Structures and Ground State Spin Multiplicities of Poly-Radical-Ions of Homo- and Heteronuclear Dendralenes

Henryk Vogel [a] , Anna Schleitzer [a] , Fritz Dietz [a] & Nikolai Tyutyulkov [b]

[a] University of Leipzig, Institute of Physical and Theoretical Chemistry, Leipzig, Germany

[b] University of Sofia, Faculty of Chemistry, Sofia, Bulgaria

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STRUCTURES AND GROUND STATE SPIN MULTIPLICITIES OF POLY-RADICAL-IONS OF HOMO- AND HETERONUCLEAR DENDRALENES

HENRYK VOGEL, ANNA SCHLEITZER, FRITZ DIETZ

University of Leipzig, Institute of Physical and Theoretical Chemistry, Leipzig, Germany

NIKOLAI TYUTYULKOV

University of Sofia, Faculty of Chemistry, Sofia, Bulgaria

Abstract The ground state spin multiplicity and the geometry of the reductively and oxidatively doped homo- and heteronuclear dendralenes were investigated by means of *ab initio* calculations. The results were compared with the calculated effective Heisenberg exchange integral for doped infinite dendralenes.

INTRODUCTION

Organic π-systems with high spin multiplicity have received much attention recently.[1] They can be used as models for the investigation of the character of the exchange interaction between the unpaired spins and are possible "building blocks" for organic ferromagnets.[2-5] In contrast to the doped polyenes and annulenes, little investigation has been done in the field of the reductively or oxidatively doped topological isomers - dendralenes DE and radialenes.[6] Yamaguchi et al.[7,8] have investigated model systems of high spin ion radicals of polyenes by *ab initio*, *ab initio* post HF and semiempirical MO calculations to confirm their spin polarization and spin delocalization rules[9,10] for ion

radicals. The vinylidene group was used as the coupling unit which is connected at one

and the same C atom with two precursors for ion radical groups[7].

The classical DEs are the simplest examples of a large class of π-conjugated systems of

the general topological model TM:[11,12]

where $\overset{\textcircled{\pi}}{}$ is an arbitrary even alternant homonuclear or heteronuclear system connected

with vinylidene groups at two or one starred π-centers, e.g.:
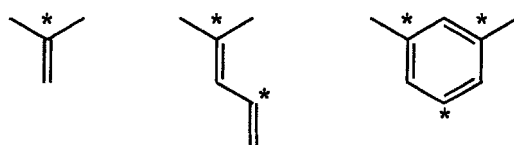
In recent papers[11,12] it was shown that the reductively or oxidatively doped

dendralenes are high spin systems with ferromagnetically coupled electrons within the

half-filled band of the infinite one-dimensional (1-D) chain. The magnetic properties of

this new class of 1-D polaronic ferromagnets are caused by the topology of the DEs. In

contrast to the doped polyacetylenes where the polaron has a different width[13,14] a

polaron of a doped DE is localized in one elementary unit (EU).

n = 1, 2, 3, ...
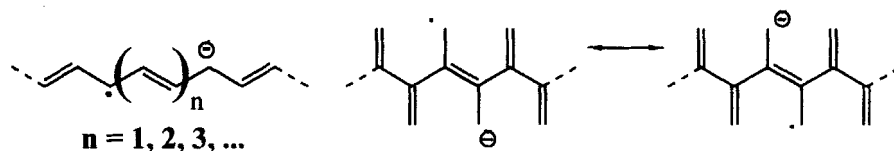
A structural relaxation corresponding to a polaron delocalized over more than one EU

is not possible. For such a polaron there is no corresponding valence formula.

In this paper we report the first results of systematic *ab initio* investigations of the structure and the ground state multiplicity of polyradical ions of homonuclear and heteronuclear DE fragments of infinite 1-D high spin polymers (real or hypothetical) with magnetic ordering.

