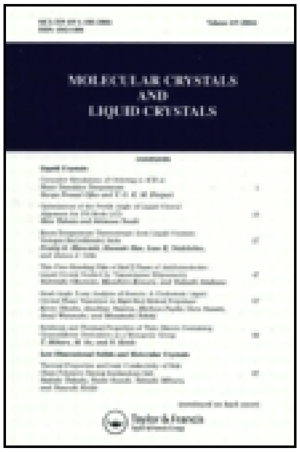

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# On the Ground State Multiplicity of Donor-Substituted Cyclopentadienyl Cations

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# ON THE GROUND STATE MULTIPLICITY OF DONOR-SUBSTITUTED CYCLOPENTADIENYL CATIONS

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Abstract It is shown that amino-substituted cyclopentadienyl cations (CPC) and benz-annelated amino CPCs might form a triplet ground state at torsion of the amino group out of the plane of the anti-aromatic CPC ring.

## INTRODUCTION

Much attention, both experimental and theoretical, has been focused recently on anti-aromatic ring systems since some of them may have a triplet ground state[1]. Therefore, they could serve as building blocks for purely organic one-dimensional (1-D) polymers with a narrow energy band gap[2] and/or with magnetic ordering.[3,4]

The cyclopentadienyl cation (CPC) with $D_{5h}$ symmetry was found to have a triplet ground state[5] as was the pentachloro CPC.[6] The unsubstituted CPC with $D_{5h}$ symmetry is characterized by degenerate highest singly occupied MOs and degenerate lowest unoccupied MOs. The species is a typical Jahn-Teller (JT) active system. A significant second order JT effect[1] leads to a decrease in the symmetry of the molecule ($D_{5h} \rightarrow C_{2v}$) with an anomalous alternation of the bond distances within the ring. *Ab initio* calculations[1,7-9] indicate that the JT distortion of the CPC leads to two JT structures, qualitatively shown in Figure 1. From the *ab initio*-CI results[1,3] it was shown that the singlet-triplet energy gap is smaller than 10 kcal $mol^{-1}$.

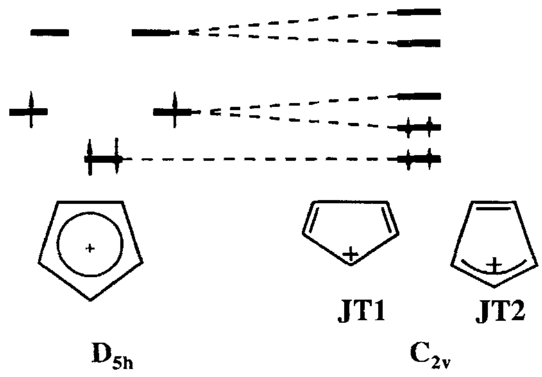

FIGURE 1 Energy levels of the Jahn-Teller structures of CPC

Most anti-aromatic systems investigated so far are very unstable, both thermodynamically and kinetically. However, it was shown experimentally[10] that substitution and ring annelation result in a stabilization of the anti-aromatic species. A partial compensation of the positive charge of the CPC fragment can be achieved by donor substituents, e.g. amino groups. A twisting of the amino group(s) could open the possibility to create species with a triplet ground state.[3] Recently, it has been shown[11] experimentally that specific compounds with large distorted spin carriers have a high-spin ground state.

The aim of this paper is to show that the introduction of suitable substituents, a torsion of these substituents out of the plane of the anti-aromatic CPC ring and/or annelation of a benzenoid system on the substituted CPCs can open possibilities to stabilize triplet states.

## COMPUTATIONAL DETAILS

The geometries of the considered compounds have been investigated by *ab initio* calculation on RHF/ROHF (all investigated molecules), and on CASSCF (compounds **1**-**3**) levels. In each case, the RHF/ROHF optimizations have been followed by a CISD single point calculation. The active space consisted of all MOs with exception of the lowest-lying MOs formed by 1s AOs and their virtual analoga. Optimizations on CASSCF level have been carried out with an active space including all π MOs.

