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The Stable Pentamethylcyclopentadienyl Cation**

Joseph B. Lambert,* Lijun Lin, and Vitaly Rassolov

The cyclopentadienyl anion, $C_5H_5^-$ (**1**, Cp^-), was first prepared one hundred years ago.[1] In due course it became a classic example of aromaticity, exemplifying the Hückel $4n+2$ rule for π electrons, along with benzene (**2**) and the tropylium cation (**3**).[2–4] In contrast, the cyclopentadienyl cation, $C_5H_5^+$ (**4**, Cp^+) has languished experimentally as an elusive charge variant. It shares with cyclobutadiene[5–7] (**5**) and the cycloheptatrienyl anion[8] (**6**), among others, the characteristics of possessing $4n$ π electrons and thus potentially being antiaromatic.


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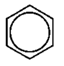
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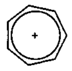
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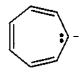
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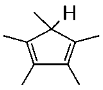
No simple cyclopentadienyl cation has been structurally characterized. Several studies have reported electron spin resonance (ESR) spectra,[9] and some studies have implied the species as an intermediate.[10] These investigations variously looked at the pentachloro, pentaphenyl, and pentamethyl derivatives as well as the unsubstituted molecule. In general, the observed cations were relatively unstable, possessed triplet multiplicity, and needed protective environment.

We now report the preparation of the pentamethylcyclopentadienyl cation $C_5Me_5^+$ (Cp^{*+}) as the tetrakis(pentafluorophenyl)borate ($TPFPB^-$) salt. The crystalline material obtained is stable for weeks at room temperature and can be left exposed to the open atmosphere without serious decomposition. We have solved the X-ray structure and obtained NMR spectra in the solid state and in solution. This material may be obtained in one step at room temperature by hydride abstraction from commercially available pentamethylcyclopentadiene [Eq. (1)].[11, 12] The trityl cation (Ph_3C^+, with the anion $TPFPB^-$) is converted into triphenylmethane, whereas pentamethylcyclopentadiene is converted into the corresponding cation. Crystals of the product began forming immediately and spontaneously. The overall yield is nearly quantitative, and yields of crystals have reached 40%. The reaction has been carried out in several solvents (benzene, toluene, dichloromethane) and with alternative (silyl) leaving groups.



$$+\ Ph_3C^+TPFPB^- \longrightarrow Ph_3CH + Cp^{*+}TPFPB^- \qquad (1)$$

The remarkable stability of this material may be attributed to a number of factors. First, the methyl groups clearly are critical, as analogous experiments with the unsubstituted system were unsuccessful. The methyl group serves as an electron donor and also may play a steric role, as described subsequently. The second key factor is the choice of the counteranion. Many anions of low nucleophilicity now are available.[13] We previously utilized $TPFPB^-$ in the preparation of the first silylium cation[14] and employ this same anion in the present study. Finally, choice of solvent also is critical, as

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

solvents with higher nucleophilicity than those of arenes or halocarbons react with the cation.

The crystal structure[15] of the cation with its anion is depicted in Figure 1. As the edge view (Figure 2a) shows, the molecule is modestly nonplanar (the five internal ring dihedral angles are 4.1(6), 6.6(6), 4.6(5), 6.9(6), and 0.5(5)°). Three carbon atoms (C1, C2, C3) and their attached methyl groups form a nearly planar substructure closely resembling a 1,2,3-trimethylallyl group. Atoms C4 and C5, respectively, are below and above this plane, and their attached methyl groups protrude appreciably from the plane, the CH_3-C4-C5-CH_3 dihedral angle being 106.9(6)°.

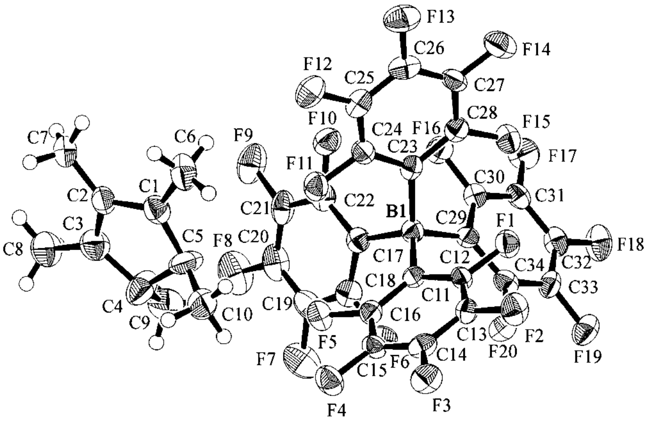


Figure 1. The crystal structure of pentamethylcyclopentadienyl tetrakis(pentafluorophenyl)borate. There is no covalent bonding between the cation on the left and the anion on the right.

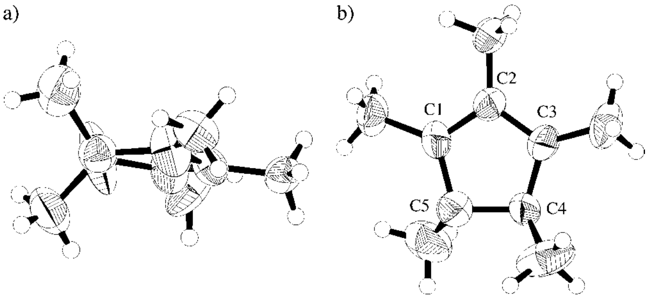
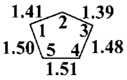


Figure 2. a) Edge view of the pentamethylcyclopentadienyl cation, sighting down the C4-C5 bond on the left. The nearly planar allyl portion is on the right. b) Top view.