We consider the following oxidatively and reductively doped homonuclear and heteronuclear dendralenes:
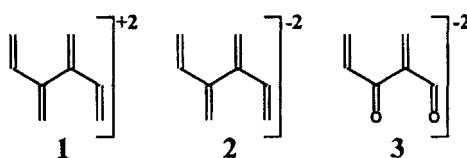

These structures constitute the basic theoretical models. More realistic structures are those in which the polarons are stabilized in the EUs by delocalization of the negative or positive charge over odd-membered aromatic rings,[11,15-17] e. g. a cyclopentadienide anion or a tropylium cation, respectively. The radical sites could be stabilized in a diphenylmethyl structure:
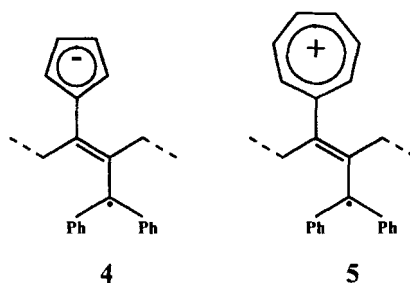
METHODS OF INVESTIGATION

The molecular geometries of the structures have been optimized by means of *ab initio* calculations using the GAMESS-UK program package.[18] Stationary points on the potential energy surfaces were located at the restricted HF level (standard split valence basis set 6-31G*). All bond lengths and bond angles of the elementary units are fully

optimized within the symmetry point group C_l. To determine the singlet-triplet splitting, Direct CISD calculations (including all singly and doubly excited electronic configurations) have been performed based on the wave functions and optimized geometries of the appropriate singlet and triplet states.

RESULTS AND DISCUSSION

Figure 1 shows the optimized geometries of the models 1-3 in their ground states. The ground state of structure 1 is a closed shell singlet state containing a five-membered ring (1a). This structure is about 1.90 eV more stable than the lowest open shell singlet state (1b) and about 1.91 eV more stable than the lowest triplet state (1c). Both positive charges are delocalized within two allyl fragments. If the methylene groups are included in bulky fragments, like structure 4, a triplet ground state may be stabilized caused by a stronger (larger) torsion of the butadiene units.

The lowest open shell singlet state and the lowest triplet state of the compounds 2 and 3 are nearly degenerate.
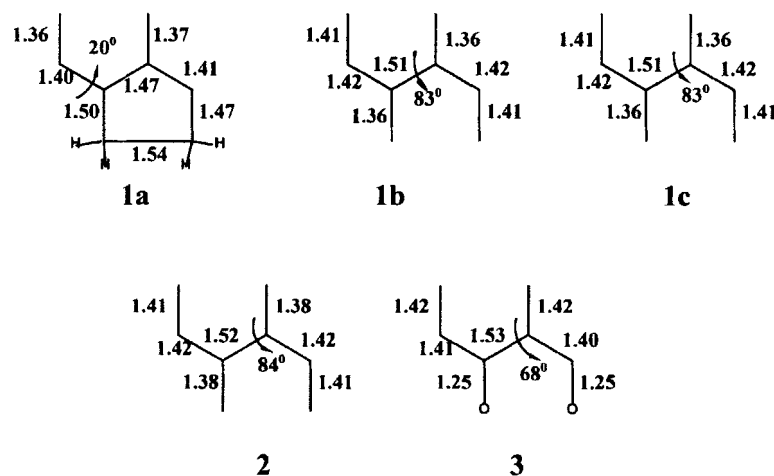

FIGURE 1   Optimized geometries (bond lengths in Å) of the triplet states (basis set 6-31G*) of structures 1-3 (1a: singlet ground state, 1b: lowest open shell singlet state, 1c: lowest triplet state).

A small singlet-triplet splitting ($\Delta E^{S-T} = E^S - E^T$) in favor of the triplet ground state has been calculated (6-31G*, CISD) for the species **2** ($\Delta E^{S-T} = 0.01$ eV) and **3** ($\Delta E^{S-T} = 0.01$ eV).

The species **1-3** can be regarded each as representing two EUs of the infinite 1-D systems of dendralene polyradical ions. The effective exchange interaction integral in the Heisenberg Hamiltonian between the unpaired electrons within the half-filled band (HFB) J_{eff} for the corresponding polymer of **2** has been evaluated as the sum of a direct or Coulomb (J), a kinetic (J_{kin}) and an indirect (spin polarization) (J_{ind}) contribution:[11]

$$J_{eff} = J + J_{kin} + J_{ind} .$$

For the infinite dendralene polyradical polyanion (which corresponds to **2**) a value of $J_{eff} = 0.058$ eV has been calculated.

In the case of the more realistic models **4** and **5**,[11] the effective exchange integrals have been calculated to be $J_{eff}(4) = 0.257$ and $J_{eff}(5) = 0.251$ (assuming models in which the cyclopentadienide and tropylium rings, the diphenyl-methyl fragments and the EUs are distorted with dihedral angles of 60°, the phenyl groups are twisted by 30°), i.e. the interaction is ferromagnetic in all cases with a predominant contribution of the direct Coulomb exchange.

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