A 3-21G standard basis set has been used throughout. By selected calculations on **1**, **2**, and **5** it has been shown that the application of a 6-31G* basis set does not influence the results qualitatively. For this reason, only the results obtained with the 3-21G basis set are given in this paper. The program package GAMESS-UK[12], version 5.1, has been used.

## RESULTS AND DISCUSSION

The optimized geometries of the investigated species are given in Figures 3 and 4. The singlet-triplet splittings $\Delta E^{ST}$ of all molecules in their equilibrium geometries and for the structures with distorted amino group(s) ($\Theta = 90°$) are summarized in Table 1. In addition, the sums of the π-net charges of the carbon atoms of the CPC ring are given.

### Amino CPC

The optimized ground state of amino CPC (**1**) is a singlet state with $C_{2v}$ symmetry. The geometry corresponds to that of the JT1 structure of the unsubstituted CPC (see Figures 1 and 3). The singlet-triplet splitting has been calculated (CISD based on RHF/ROHF optimized geometries) to be −17.9 kcal mol$^{-1}$. At torsion of the amino group out of the plane of the anti-aromatic CPC ring from $\Theta = 0°$ up to $\Theta = 90°$, the total energy of both singlet and triplet states increases to a different extent, and the singlet-triplet splitting decreases with increasing Θ. At about $\Theta = 70°$, the lowest-lying singlet and triplet states are degenerate. For values of $\Theta > 70°$, a triplet state is the ground state. The maximum singlet-triplet splitting ($\Theta = 90°$) has been calculated to be about +8 kcal mol$^{-1}$. Regardless of the torsion angle Θ, the amino group remains planar (no pyramidalization).

A multiconfigurational treatment (CASSCF optimization) of the amino CPC does not change the results qualitatively, but rather quantitatively: At this level of computation, the singlet-triplet splitting amounts to −32.1 kcal mol$^{-1}$ for the planar equilibrium geometry ($\Theta = 0°$, singlet ground state) and +0.7 kcal mol$^{-1}$ for the fully distorted geometry ($\Theta$ = 90°, triplet ground state), respectively. The torsion angle at which both states are degenerate was estimated to be about $\Theta$ = 82°.

In Figure 2, the relative energies of the singlet and triplet states are presented as a function of the torsion angle $\Theta$. Figure 3 shows the geometries of both the singlet and the triplet states for the planar amino CPC with $C_{2v}$ symmetry and for the fully distorted structure with $\Theta$ = 90°. Whereas the geometry of the singlet state corresponds to that of the JT1 structure of the unsubstituted CPC, the geometry of the triplet ground state ($\Theta$ = 90°) shows the tendency to an equalization of the bond lengths (in analogy to the $D_{5h}$ symmetry of the triplet ground state of the unsubstituted CPC).

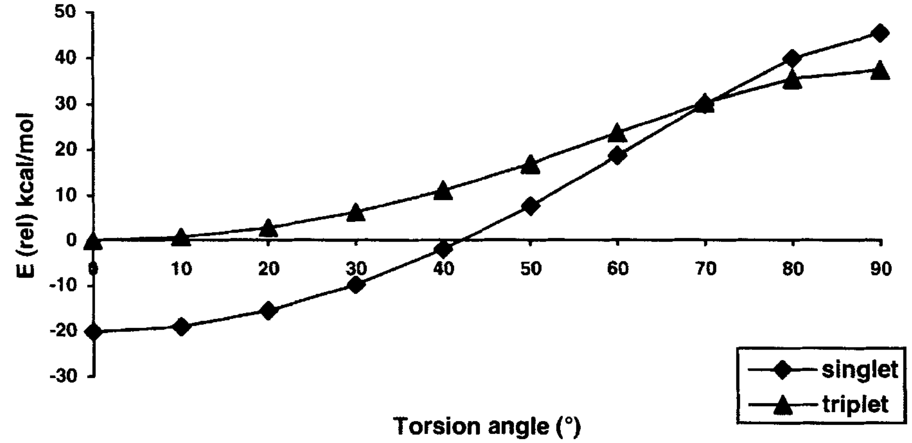

FIGURE 2 CISD energies of the lowest-lying triplet ($^3B/^3B_2$) and singlet states of the amino CPC in dependence of the torsion angle $\Theta$. Reference: $^3B_2$ energy for $\Theta$=0° ($C_2/C_{2v}$ symmetry, 3-21G optimized geometries).

