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What is the Preferred Structure of the Singlet Cyclopentadienyl Cation?

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Pseudorotation of the singlet cyclopentadienyl cation (a C_{2v} 'ethylene'-type structure **2**) proceeds through the 'allylic'-type C_{2v} singlet **3** as the transition state with an extremely low barrier [0.09] kcal mol^{-1} at MP4SDTQ/6–31G(2d,p)//MP2(full)/6–13G*] and the $C_5H_5^+$ nuclear configuration oscillates among the degenerate C_{2v} minima **2,2a,2b**, *etc.*

The ground state of the cyclopentadienyl cation has been found experimentally to be a triplet ($^3A_2'$, D_{5h} structure **1**).[1,2] The $^1E_2'$ singlet D_{5h} structure undergoes a first-order Jahn–Teller distortion.[3] Also, a second-order Jahn–Teller effect is pronounced in this state which, as a result of the e_2' distortion, interacts with the low-lying $^1A_1'$ state.[3] Two singlet structures of C_{2v} symmetry, **2** and **3**, have been suggested to be involved in pseudorotation, Scheme 1.[3,4]

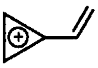
MINDO/3 calculations indicate that neither **2** and **3** are minima and a non-planar C_s structure **4** is lower in energy.[5] However, earlier *ab initio* calculations [3,6] found **3** to be a minimum and a 'symmetrical' (see ref.6) C_{2v} structure **2** was suggested to be a transition state.[6] Geometry optimization of **4** led to **2** or to **3**.[6] The most stable isomer of $C_5H_5^+$ was claimed to be the vinylcyclopropenium cation **5**, which is 16.4 kcal mol^{-1} lower in energy than **1** at MP2/6–31G**//HF/6–31G*.[6] Both singlets, **2** and **3**, having almost equal energies, are 9.2 kcal mol^{-1} lower in energy than **1**.

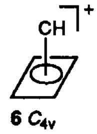

1 D_{5h}


2 C_{2v}


3 C_{2v}


4 C_s


5 C_s



6 C_{4v}


(1)

2 **3** **2a** **3a** **2b**

Is it "likely that a better calculation will show that the symmetrical structure **2** is a transition state between rotational isomers"?[6] Indeed, correlation effects may influence the nature of stationary points for **2** and **3** considerably. What structure does the singlet cyclopentadienyl cation have at a higher level?

The GAUSSIAN-92 program[7] was employed for calculations. The results obtained are given in Table 1 and Fig. 1. For **2** and **3**, harmonic frequencies were calculated at MP2(fc)/6–31G*. The final energies for the $C_5H_5^+$ isomers **1**–**3**, **5** and **6** were computed at MP4SDTQ(fc)/6–31G**//MP2(full)/6–31G* + ΔZPE(HF/6–31G*) and refined, for **2** and **3**, at MP4SDTQ(fc)/6–31G(2d,p)//MP2(full)/6–31G* + ΔZPE(MP2(fc)/6–31G*). Projections to the pure spectroscopic state of the triplet **1** ($^3A_2'$) (PMP2 and PMP4)[8] were carried out.

Table 1 Total (a.u.) and relative (kcal mol^{-1}) energies of the $C_5H_5^+$ isomers **1–6** calculated at various computional levels

	HF/6–31G*		MP2(full)/6–31G* //MP2(full)/6–31G*		MP4SDTQ/6–31G**// MP2/6–31G*	
2 C_{2v}	–191.90215(1)[a]	0	–192.52005(0)[a]	0	–192.60567 [–192.64529]e	0
3 C_{2v}	–191.90235(0)	–0.1(0.2)[b]	–192.51986(1)	0.1(–0.2)[b]	–192.60554 [–192.64515][e]	0.08[0.09][e] (–0.2)[d,e]
1 D_{5h}	–191.93339(0)	–19.6(–19.0)	–192.53977[c]	–12.3	–192.61954[c]	–8.7[g]
5 C_s	–191.91827(0)	–10.1(–9.7)	–192.53552	–9.7	–192.61532	–6.1
6 C_{4v}	–191.86520(0)	23.2(23.7)	–192.51446[f]	3.5	–192.58611	12.3

[a] Number of imaginary frequencies is shown in parentheses. [b] Relative energies with ΔZPE(HF/6–31G*) correction (scaling factor is 0.91) are shown in parentheses. ZPE(**2**) = 53.1 kcal mol^{-1}. [c] PMP2 and PMP4 values are given for the triplet **1**. [d] Relative energies with ΔZPE(MP2(fc)/6–31G*) correction (scaling factor is 0.96) are shown in parentheses. ZPE(**2**) = 53.1 kcal mol^{-1}. [e] Total and relative energies calculated at MP4SDTQ/6–31G(2d,p)//MP2(full)/6–13G* are indicated in square brackets. [f] The geometry of **6** , optimized at MP2/6–31G*, has been taken from ref. 13. [g] At QCISD (T)/6–31G**//MP2/6–31G*, **1** ($E = -192.61910$ a.u.) is 2.0 kcal mol^{-1} more stable than **5** ($E = -192.61596$).

