Bond-Stretch Isomerism

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The Two Structures of the Hexafluorobenzene Radical Cation $C_6F_6^{\bullet+}$ [**]

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Benzene is the archetypical aromatic species, with regular D_{6h} symmetry, aromaticity, ring current, special chemistry, and stability. It is to be expected that a change in the electron count should have a severe effect in these ring systems: for example, the global minimum of the $C_6H_6^{2+}$ dication is a fulvene dication.[1] The six-membered-ring singlet dication is predicted to have a nonplanar "bisallyl" structure. The $C_6(CH_3)_6^{2+}$ ion even has an experimentally established pentagonal-pyramidal skeleton.[2]

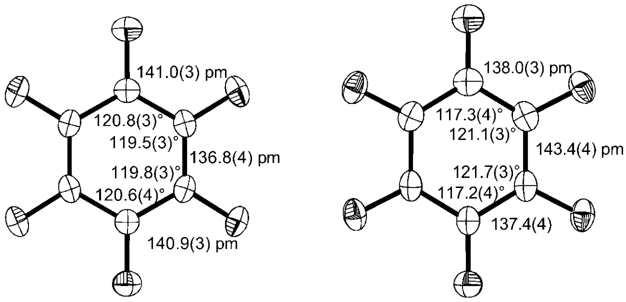
The loss of one electron from benzene could have a less drastic effect. If the six-membered ring skeleton is retained, the least that is expected is a Jahn–Teller distortion away from the regular hexagonal structure, possibly of the dynamic type. Calculations have predicted that a compression of the regular six-membered ring would be the ground state for the radical cations $C_6H_6^{\bullet+}$, $C_6F_6^{\bullet+}$, and $C_6H_3F_3^{\bullet+}$. A low-lying saddle point corresponded to an elongated structure.[3–5]

Isolation of salts with the radical cation $C_6H_6^{\bullet+}$ remains a challenge. Although the first ionization potential, and therefore the oxidation potential, of C_6F_6 is higher than for C_6H_6,[6] so that a stronger oxidant is needed for the production of the radical cations, the organic-bound fluorine atoms lend better protection during and after the oxidation step. Indeed as early as 1974 it was observed that C_6F_6 can react with $O_2^+AsF_6^-$, and the unstable yellow solid product was clearly $C_6F_6^{\bullet+}AsF_6^-$.[7,8] Also $CrF_5{\cdot}2SbF_5$ can oxidize C_6F_6.[9]

For a successful isolation and complete structural characterization of $C_6F_6^{\bullet+}$ salts there are several requirements: a) The oxidation power of the oxidant should not be much higher than just necessary, so as to avoid secondary reactions; b) the counterion should have low symmetry so that it should not enforce disorder on the $C_6F_6^{\bullet+}$ ion; c) the counterion should be as weakly coordinating as possible, so that its influence on the structure of the cation is minimized. With OsF_6 we accidentally found the proper oxidant.

C_6F_6, dissolved in HF, is not oxidized by OsF_6. However addition of SbF_5 increases the oxidation strength of OsF_6 just enough so that an electron transfer occurs smoothly, and upon cooling, brown crystals are found in good yield. According to the crystal-structure analysis the compound is $C_6F_6^{\bullet+}Os_2F_{11}^-$. Surprisingly there are two crystallographically different $C_6F_6^{\bullet+}$ ions with distinctly different structures. The $Os_2F_{11}^-$ ion has a fluorine-bridged structure, very similar to the established $Sb_2F_{11}^-$ anion, but to our knowledge, $Os_2F_{11}^-$ is formed for the first time. As osmium appears in many oxidation states, and to rule out any doubt that we have Os^V (and therefore with $C_6F_6^{\bullet+}$), we attempted the synthesis with the $Sb_2F_{11}^-$ ion.

