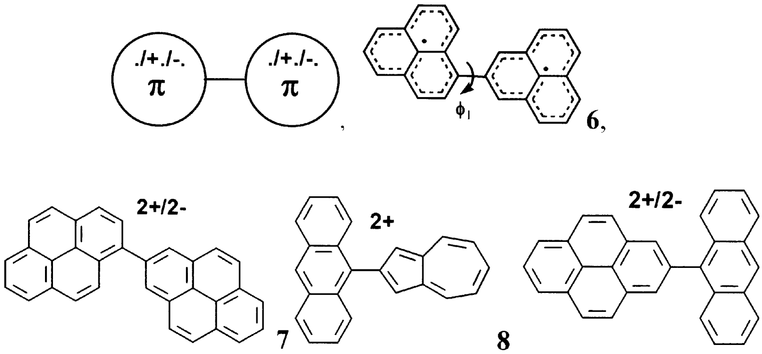
SCHEME 2: benzotrithiophene (**3**), methyl-triphenylene(**4**), bistriphenylene-benzene (**5**).

Upon charging with K/THF, first the monoanion was evidenced with λ_{max}= 862 nm, where the spin density distribution from EPR/ENDOR spectroscopy was hinting towards a charged meta-quinquephenyl rather than a substituted triphenylene.

Upon dianion formation (λ_{max}= 703, 932 nm) many new zfs-components in the frozen solution EPR spectra could be obtained with splittings of up to 29.6, 33.0, 41.4 mT much larger than for any single dianion biradical predicted by the point dipole approach. Therefor higher spin states seem to be involved either intra- or intermolecular with $S = 3/2$ or $S = 2$. The clear identification of more well defined spin species has to await further experiments.

Earlier we had tested many bi- and oligoarylenes for high spin formation, even mixed dimers (originally thought for charge switches).[19] As long as large torsions prevail brought about through an anthracene unit biradical dianions and dications are formed, but as in the series of oligoanthrylenes they are thermally activated. According to the rules for spin coupling units a single bond should act as an antiferromagnetic (afm) coupling unit. [1,2,20]

We therefore thought if we can overcome the classical rules for function of spin couplers using delocalized radicals and radical ions. As model we depicted cases with large alternation of sign of spin density in the periphery as known for the phenalenyl radical. In order to reproduce the experimentally verified spin density distribution, semiempirical calculations with extended CI showed best agreement, much superior over any unrestricted open shell approach.[22] An asymmetric bridging as in 1,2'-bisphenalenyl (**6**) should then revert the usual meaning of coupling units and a fm exchange coupling with $\Delta E_{ST} \sim +2.5$ kcal/mol is predicted. The fm exchange is also foreseen for extended 1,2-ethenyl or 1,4-phenylene bridged dimers. Phenalenyl, on the other hand is known to undergoe 1,1'-dimerization and we predicted other stable radical ions with strong spin alternation in the periphery to be combined with themselves or similar redox active units yielding high spin ground states, as e.g. 1,2-bipyrene (**7**), 9-anthryl-2-azulene (**8**), 9-anthryl-2-pyrene (**9**). The last (**9**) can even be extended to higher alternating oligomers also synthetically.[22]



6, 7 8 9

SCHEME 3: Bridging of delocalized radicals and radical ions with high spin ground states.

