# Excited states of cyclic-conjugated anions: a theoretical study of the photodecarboxylation of cycloheptatriene and cyclopentadiene carboxylate anions

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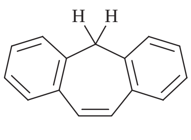
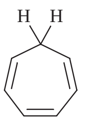
**Correlation diagrams and semiempirical calculations suggest that the same carbanion intermediates are involved in both the photodecarboxylation reaction of cycloheptatrienyl and cyclopentadienyl carboxylate anions and the photodeprotonation reaction of cycloheptatriene and cyclopentadiene; therefore, the same '4*n* rule' applies to both processes, which can proceed only on the HOMO→LUMO excited potential energy surface of A″ symmetry. This is confirmed by *ab initio* CASSCF calculations which show that the second excited singlet state of cycloheptatriene carboxylic acid is of A″ symmetry, and that photodecarboxylation proceeds without barriers only on this A″ potential energy surface. This validates the proposition that the difference in excited-state acidity of suberene and the parent compound cycloheptatriene is due to a different ordering of the excited states.**

## Introduction

Photoinitiated generation of conjugated cyclic carbanions has been reported recently,[1] and it was suggested that a simple 'electron-count' rule applies for predicting the relative reaction efficiencies when dealing with photochemical reactions that can proceed *via* charged cyclic arrays as intermediates.[2] In the excited state the 4*n*-electron count is favoured over the usual 4*n* + 2 count commonly observed in ground-state systems. That is, there appears to be an inherent stabilization effect of the 4*n* array of electrons of these compounds on the excited-state surface, analogous to the well-known aromatic stabilization associated with the 4*n* + 2 systems in the ground state. Simple correlation diagrams for the deprotonation reaction in fact show that the HOMO→LUMO excited configuration $\Phi_{H\rightarrow L}$ of cycloheptatriene correlates with a configuration of the anion which is degenerate with the ground state configuration $\Phi_0$, while for cyclopentadiene $\Phi_{H\rightarrow L}$ correlates with a high lying excited configuration of the anion.[3] Thus, the photogeneration of a conjugated cyclic anion is symmetry allowed or forbidden, depending on the electron count. This nicely explains why photolysis of dibenzo[*a*,*d*]cycloheptene (suberene, **SUB**) in $D_2O$–$CH_3CN$ results in exchange of the benzylic proton with deuteron, while the related compounds such as fluorene and dibenzo[*a*,*d*]cycloheptane are totally unreactive.[4] However, the parent 4*n* compound cycloheptatriene (**CHT**) undergoes a photochemical sigmatropic [1.7]hydrogen shift reaction,[5] but does not at all exhibit excited state carbon acidity.



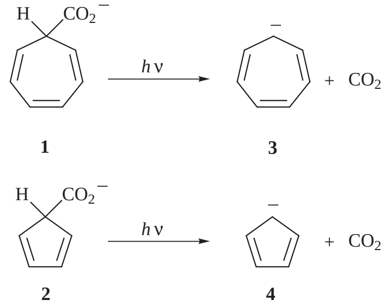
**SUB**



**CHT**

Based on semiempirical configuration interaction (CI) calculations[6] we suggested that the different behavior of **SUB** and **CHT** is due to the fact, that for **SUB** the HOMO→LUMO excited A″ state, which according to the correlation diagram is responsible for photogeneration of an anion, is the lowest excited singlet state, but not for **CHT**; instead, there is a lower-lying A′ state that dominates the photochemical reactivity of **CHT**.[3,7] In order to prove this suggestion, it has to be shown that **CHT** undergoes the observed sigmatropic [1.7]hydrogen shift reaction on a potential energy surface of A′ symmetry, while carbon acidity is expected for the HOMO→LUMO excited A″ state of **CHT** and is not observed experimentally because of Kasha's rule.[8]

In this paper we will show that for **CHT** the carbanion generation indeed could take place on a potential energy surface of A″ symmetry. Since in isolated molecule calculations on the deprotonation reaction R–H + B⁻→R⁻ + HB high lying orbitals of the base cause considerable problems, we use as model reaction the photodecarboxylation of cycloheptatriene carboxylic acid (Scheme 1). This is suggested by the fact that



**Scheme 1**

Krogh and Wan[9] have shown that photodecarboxylation of diarylacetic acids may proceed *via* the same carbanion intermediates that are generated by photodeprotonation; this is concluded from the quantum yield $\Phi = 0.6$ for the decarboxylation of suberenyl carboxylic acid as compared to $\Phi = 0.01$ for fluorenyl carboxylic acid, which reflect the stabilities of the corresponding excited-state antiaromatic and aromatic carbocyclic anions. Thus, these reactions should follow the same '4*n* rule' as the corresponding photodeprotonation reactions.