This reaction of C_6F_6 with $O_2^+Sb_2F_{11}^-$ is difficult to control due to the higher oxidation power, but finally the product $C_6F_6^{\bullet+}Sb_2F_{11}^-$ is obtained as a yellow crystalline solid. This compound has a similar composition to the fluoroosmate $C_6F_6^{\bullet+}Os_2F_{11}^-$, and the compounds are crystallographically virtually identical. The precision of the $C_6F_6^{\bullet+}Sb_2F_{11}^-$ structure determination is even higher, possibly due to lower X-ray absorption (Figure 1).[10]



I, Quinoid Cation

II, Bisallyl Cation

Figure 1. The two experimental structures of the $C_6F_6^{\bullet+}$ ion in the salt $C_6F_6^{\bullet+}Sb_2F_{11}^-$. Both cations have a twofold crystallographic axis, so that bond lengths and angles on the left side are the same as on the right side. Furthermore both cations have, within the error limits, D_{2h} symmetry. The structure of the compound $C_6F_6^{\bullet+}Os_2F_{11}^-$ is virtually identical in all details.

In both cases the original C_6F_6 hexagon is strongly distorted. This distortion is most clearly seen in the bond-length variations within the two rings, which are far above the error limits. Both cations have D_{2h} symmetry. Cation I is a compressed hexagon, and could be called a "quinoid" structure, cation II resembles an elongated hexagon, and could be called a "bisallyl" structure. The geometries can be represented by the Lewis structures as shown in Scheme 1.

The terms "compressed" and "elongated" hexagons may be misleading. In comparison to the C–C bond lengths of neutral C_6F_6 (average value: 137.8(2) pm at −140°),[11] the quinoid form has four elongated bonds, the bisallyl form two. All the C–F bond lengths in the two forms of $C_6F_6^{\bullet+}$ are shorter than in C_6F_6 (average value: 133.3(2) pm, see Table 1). This change reflects the positive charge of the rings. Differences between C–F bond lengths within each of the cations are predicted to be very small, they are on the border of the experimental accuracy, but the predicted trends seem to be

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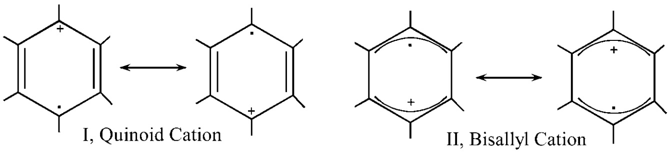

Scheme 1. The Lewis structures for cations I and II.

obeyed. Only a qualitative answer can currently be given to the question of the influence of the anions on the two cations. Number and lengths of $F_{anion}\cdots C_{cation}$ contacts seem to be quite similar for both cations.

In solution the EPR spectrum shows a symmetrical binominal septet, indicating a rapid interchange of both structures in solution ($g = 2.0022$, $a_F = 13.65$ G, −20 °C in SO_2FCl).

The observation of two distinctly different isomers is also verified by our DFT calculations.[12] Different methods and different basis sets reproduce the bond lengths to within ±1 pm. The results are shown in Table 1 along with the experimental values. An important fact is that both isomeric forms have the same energy within 0.1 kcal mol^{-1}, so that the question of which isomer represents the global minimum remains open, although even the most sophisticated method suggests the quinoid structure to be the slightly more stable one.

Table 1: Calculated[a] and experimental (in parentheses) bond lengths [pm] and angles [°] of $C_6F_6^{\bullet+}$ radical cations.

Bond	Quinoid $C_6F_6^{\bullet+}$	Bisallyl $C_6F_6^{\bullet+}$
C–C 2×	137.1 (136.8 (4))	144.9 (143.4(4))
C–C 4×	142.7 (141.0, 140.9(3))	138.9 (138.0, 137.4(4))
C–F 2×	128.8 (129.6, 130.1(4))	130.9 (131.3, 130.5(5))
C-F 4x	130.3 (130.6, 131.2(3))	129.3 (130.2, 130.6(4))
C–C–C 2×	122.4 (120.8, 120.6(4))	117.7 (117.3, 117.2(4))
C–C–C 4×	118.8 (119.5, 119.8(3))	121.2 (121.1, 121.7(3))
$E_{rel.}$ [kcal mol^{-1}]	0.0	0.09

[a] B3LYP calculations in D_{2h} symmetry with a TZPP basis set.

