On the Ground State Multiplicity of Amino-substituted Cyclopentadienyl Cations

Ronald Beust[a], Anna Schleitzer[a], Henryk Vogel[a], Nikolai Tyutyulkov[b], and Fritz Dietz[a]*

[a]*University of Leipzig, Institute of Physical and Theoretical Chemistry Augustusplatz 10–11, D-04109 Leipzig, Germany*

[b]*University of Sofia, Faculty of Chemistry, BG-1126 Sofia, Bulgaria*

It has been investigated by means of *ab initio* quantum chemical methods (optimizations on SCF level followed by single point CISD calculations; optimizations on CASSCF level), how the singlet-triplet splitting of the mono-, 1,3-di- and 1,2,4-triaminocyclopentadienyl cation depends on the out-of-plane angle between the substituent(s) and the antiaromatic ring fragment. It has been found that all these molecules are ground state singlets in their planar equilibrium geometries. However, singlet and triplet states are nearly degenerate, if the substituent(s) is/are rotated out of the ring plane by 90°. The impact of this finding for the search for molecules with a stable high spin ground state, which may serve as building blocks for polymers with magnetic ordering, is discussed.

INTRODUCTION

Much attention, both experimental and theoretical, has been focused recently on antiaromatic ring systems since they may have a triplet ground state. Therefore, they could serve as building blocks for purely organic polymers with magnetic ordering, ferromagnetic or anti-ferromagnetic, respectively.

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* Author to whom correspondence should be addressed.

A number of antiaromatic molecules have been prepared, especially unsubstituted or symmetrically substituted five-, six- and seven-membered rings. For instance, the cyclopentadienyl cation (cpc) was found to have a triplet ground state[1] as well as the pentachloro cpc,[2] for the cycloheptatrienid anion (cha), a triplet ground state has been predicted according to PPP calculations.[3] In contrast, the pentaphenyl cpc[4] and the heptaphenyl cha[5,6] are ground state singlets. All systems investigated so far are very unstable, both thermodynamically and kinetically. In order to stabilize antiaromatic molecules, substituents with suitable steric and electronic properties could be used. However, experimental results show that the introduction of large substituents or other structural elements in a large number of cases alters the ground state into a singlet.

Breslow explained this effect presuming that spin pairing and hence a singlet ground state are favourable if the molecular orbitals, which are singly occupied in a triplet state, are localized on positions of the molecule remote to one another.[2] Consequently, an extension of the conjugated system, for instance by substitution or annelation of benzoid fragments, may favour a singlet ground state for the molecule.

In this paper, we want to present the results of a theoretical investigation on the ground state multiplicity of the amino cpc and related species as a function of the angle between the antiaromatic ring fragment and substituent planes.

COMPUTATIONAL DETAILS

Geometries of the mono-, di- and triamino cpc have been optimized by several values of the angle Θ between the antiaromatic ring fragment and the substituent(s) both on SCF and on CASSCF levels. Two amino cpcs, further substituted by aliphatic groups, have been optimized on SCF level only.

In each case, optimization on SCF level has been followed by a single point CISD calculation. The active space consisted of all MOs, with the exception of the lowest lying MOs formed by 1s AOs and their virtual analognes.

Optimizations on CASSCF level have been carried out with all π MOs included in the active space.

The amino groups have been kept planar in optimizations of the distorted species of the di- and triamino cpc and in all CASSCF optimizations.

The basis set used was 3-21G, for some more detailed studies on the monoamino cpc 6-31G*. The results are not influenced qualitatively by the basis set extensions; singlet-triplet splittings vary by at most 2.2 kcal mol^{-1} (*ca.* 11%).

For this reason, all numerical values given herein are calculated with the 3-21G basis set.

The program GAMESS-UK, version 5.1, has been used for all steps of calculation.[7]

RESULTS AND DISCUSSION

Amino Cyclopentadienyl Cation

The amino cpc has been optimized without any geometrical restriction. The molecule was found to be planar in its equilibrium geometry (molecular symmetry C_{2v}) regardless of the multiplicity. Planarity has been confirmed by performing a frequency analysis with the 6-31G* basis set for both multiplicities.

The singlet-triplet splitting on this level of computation (including a CISD calculation, based on the SCF optimized geometries, 3-21G basis set) amounts to 17.9 kcal mol^{-1}, i.e. the amino cpc is a ground state singlet as expected (triplets $^3B_2/^3B$ have been found to be the lowest-lying ones with respect to the energy for all systems in this work having C_{2v}/C_2 symmetry).

It has to be noted that the geometry of the singlet state refers to the Jahn-Teller structure of the parental unsubstituted cpc with a comparatively long C3-C4 bond (see Figures 1 and 3).[8]

These calculations have been followed by geometry optimizations with the torsion angle Θ (see Figure 1) constrained to several values.