## Results and discussion

### Methods of computation

Quantum chemical calculations on the mechanism of photoreactions are rather demanding since excited states can be described only by taking into account a sufficient amount of configuration interaction (CI). We therefore use the semi-

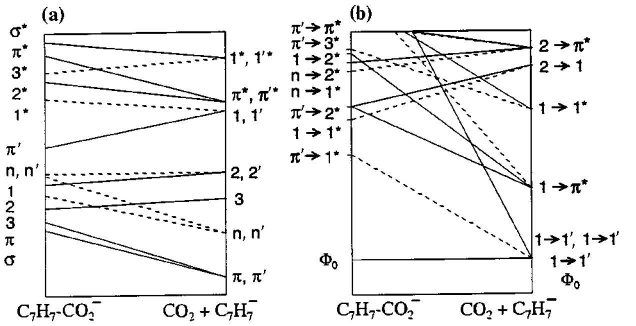


**Fig. 1** (a) Orbital correlation diagram and (b) configuration correlation diagram for the decarboxylation of the cycloheptatriene carboxylate anion **1**. Solid and broken lines refer to A′ and A″ symmetry, respectively. The CO$_2$ group is assumed to be coplanar with the π system of the ring (see text). For the ring π MOs $\varphi_i$ and $\varphi_j^*$ the short-hand notation *i* and *j** is used. σ and σ* are the MOs describing the C–CO$_2^-$ bond. $\Phi_0$ denotes the ground configuration and excited configurations $\Phi_{i\rightarrow j^*}$ are abbreviated by $i\rightarrow j^*$.

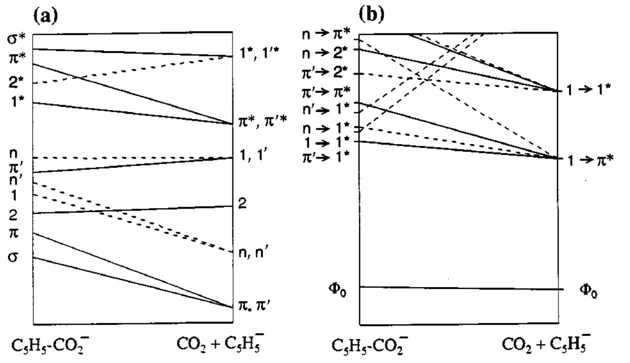


**Fig. 2** (a) Orbital correlation diagram and (b) configuration correlation diagram for the decarboxylation of the cyclopentadiene carboxylate anion **2**. Solid and broken lines refer to A′ and A″ symmetry, respectively. For further details see Fig. 1.

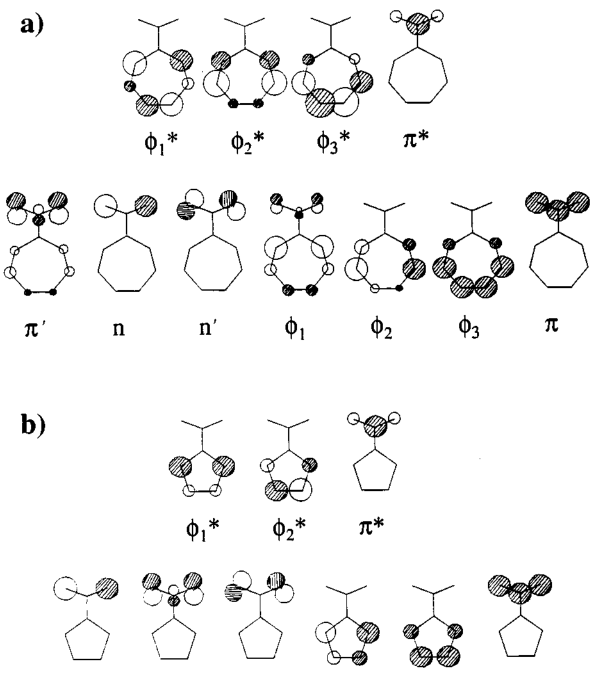


**Fig. 3** Schematic representation and notation of some MOs (a) of the cycloheptatriene carboxylate anion **1**, and b) of the cyclopentadiene carboxylate anion **2**