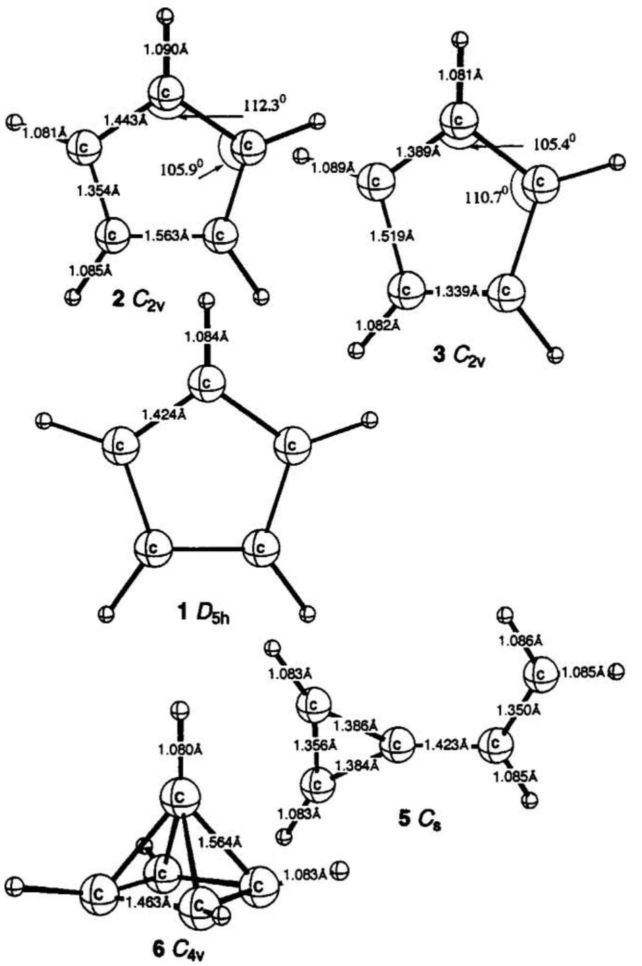
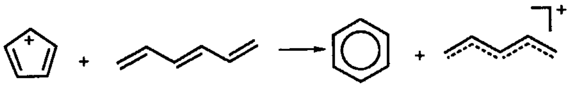


Fig. 1 Geometries of **1–6** optimized at MP2(full)/6–31G*. The geometry of **6** has been taken from ref. 13.

Planar **3** is a minimum [the lowest frequency $\nu(b_2) = 248$ cm^{-1}] while **2** is a transition state at HF/6–31G* (Table 1). Since the RHF solution for **3** is singlet stable [$^s\lambda_+$, the lowest eigenvalue in the singlet instability ($^sA + {}^sB$) matrix is 1.57 eV],[9] the RHF/6–31G* frequency calculations are reliable. However, the nature of the stationary points for **2** and **3** changes at MP2(fc)/6–31G*, where **2** becomes a minimum [the lowest frequency $\nu(b_2) = 226$ cm^{-1}], while **3** turns out to be a transition state [$\nu(b_2) = 231i$ cm^{-1}].

Both at HF/6–31G* and at MP2/6–31G*, the energy difference between **2** and **3** is extremely small. At MP4SDTQ(fc)/6–31G(2d,p)//MP2(full)/6–31G*, **2** is only 0.09 kcal mol^{-1} lower in energy than **3** (Table 1). Moreover, when the ΔZPE(MP2(fc)/6–31G*) correction is taken into account, the order reverses, and **3** is 0.2 kcal mol^{-1} lower in energy than **2**. Hence, the singlet cyclopentadienyl cation exemplifies a structurally non-rigid molecule.[10] The pseudorotation in Scheme 1 should be very fast and the $C_5H_5^+$ nuclear configuration oscillates among the degenerate C_{2v} minima **2**, **2a**, **2b**, ...

The singlet cyclopentadienyl cation is considered to be an antiaromatic species.[2] Indeed, singlet **2** is destabilized with respect to the corresponding open-chain pentadienyl cation, in contrast to benzene which is stabilized with respect to hexatriene as shown by the energy of the homodesmotic reaction 2.

 (2)

$\Delta E = -68.1$ kcal mol^{-1}
MP4SDTQ/6–31G**//MP2/6–31G*

In contrast to the MP2/6–31G*//HF/6–31G* results,[6] we have found triplet **1** to be 2.6 kcal mol^{-1} more stable than **5**, which was claimed to be the most stable $C_5H_5^+$ isomer.[6] Moreover, **1** is lower in energy than singlets **2** and **3**. The pyramidal C_{4v} structure **6**, possessing three-dimensional aromaticity, [11,13] has 12.3 kcal mol^{-1} higher energy than the planar singlet **2** at MP4SDTQ/6–31G**//MP2/6–31G* (Table 1).

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