## 1,2- and 1,3-Diamino CPCs

The CPC structure may be stabilized by multiple substitution. Various stable substituted 1,2- and 1,3-diamino CPC salts have been synthesized and characterized by Gompper *et al.*[10] As model systems, we have used 1,2-diamino CPC **2** and 1,3-diamino CPC **3**. *Ab initio* investigations[13,14] revealed that the energetically lowest-lying state is a singlet in both cases which corresponds to the JT1 of the unsubstituted CPC for **2** and to JT2 for **3**, respectively.

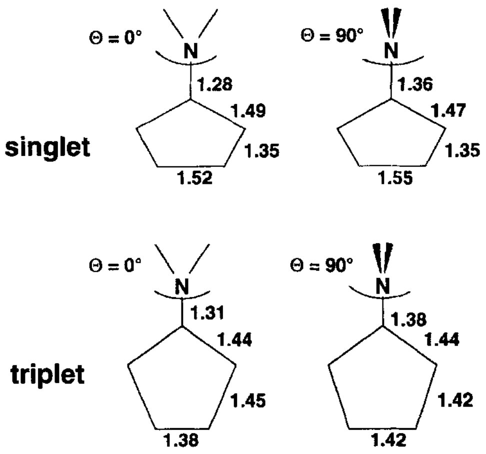

FIGURE 3 CASSCF optimized geometries of amino CPC **1** in the singlet and triplet states with Θ = 0° and Θ = 90°, bond lengths in Å, Θ in degree.

It has been found that **3** has a singlet ground state in its planar geometry ($C_{2v}$) as well as in its fully distorted geometry (Θ = 90°). However, the singlet-triplet splitting is significantly reduced from about –36.3 kcal mol$^{-1}$ for the planar geometry to about –1.0 kcal mol$^{-1}$ for Θ = 90° (CASSCF optimization, in the singlet state at Θ= 90° the amino groups are pyramidalized). This means that the lowest-lying singlet and triplet states are nearly degenerate at this conformation. As in the case of amino CPC, the C–C bond lengths in the five-membered ring are nearly equalized in the triplet state (1.42 to 1.43 Å). This is depicted in Figure 4.

The 1,2-diamino CPC **2** in its equilibrium geometry has a singlet ground state. The molecule is surprisingly non-planar: one amino group is pyramidalized and rotated out of the plane of the anti-aromatic CPC ring by $\Theta_1$ = 90° while the other amino group is co-planar with the CPC ring ($\Theta_2$ = 0°). This singlet state is stabilized in relation to a planar triplet state ($C_{2v}$ symmetry) by about 20.7 kcal mol$^{-1}$. If both the amino groups are rotated out of the plane of the CPC ring, the singlet and triplet states are almost degenerate. The singlet-triplet splitting was calculated to be about +0.1 kcal mol$^{-1}$ (CASSCF optimization, both amino groups are pyramidalized regardless of the multiplicity at $\Theta_1 = \Theta_2$ = 90°).