In our earlier experimentally efforts towards intermolecular alignment we have tried to extend the principles of benzophenone dimerization which results in triplet state upon charging.[23,24] We could demonstrate higher spin states for dimerized bisbenzoylbenzenes (S=3/2, S=2) and this holds although for exchange of the central benzene ring by pyridine, where slightly smaller D-values were found in 1995 (S = 3/2: D = 6.72mT; S = 2: D = 5.58 mT, unpublished) in agreement with results from Takui et al. last year [25]. For extended oligophenylketones, on the other hand, we could not find higher charged states, since charging of a ketyl unit in between two charged benzophenones competes with doubly charging of a benzophenone leading to lower spin states. This seems to be one of the inherent problem of polaronic ferromagnets as discussed earlier.[26] We therefore considered fuchsones and extended oligo-semiquinone-methides (**10**,**11**) as building blocks since the reduction potential of fuchsone (-1.78 V) is considerably lower than for benzophenone (-2.15 V) with ΔEred ~ 0.37 V). The synthesis of the oligosemiquinonemethides followed the outline by Becker [27] starting from the oligoalcohols. They are coupled acid catalyzed with di-*t*but-phenol (> 90 %) and finally oxidized with MnO_2 (> 90%) to the desired products **10**,**11**.

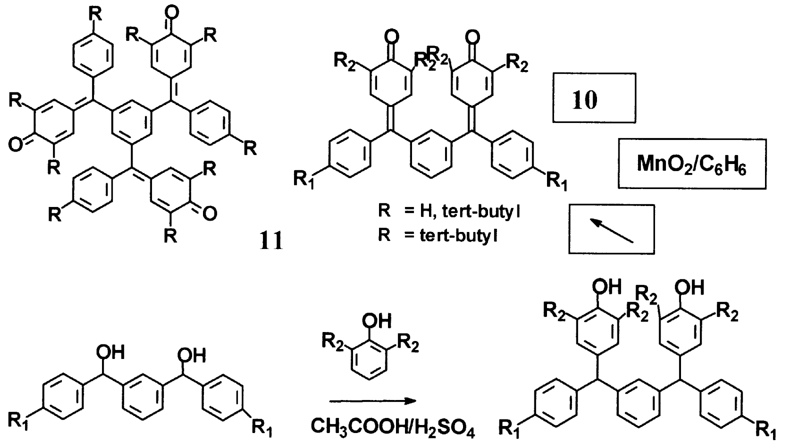


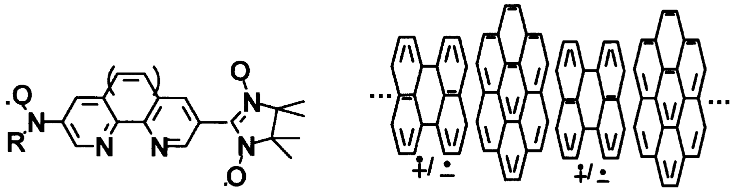
FIGURE 1: Seminquinonemethides and their synthesis [28]

The cyclic voltammetry of the oligosemiquinonemethides show reduction waves at much lower potential than the corresponding ketones e.g. for 1,3,5-benzene substituted trimer **11** three reversible reduction waves appeared at –1.68, -1.87, –1.99 V (TBAHFP/THF) (**10**: -1.72, -

1.90 V). The charging with potassium also enabled formation of diradical dianions of **10** (D' = 7.8 mT) and **11** and triradical trianions of **11** (S = 3/2, D = 4.2 mT). However no higher spin states for intermolecular aggregates could be identified by cw-EPR yet.

SUMMARY AND OUTLOOK

From the outline above, further work is devoted to the bridged triphenylenes **5** in order to identify pure intramolecular coupled species and to study their aggregation. The same holds for the novel semiquinonemethides, where also ion exchange is in progress. Towards novel stable high spin molecules for aggregation two new projects have been started. The first involves stable biradical high spin ground states for asymmetric substituted bipyridines and phenanthrolines with nitroxide and nitronyl nitroxide radical sites. The second approach involves mixed radical ion crystals where fm exchange is predicted for face to face alignment of radical ions separated by neutral conjugated molecules. Here the demanding task consists of finding suitable charged and neutral molecules as the suggested alternating stack of perylene radical ions and neutral coronene,



SCHEME 4: new models for high spin formation.

while theoretically many stacks with ferromagnetic exchange can be predicted. [29]

ACKNOWLEDGEMENT

Financial support by the DFG (MB, DC) and the FCI is gratefully acknowledged.

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