empirical MNDOC-CI method (**m**odified **n**eglect of **d**iatomic **o**verlap parameterized for taking into account **c**orrelation effects explicitly)[6] to explore excited state geometries and potential energy surfaces before using *ab initio* CASSCF methods (**c**omplete **a**ctive **s**pace **s**elf **c**onsistent **f**ield) to get the final results. The MNDOC-CI method is based on spin-adapted CFS's (configurational state functions) and includes single and double excitations with respect to one or several reference configurations within an active space of 10–12 orbitals involved in the process under consideration. For the CASSCF calculations the two-step quasi-Newton method[10] included in the GAUSSIAN 94 package[11] was employed. A minimal basis (STO-3G) and a variation of the active space was used for selecting the orbitals to be included, which turned out to be all six π MOs as well as the HOMO, which is highly localized in the CO$_2$ group and carries the negative charge. Thus, final results were obtained for eight electrons in seven orbitals using the 6-31+G* basis set, which includes diffuse basis functions for the description of anionic species.

## Correlation diagrams and results of semiempirical calculations

In the study of photochemical reactions it is in general quite useful to consider first correlation diagrams for the process under investigation. In Figs. 1 and 2 orbital correlation diagrams and the corresponding configuration correlation diagrams are given for the decarboxylation of the cycloheptatriene (**1**) and cyclopentadiene carboxylate anion (**2**), respectively. These diagrams were constructed on the basis of orbital and configurational energies obtained from MNDOC-CI calculations. For the carboxylate anions **1** and **2** the MOs used in the correlation diagrams are shown together with their denotation in Fig. 3; for the anions **3** and **4** the π MOs occupied in the ground configuration $\Phi_0$ are numbered 1,2,... starting from the degenerate HOMO, and the unoccupied degenerate LUMO is denoted by 1*.

From Figs. 1b and 2b it is seen that, as in the case of the deprotonation reaction discussed earlier, neither for **1** nor for **2** a symmetry induced barrier exists for the ground-state reaction; decarboxylation in the S$_0$ is therefore allowed and its occurrence will be determined entirely by the heat of reaction. The configuration correlation diagram of the excited-state decarboxylation of **1** also appears to be very similar to the corresponding diagram for deprotonation, as both the singly and the doubly π′→1*-excited configurations correlate with the triply degenerate ground configurations that yield the three lowest singlet states of the heptatrienyl anion **3**, indicating a barrierless and exothermic reaction in the A″ excited state. In the case of **2**, however, the allowed excited-state correlations correspond to a homolytic cleavage of the exocyclic CC bond yielding a cyclopentadienyl radical and CO$_2$ radical anion; the formation of the cyclopentadienyl anion will be described by a correlation of the 1→1* excited reactant configuration of A″ symmetry with the corresponding 1→1* configuration of the resulting anion. The crossing of several excited-configuration correlation lines thus indicates a barrier for the excited-state decarboxylation reaction in close analogy with the deprotonation reaction.

These conclusions from the correlation diagrams are fully confirmed by the results of MNDO-CI reaction path calculations, in which the CC distance between the ring and the CO$_2$ group was varied between 1.6 and 3.4 Å in steps of 0.2 Å with the other geometry parameters optimized for the state under consideration. Some typical results are shown in Fig. 4. It is seen that the decarboxylation of **1** yielding the antiaromatic cycloheptatrienyl anion **3** proceeds in the A″ excited state easily and without a barrier. In the S$_1$ excited state of **2**, on the other hand, radical fragmentation occurs producing a CO$_2$ radical anion and a cyclopentatrienyl radical, while the aromatic cyclopentadienyl anion **4** is formed only in one of the higher excited states. The ground-state reactions, however, are calculated to be very similar for both systems, with barriers of 43.9 and 38.9 kJ mol$^{-1}$, and heats of reaction $\Delta H_R = -0.8$ kJ mol$^{-1}$ and $\Delta H_R = -39.4$ kJ mol$^{-1}$, respectively. The difference of 38.6