To analyze the transitions between the two states we have calculated the two-dimensional potential-energy surface resulting in a "mexican hat" (Figure 2).

There is a path from the bisallyl structure to the chinoid structure without a barrier (Figure 3). This path is along the brim of the "mexican hat" in Figure 2. If D_{2h} symmetry is retained during the interchange, than a barrier of 3.1 kcal mol^{-1} is calculated, in good agreement with a spectroscopically determined value of 2.3 kcal mol^{-1} in the gas phase.[13] This transition state is represented by the tip of the "mexican hat" in Figure 2. A related system is found for the Jahn–Teller distortion in AuX_3 (X = F, Cl) molecules, except that all the energy differences are about one order of magnitude larger so that the global minimum can clearly be located.[14]

In Figure 4 the two highest occupied (one singly, one doubly occupied) orbitals are shown for both isomers. The two isomers differ only in the order of these two π orbitals.

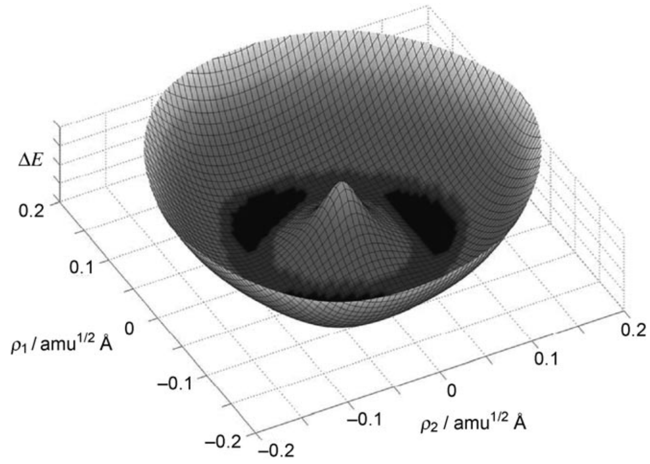

Figure 2. The "mexican hat" potential energy surface (PES) of $C_6F_6^{\bullet+}$ at the B3LYP level, generated along the normal coordinates of the frequency 437 cm^{-1} from the bisallyl cation based on the D_{6h} symmetry point in the center. ρ_1 and ρ_2 describe the change of the structure. The dark areas represent the quinoid structure separated by three bisallyl structures marginally higher in energy.

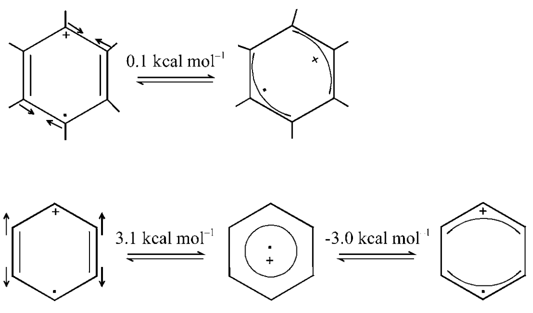

Figure 3. Schematic transitions of low (top) and high (bottom) energy between the quinoid and bisallyl cation $C_6F_6^{\bullet+}$. Top: Barrier-free path, bottom: path via a D_{6h} transition state with a 3 kal mol^{-1} barrier. The arrows show the principal movements during the transitions.

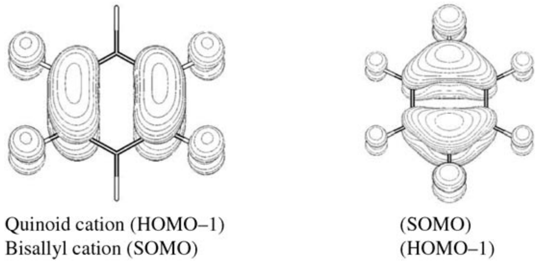

Figure 4. View of the two occupied (π) orbitals with highest energy of cations I and II

Areas of double bonding and positions of the unpaired electron support the Lewis structures.