The view from the top (Figure 2b) shows an irregular pentagon. The irregularity is quantified in structure **7** (the methyl groups are omitted from the following structures for clarity). The bond lengths in the allyl-like portion across the top of the drawing are relatively short, that is, approximately 1.40 Å (benzene-like), as expected for charge delocalization. The other bond lengths are somewhat shorter than a single bond between sp^3 carbon atoms (typically ca. 1.54 Å) and longer than a single bond between unconjugated sp^2 carbon atoms (typically ca. 1.48 Å).



7

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9

10

Several valence bond structures may be considered.[3] The fully delocalized form **8**, which would suffer from antiaromaticity, is eliminated because of the observed irregularity of the pentagon. Structure **9** requires a localized cation at C1 and localized double bonds, whereas the observed C3–C4 and C1–C5 lengths are closer to single bonds. Structure **10** best describes the C1-C2-C3 (allyl-like) portion. The observed C4–C5 bond is closer to a single bond and is poorly depicted by all the structures.

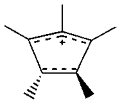
The best reported calculations on the pentamethyl derivative[16] indicate strong bond alternation resembling **9**, with a nearly single C4–C5 bond (1.56 Å) but no pyramidalization at these carbon atoms. Our own calculations on the pentamethyl derivative[17,18] at higher level, however, favor structure **10**, with lengths of 1.38 and 1.39 Å (observed 1.406(6) and 1.394(6) Å) for the bonds (C1–C2, C2–C3) in the allyl portion, 1.52 and 1.53 Å (observed 1.500(6) and 1.481(6) Å) for the next adjacent bonds (C1–C5 and C3–C4), and 1.36 Å (observed 1.510(6) Å) for the bond (C4–C5) opposite the allyl portion. All calculations[16,17] have indicated a planar structure. Thus the major differences between our calculations and observations are an observed lengthening of C4–C5 by 0.15 Å and pyramidalization of C4 and C5.[19]

The solid-state ^{13}C NMR spectrum reflects the nonequivalence of the five ring carbon atoms in the crystal. As a result, all ten carbon atoms in the molecule give distinct or nearly distinct peaks. There are five methyl resonances in the region $\delta = 7-22$. The cationic region contains two equal peaks at $\delta = 243$ and 250, corresponding to C1 and C3. The central carbon atom (C2) in the allyl-like fragment gives a sharp signal at $\delta = 153$, indicative of the absence of charge at the nodal position of the allyl group. The resonances for C1-C2-C3 closely resemble those for the 1,3-dimethylallyl cation ($\delta = 236$ and 147).[20] Finally, a peak at $\delta = 60$ is intermediate between the normal alkane and alkene regions and fits well for the pyramidalized carbon atoms, C4 and C5. Higher symmetry is indicated in solution, as the C1/C3 resonances appear at the approximate average positions of those in the solid.

The unsaturated region of the ^{13}C NMR spectrum is best attributed to the allyl fragment of **10** (two carbon atoms bearing positive charge, plus one on the node). Structure **9** has only one carbon atom bearing positive charge. Thus NMR spectroscopic analysis confirms the conclusions from the crystal structure that **10** best describes the pentamethylcyclopentadienyl cation.

To probe the spin multiplicity of this cation, we examined pure crystals and diluted powder by ESR spectroscopy. No significant signals were obtained at either 77 or 298 K. A triplet state thus is unlikely. The sharpness of the NMR signals both in the solid and in solution strongly supports the absence of unpaired electron spins, which should have broadened the signals. The pentamethylcyclopentadienyl cation therefore appears to be a stable singlet molecule. Our calculations[17] found the planar singlet state of the pentamethyl derivative to be lower by 1.5 kcal mol^{-1} than the symmetrical (D_{5h}) triplet state.

Crystallography, NMR spectroscopy, and theory support a structure most closely resembling **10**. The pyramidality of C4 and C5 and the Me-C4-C5-Me dihedral angle in the crystal (107°), however, indicate significant deviations from a double bond. The estimated barrier to torsion around the C4–C5 bond is quite small, perhaps under 100 cal mol^{-1}. Thus in both calculation and observation, this formally double bond is very unusual. The pyramidality seems to imply a fourth coordination, yet there is no fourth atom within the sum of the ionic radii. The closest atom to C4 is F6 (3.092 Å) from the counteranion (Figure 1), and the closest atom to C5 is F14 (3.394 Å) from the second anion in the asymmetric unit. Fluorine atoms at 3.1–3.4 Å distance can provide only a very small perturbation to pyramidalize C4 and C5 and lengthen C4–C5. In the solid state, there is a fluorine atom on the anion close to a hydrogen atom on each of the methyl groups on C4 and C5 (H12····F20 2.70 Å, H14····F18 2.50 Å). These distances would be about 1 Å shorter if the ring substituents moved into the plane of the ring. Crystal packing between the anion and the cation pyramidalizes C4 and C5, a distortion permitted by the weak π bonding. These are noncovalent, nonbonded interactions. The resulting deformations are a tradeoff between coulombic attractions and nonbonded repulsions.



11

In summary, we have observed that the pentamethylcyclopentadienyl cation is a stable singlet with a largely localized electronic structure best described by **11**.

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[17] Geometry optimization and energy calculations were carried out at the CASSCF(4.5)/6-31G* level of theory with the GAMES program.[18] Inclusion of nondynamic correlation effects allows mixing of electronic configurations for **9** and **10** and favors geometry **10** with a singlet ground state. The MP2 calculations used by previous authors[15] for geometry optimization are based on a single determinant reference and, therefore, do not permit such mixing. These calculations favor molecular structure **9** rather than **10** and the triplet rather than the singlet.

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[19] The C4–C5 bond is clearly a double bond in calculation and must be considered formally to be a double bond in observation to account for all the π electrons. Because of pyramidalization, however, its length is closer to that of a single bond.

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