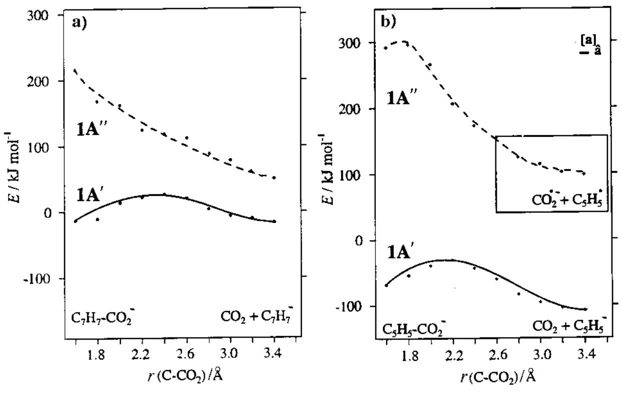


**Fig. 4** MNDOC-CI reaction path calculation for the photodecarboxylation a) of cycloheptatrienyl carboxylate **1** and b) of cyclopentadienyl carboxylate **2**. For the distances $r$(C–CO$_2$) shown all geometry parameters are optimized for each state separately; energies of different states for a given $r$(C–CO$_2$) may therefore correspond to different structures. Solid and broken lines refer to A′ and A″ symmetry, respectively. Smooth lines have been drawn although the calculated points scatter somewhat due to the restricted nature of the CI. In b) the broken line corresponds to homolytic cleavage; the cyclopentadienyl anion **4** is formed only in one of the higher excited states as indicated by [a] for $r$(C–CO$_2$) = 3.4 Å.

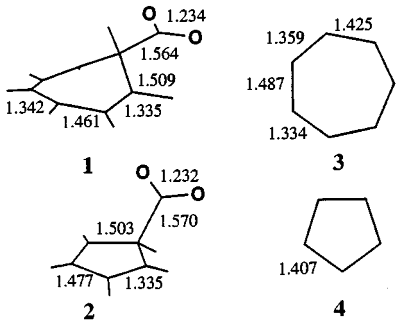


**Fig. 5** RHF/6-31+G*-optimized ground state geometries of cycloheptatrienyl carboxylate (**1**), cyclopentadienyl carboxylate (**2**), cycloheptatrienyl anion (**3**) and cyclopentadienyl anion (**4**). **3** and **4** are planar, while the puckering angles in **1** and **2** are 46 and 2°, respectively.

kJ mol$^{-1}$ in $\Delta H_R$, although favouring the formation of the aromatic anion, is much smaller than expected. This may be due to the fact that aromatic stabilization energies are generally underestimated by semiempirical methods;[12] but a more important reason may be that minimal basis set calculations are not able to describe anionic systems correctly. Therefore, *ab initio* calculations including diffuse basis functions were performed to get more quantitative data for the decarboxylation reaction discussed here.

## Results of *ab initio* calculations

In order to determine the ground state heats of reaction, RHF calculations for the reactants **1** and **2** and the products **3** and **4** as well as CO$_2$ were carried out. The optimized geometries are shown in Fig. 5, and the calculated energies are collected in Table 1. The global minimum of **1** occurs for a boat conformation with the carboxylate group in equatorial position and coplanar with the ring. MNDOC-CI calculations yield the same minimum, although another minimum with an axial carboxylate group perpendicular to the ring is 8 kJ mol$^{-1}$ lower in energy. On the *ab initio* level, however, such a conformation is not possible, since the more pronounced boat form would lead to strong steric interactions between the carboxylate oxygen and the ring carbons. Both anions **3** and **4** are calculated to be planar, the aromatic system **4** is completely delocalized. The deficiency of the semiempirical method to describe anions is reflected in the heats of reaction, which are now positive ($\Delta H_R$ = 160.8 kJ mol$^{-1}$ and 33.5 kJ mol$^{-1}$, respectively). The

**Table 1** RHF/6-31+G* results for the ground states of the reactants cycloheptatrienyl carboxylate **1**, cyclopentadienyl carboxylate **2** as well as CO$_2$ and the products cycloheptatrienyl anion (**3**) + CO$_2$ and cyclopentadienyl anion (**4**) + CO$_2$

| | $E$/au | $\Delta H_R$/ kJ mol$^{-1}$ | $\Delta H_R$ (MNDOC-CI)/ kJ mol$^{-1}$ |
|---|---|---|---|
| CO$_2$ | −187.638 77 | | |
| **1** | −456.757 28 | | |
| **3** | −456.296 02 | 160.8 | −0.8 |
| **2** | −379.860 20 | | |
| **4** | −379.847 43 | 33.5 | −39.4 |