In the early 1970s, the occurrence of two isomers that differ only in bond lengths was predicted by theory and called bond-stretch isomerism.[15] Experimentally confirmed cases are rare.[16,17]

Other cases for bond-stretch isomerism could be isomers of Jahn–Teller expanded and compressed octahedral metal complexes. But the original findings of unusual compressed MnF_6^{3-} octahedra turned out to be crystallographical artifacts caused by twinning.[18] Bond-stretch isomers as postulated in *mer*-$[(R_3P)_3MoCl_2O]$, which seemed to exist in two isomers with different Mo=O bond lengths and colors[19,20] are also an artifact arising from the existence of mixed crystals of different compounds.[21]

In conclusion we showed experimentally and theoretically that the hexafluorobenzene radical cation exists in two forms.

Experimental Section

Reactions were performed in PFA (Poly perfluorovinylether tetrafluoroethylene copolymer) tubes, volatile materials (anhydrous HF, C_6F_6, OsF_6) are handled in a stainless steel vacuum line. $O_2^+SbF_{11}^-$ was prepared from O_2, F_2, and SbF_5.[22] C_6F_6 (99.5%, Aldrich Co) must be highly pure since contaminants are oxidized preferentially.

$C_6F_6^{\bullet+}$ $Os_2F_{11}^-$: OsF_6 (100 mg), HF (2 mL), and C_6F_6 (300 mg) were condensed into a PFA tube, which contained SbF_5 (50 mg). The reaction mixture was slowly warmed to room temperature, affording a yellow brown clear solution. To remove excess C_6F_6 all volatiles were removed under vacuum, then HF (2 mL) was condensed in. Slow cooling of the mixture to −78° gave a large crop of brown crystals.

$C_6F_6^+$ $Sb_2F_{11}^-$: $O_2^+Sb_2F_{11}^-$ (100 mg) was place into a PFA tube and C_6F_6 (300 mg) condensed on it. Very slow warming to −20 °C afforded a yellow, clear solution. At −20° the excess C_6F_6 was removed under vacuum, then HF (2 mL) was condensed in. Recrystallization from −30° to −78 °C affords yellow crystals. Care must be taken that the temperature never exceeds −20 °C throughout the entire procedure.

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[10] X-ray data for $C_6F_6Os_2F_{11}^-$: $a = 898.58(4)$, $c = 28.7388(18)$ pm, $\gamma = 120°$, $V = 2009.6 \times 10^6$ pm^3, trigonal, space group $P3_121$, $Z = 6$, $\theta_{max} = 46.5°$, 11 890 unique reflections, 230 parameters, $R_1 = 0.0251$, $wR_2 = 0.0543$. X-ray data for $C_6F_6^{\bullet+}Sb_2F_{11}^-$: $a = 905.80(7)$, $c = 290.79(42)$ pm, $\gamma = 120°$, $V = 2066.2 \times 10^6$ pm^3, trigonal, space group $P3_221$, $Z = 6$, $\theta_{max} = 30.5°$, 4208 unique reflections, 230 parameters, $R_1 = 0.0152$, $wR_2 = 0.0336$. CCDC 703432 and 703433 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] X-ray data of C_6F_6: −140°, $a = 590.4(1)$, $b = 911.7(2)$, $c = 1677.5(3)$ pm, $\beta = 94.016(4)°$, $V = 900.8 \times 10^6$ pm^3, space group $P2_1/n$, $Z = 6$, $\theta_{max} = 30.6°$, 2757 unique reflections, 163 parameters, $R_1 = 0.0402$, $wR_2 = 0.1147$, CCDC 703623 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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