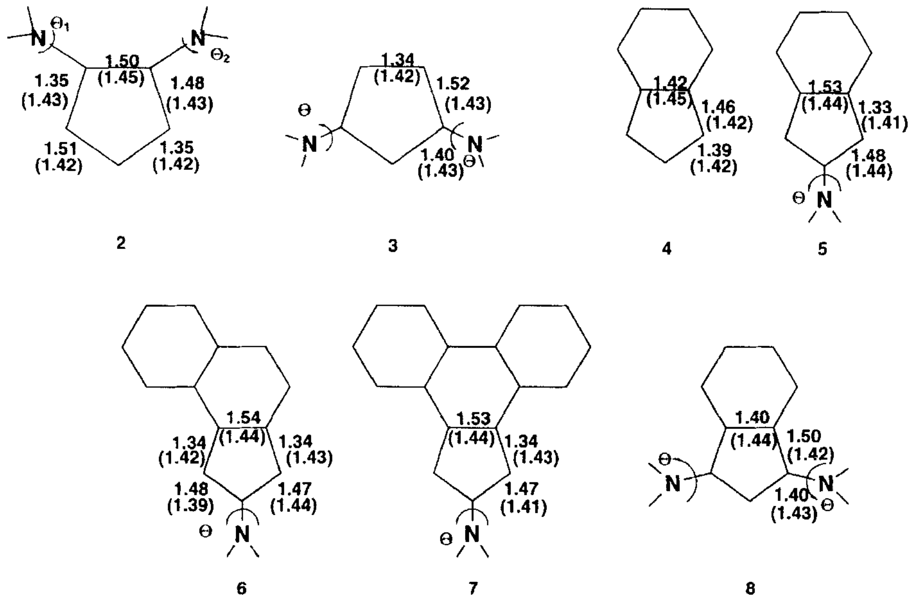

FIGURE 4 Optimized structures (bond lengths in Å) of the investigated compounds in the singlet (at Θ = 0°) and triplet states (at Θ = 90° except for structure **4**, values in brackets). Structures **2** and **3** are CASSCF optimized, structures **4** to **8** are RHF/ROHF optimized.

Cata-condensed CPCs

The optimized geometries are given in Figure 4, the singlet-triplet splittings ($\Delta E^{ST} = E^S - E^T$) of all the investigated compounds are summarized in Table 1. The geometry of the unsubstituted indenyl cation (IC) **4** in its singlet ground state corresponds to the JT2 of the CPC. The S-T splitting amounts to about −9.7 kcal mol$^{-1}$ (3-21G, CISD).

Amino substitution (amino IC **5**) reduces the S-T gap so that the singlet and triplet states are approximately degenerate (singlet JT1; $\Delta E^{ST}$ = +3.5 kcal mol$^{-1}$) if the amino group is co-planar with the IC fragment. The geometry of the most stable singlet state corresponds to the JT1 structure of the CPC while the geometry of the triplet state is characterized by a maximum equalization of the bond lengths. The S-T splitting (singlet JT2) increases to about −21.4 kcal mol$^{-1}$ at torsion of the amino group out of the IC plane by Θ = 90°.

TABLE 1 S-T splitting, $\Delta E^{ST} = E^{S} - E^{T}$ (in kcal mol$^{-1}$), of the investigated compounds (see Figure 4, Θ in degree) and sum of the π-net charges of the carbon atoms of the CPC ring, $\Sigma q^{\pi}$ (Mulliken analysis).

| Structure | Θ | ΔE* | ΔE** | $\Sigma q^{\pi}$* | $\Sigma q^{\pi}$** |
|---|---|---|---|---|---|
| **1** | 0 | −20.2 | −32.1 | $0.521^{d}$ | $0.403^{d}$ |
| **1** | 90 | +8.0 | +0.7 | $0.964^{e}$ | $0.964^{e}$ |
| **2** | $0^{a}$ | −2.6 | −20.7 | $0.480^{d}$ | $0.364^{d}$ |
| **2** | $90^{b,c}$ | +12.2 | +0.1 | $0.928^{e}$ | $0.929^{e}$ |
| **3** | 0 | −27.7 | −36.3 | $0.283^{d}$ | $0.132^{d}$ |
| **3** | $90^{c}$ | +5.7 | −1.0 | $0.932^{e}$ | $0.933^{e}$ |
| **4** | -- | −9.7 | -- | $0.504^{d}/0.676^{e}$ | -- |
| **5** | 0 | +3.5 | -- | $0.735^{d}$ | -- |
| **5** | 90 | −8.3 | -- | $0.659^{e}$ | -- |
| **6** | 0 | −6.3 | -- | $0.369^{d}$ | -- |
| **6** | $90^{c}$ | −2.4 | -- | $0.576^{e}$ | -- |
| **7** | 0 | −11.3 | -- | $0.354^{d}$ | -- |
| 7 | $90^{b,c}$ | +11.4 | -- | $0.606^{e}$ | -- |
| **8** | 0 | −44.3 | -- | $0.120^{d}$ | -- |
| **8** | $90^{c}$ | −14.6 | -- | $0.637^{e}$ | -- |