**Table 2** CASSCF/6-31+G* results for the singlet states 1A′, 2A′ and 1A″ of cycloheptatrienyl carboxylate **1**. Reference configurations $\varphi_i$ at the CASSCF optimized geometries.[a]

| Irrep. | $E$/au | $E_{rel}$/kJ mol$^{-1}$ | $\Psi$[b] |
|---|---|---|---|
| **1A′** | **−456.834 58** | **0.0** | $\mathbf{\Phi_0}$ |
| 2A′ | −456.620 60 | 561.9 | $\Phi_{H\to L,H\to L}$, $\Phi_{H-1\to L}$, $\Phi_{H-1\to L+1}$ |
| 1A″ | −456.602 17 | 610.0 | $\Phi_{H\to L}$ |
| 1A′ | −456.757 97 | 201.0 | $\Phi_0$, $\Phi_{H\to L,H\to L}$ |
| **1A″** | **−456.754 83** | **209.3** | $\mathbf{\Phi_{H\to L}}$ |
| 2A′ | −456.741 24 | 244.5 | $\Phi_{H\to L,H\to L}$, $\Phi_0$ |
| **2A′** | **−456.677 63** | **412.0** | $\mathbf{\Phi_{H\to L,H\to L}}$, $\mathbf{\Phi_{H-1\to L}}$, $\mathbf{\Phi_{H-1\to L+1}}$ |
| 1A″ | −456.639 71 | 511.6 | $\Phi_{H\to L}$ |

[a] Geometries are optimized for the state with the energies given in bold. [b] Only the dominant configurations $\Phi$ contributing to the total wavefunction $\Psi$ are given.

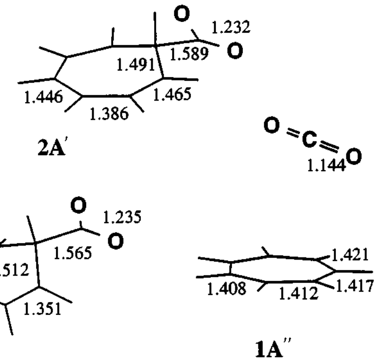


**Fig. 6** CASSCF/6-31+G*-optimized geometries of cycloheptatrienyl carboxylate **1** in its ground state S$_0$ (1A′) and in the first two excited singlet states 2A′ and 1A″. The 1A″ geometry does not correspond to a minimum, at $r$(C–CO$_2$) = 3.8 Å the 1A″ and 1A′ states are practically degenerate and optimization was cut off.

difference of 127.3 kJ mol$^{-1}$ in favour of the aromatic product is much more reasonable than the semiempirical result.

For the CASSCF optimization of the excited state of **1** all six π orbitals as well as the HOMO, which is highly localized on the CO$_2$ group and carries the negative charge, were included in the active space. In the first step the ground state S$_0$ was optimized, and starting from this S$_0$ (1A′) geometry the excited states S$_1$ and S$_2$ were optimized on the potential energy surface of the 1A″ and of the 2A′ state. The geometries are shown in Fig. 6, and the energies are collected in Table 2. In agreement with the conclusions from the correlation diagrams the CASSCF calculations demonstrate that decarboxylation proceeds without a barrier only on the potential energy surface of the 1A″ state, as no stable minimum could be detected on this surface. Instead, the optimization procedure leads to a geometry with the neutral CO$_2$ 3.8 Å away from the cycloheptatrienyl anion. At this geometry the 1A″ and 1A′ states are practically degenerate and optimization was cut off. For the 2A′ state (S$_1$), however, a true minimum was found in the Franck–Condon region. Decarboxylation on the 2A′ surface is very unlikely as indicated by the fact that the same Franck–Condon minimum is reached if the optimization is started at an MNDOC-CI optimized geometry with $r(\text{C–CO}_2) = 1.7$ Å, *i.e.* 0.11 Å longer than at the minimum.

A comparison of the CASSCF results in Table 2 and the MNDOC-CI excitation energies $\Delta E(1\text{A}'') = 283.9$ kJ mol$^{-1}$ and $\Delta E(2\text{A}') = 384.8$ kJ mol$^{-1}$ shows that the semiempirical relative energies are much lower than the *ab initio* data, and that the order of the excited states is interchanged, *i.e.* the symmetric 2A′ state lies at higher energies than the 1A″ state. The same difference between *ab initio* and semiempirical excitation energies has been observed for the unsubstituted cycloheptatriene, where an MNDOC-CI calculation with an increased and optimized CI leads to the *ab initio* order of the excited states.[13] Thus we conclude that the wrong ordering of the semiempirical excitation energies is due to the limited CI.

## Conclusions

From the results of CASSCF calculations it follows that the second excited singlet state of the cycloheptatriene carboxylic anion **1** is of A″ symmetry, and that photodecarboxylation proceeds without a barrier only on the potential energy surface of this state. This proves the suggestion that the same carbanion intermediates are involved in photodecarboxylation and photodeprotonation reactions, and that therefore the same '4*n* rule' applies to both types of processes. In particular, this validates the proposition that the difference in excited-state acidity of suberene and the parent compound cycloheptatriene is due to a different ordering of the excited states.

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