Regardless of its amount, the amino group has been found to be planar (3-21G basis set, a slight pyramidalization has been observed with the
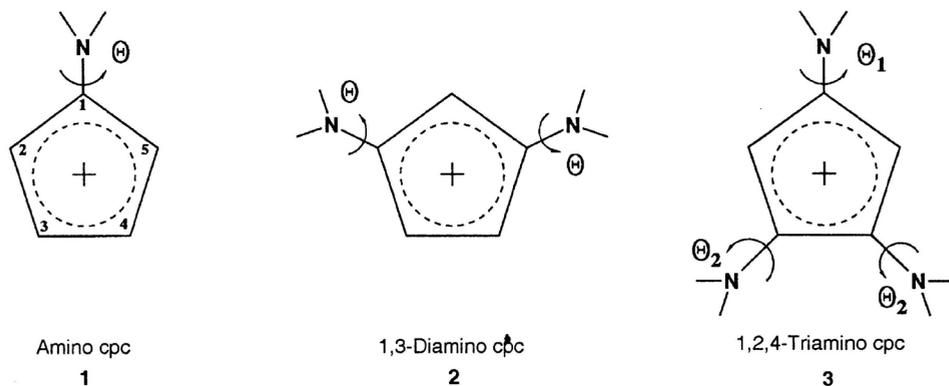

Amino cpc
1

1,3-Diamino cpc
2

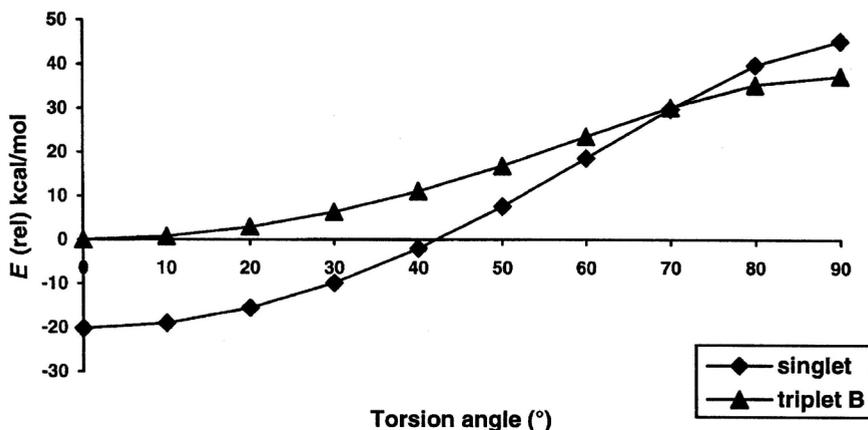1,2,4-Triamino cpc
3

Figure 1. Systems under investigation.

Figure 2. CISD energies of the lowest-lying triplet (^{3}B/^{3}B$_2$) and singlet states of the amino cpc in dependence on the torsion angle Θ. Reference: ^{3}B$_2$ energy for $\Theta = 0°$ (C_2/C_{2v} symmetry, 3-21G optimized geometries).

631G* basis set, but the influence on the total energy of the molecule of at most 0.6 kcal mol^{-1} is rather negligible). The antiaromatic ring fragment has been optimized to planarity in any respect (*i.e.* molecular symmetry C_2, C_{2v} for $\Theta = 90°$, respectively). For each value of Θ, the singlet-triplet splitting has been calculated. It has been found that turning the amino group out of the plane of the ring fragment raises the total energy of both the singlet and triplet states. Since the singlet energy increases more evidently, the singlet-triplet splitting decreases with increasing Θ. For $\Theta = 70°$, the singlet and triplet states are degenerate; for higher values of Θ, even a triplet ground state can be achieved. The maximum singlet-triplet splitting for $\Theta = 90°$ has been calculated to be appr. −8.0 kcal/mol.

In Figure 2, the relative energies of the singlet and the triplet states are presented as a function of Θ.[8]

An examination of the net spin populations (Muliken analysis) shows that the unpaired electrons of the triplet state are shifted towards the antiaromatic ring fragment when Θ is raised from 0° to 90°.[8]

It has been investigated whether sterical effects could lead to a rotation of the amino group out of the plane of the antiaromatic ring. Neither by methyl nor by *tert*-butyl groups in the vicinity of the amino group could the desired distortion be achieved. Both species, the 1-amino-2,5-dimethyl cpc and the 1-amino-2,5-di-*tert*-butyl cpc, are ground state singlets (SCF optimizations, single point CISD).[8]

Furthermore, it has been checked whether a multiconfigurational treatment (CASSCF) leads to changes regarding the geometries and singlet-triplet splitting of the amino cpc.

On this level of computation, the energy gap for the amino cpc amounts to 32.1 kcal mol^{-1} for the equilibrium planar geometry ($\Theta = 0°$, ground state singlet) and -0.7 kcal mol^{-1} for the fully distorted geometry ($\Theta = 90°$, ground state triplet). However, the torsion angle at which both states are degenerate should be larger than in the computations on a lower level. If a function of the type

$$E = A \cos 2\Theta + B \quad (A, B...\text{constants for each state, compare Figure 2})$$

is presumed (which seems to be justified since the overlap integral β depends on Θ in a similar manner), it can be estimated to be appr. 82°.