*SCF-3-21G, CISD ** CASSCF 3-21G

[a] one amino group is pyramidalized and rotated out of the plane of the CPC ring in the singlet state structure

[b] amino group(s) pyramidalized in the triplet state structure

[c] amino group(s) pyramidalized in the singlet state structure

[d] calculated for singlet state

[e] calculated for triplet state

Additional benzene rings (structures **6** and **7**, respectively, see Figure 4) stabilize the triplet state more than the singlet state (3-21G, CISD). This holds in particular for species with a fully distorted amino group (Θ = 90°).

In the case of **7**, a significantly stabilized triplet ground state should be achieved if the amino group is twisted out of the plane of the conjugated π-system.

An analysis of the geometries of the ground state multiplicity of the various investigated species shows that the lowest-lying triplet state is stabilized if the substitution and/or cata-condensation leads to a maximum equalization of the bond lengths within the anti-aromatic CPC fragment.

### Charge transfer at torsion of the amino groups

In all cases under investigation, a significant transfer of the positive charge from the N atom of the amino group to the anti-aromatic CPC ring was calculated at torsion of the amino group out of the CPC ring plane. This charge transfer is connected with a reduction of the singlet-triplet splitting. In some cases, the fully distorted structure ($\Theta = 90°$) corresponds to a triplet ground state. These structures are characterized by a maximum equilization of the bond lengths (in the CPC ring) and a concentration of nearly the full positive charge within the CPC ring fragment.

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### REFERENCES

1. W. T. Borden and E. R. Davidson, J. Am. Chem. Soc. 101, 3771 (1979), W. T. Borden, Diradicals, Wiley-Interscience, N.Y. 1982.
2. F. Dietz, K. Müllen, M. Baumgarten, and N. Tyutyulkov, Macromol. Theory Simul., 3, 241 (1994).
3. R. Beust, Diploma Thesis, University of Leipzig, 1995.
4. N. Tyutyulkov, Pure Appl. Chem., 68, 345 (1996).
5. M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman jr., C. Perchonock, E. Wasserman, R. S. Hutton and V. J. Kuck, J. Am. Chem. Soc., 95, 3017 (1973).
6. R. Breslow, R. Hill and E. Wasserman, J. Am. Chem. Soc., 86, 5349 (1964).
7. E. R. Davidson and W. T. Borden, J. Chem. Phys., 67, 2191 (1977).
8. W. J. Hehre and P. v. R. Schleyer, J. Am. Chem. Soc., 95, 5837 (1973).
9. H.-J. Köhler and H. Lischka, J. Am. Chem. Soc., 101, 3479 (1979).
10. R. Gompper and H.-U. Wagner, Angew. Chem., 100, 1493 (1988).
11. K. Okada, T. Imakura, M. Oda, H. Murai and M. Baumgarten, J. Am. Chem. Soc., 118, 3047 (1996) and references therein.
12. M. F. Guest, P. Fantucci, R. J. Harrison, J. Kendrick, J. H. van Lenthe, K. Schöffel and P. Sherwood, Gamess-UK, Computing for Science Ltd., Daresbury Laboratory, 1993.
13. N. Tyutyulkov, B. Kurtev, Y. Stefanovsky, F. Dietz, J. Fabian, A. Mehlhorn, G. Olbrich, and O. E. Polansky, J.Mol.Struct., 114, 279 (1984).
14. R. Beust, A. Schleitzer, H. Vogel, N. Tyutyulkov and F. Dietz, Croat. Chem. Acta, submitted for publication.