Figure 3 presents the essential geometrical data of both the singlet and the triplet states of the amino cpc for $\Theta = 0°$ and 90°.
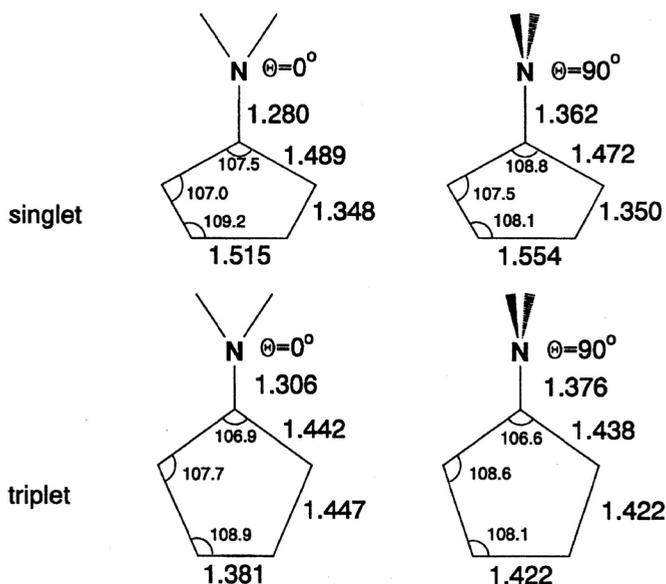

Figure 3. Geometrical data for the singlet and triplet ($^3B_2$) states of the amino cpc for $\Theta = 0°$ and 90° (CASSCF optimized, 3-21G, symmetry as decribed above), bond lengths in Å, angles in deg.

Cyclopentadienyl Cations with Two ór Three Amino Groups

For comparison with the results obtained in the case of the amino cpc, CASSCF geometry optimizations (3-21G) for both the singlet and the lowest-lying triplet states of the 1,3-diamino cpc and the 1,2,4-triamino cpc for

$\Theta = 0°$ and $90°$(**2**) and several combinations of Θ_1 and Θ_2 (**3**), respectively (see Figure 1), have been carried out.

It has been found that **2** is a ground state singlet in its planar equilibrium geometry with a singlet-triplet splitting of about 36.3 kcal mol^{-1}. However, for $\Theta = 90°$, a very small singlet-triplet splitting of about 1.0 kcal mol^{-1} has been calculated.

In the case of **3** , which is a ground state singlet in its planar equilibrium geometry with a singlet-triplet splitting of 33.8 kcal mol^{-1} ($\Theta_1 = 0°$ and $\Theta_2 = 0°$), a rotation of one amino group ($\Theta_1 = 90°$, $\Theta_2 = 0°$) and a full distortion ($\Theta_1 = 90°$, $\Theta_2 = 90°$) lead to nearly degenerate singlet and triplet states (see Table I).

TABLE I

3-21G CASSCF energies of mono-, di- and triamino cpc for several values of Θ_i; angles in deg., total energies in a.u., S-T splitting in kcal mol^{-1} ($\Delta E = E_T - E_S$)

Structure	Θ	Θ_1	Θ_2	singlet energy	triplet energy	S-T splitting
1	0			−245.71718	−245.66598	+32.1
	90			−245.60974	−245.61091	−0.7
2	0			−300.47110	−300.41319	+36.3
	90			−300.33711	−300.33556	+1.0
3		0	0	−355.20693	−355.15307	+33.8
		90	0	−355.14592	−355.13743	+5.3
		90	90	−355.06052	−355.05979	+0.5

CONCLUSION

In their planar equilibrium geometries, the aminocyclopentadienyl cations **1**, **2** and **3** have a singlet ground state with a relatively large singlet-triplet splitting of about 30 to 40 kcal mol^{-1}. In all cases, a rotation of one or more amino groups results in a destabilization of both triplet and singlet states; however, the gap between the two states reduces significantly. For this reason, the geometrical distortion discussed here could be a promising way in the search for structures with a triplet ground state being possibly applicable as building blocks for purely organic compounds with a magnetic ordering. However, since the distortion angles have to be comparatively large to achieve nearly degenerate singlet and triplet states, other manipulations of the molecular geometry in combination with the method described here might be necessary.

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SAŽETAK

O multipliciplitetu osnovnih stanja amino-supstituiranih ciklopentadienil-kationa

Ronald Beust, Anna Schleitzer, Henryk Vogel, Nikolai Tyutyulkov i Fritz Dietz

S pomoću *ab initio* kvantno-kemijskih metoda (optimizacije na SCF-razini praćene računima CISD u jednoj točki; optimizacije na CASSCF-razini) za mono-1,3-di i 1,2,4-triamino ciklopentadienil-katione istraživana je ovisnost cijepanja singlet-triplet o izvanravninskom kutu između supstituen(a)ta i aromatskog fragmenta. Pronađeno je da sve proučavane molekule imaju singletna osnovna stanja u planarnoj ravnotežnoj geometriji. Međutim, singletna i tripletna stanja gotovo su degenerirana ako se supstituent(i) zarotiraju izvan ravnine prstena za 90°. Razmatran je utjecaj tog rezultata na potragu za molekulama s visokospinskim osnovnim stanjem koje mogu poslužiti kao građevne podjedinice polimera s magnetskim uređenjem.