

# $C_6F_6^{\cdot+}$ — BOND STRETCH ISOMERISM

Bond-stretch isomerism refers to isomers that differ simply in their bond lengths.

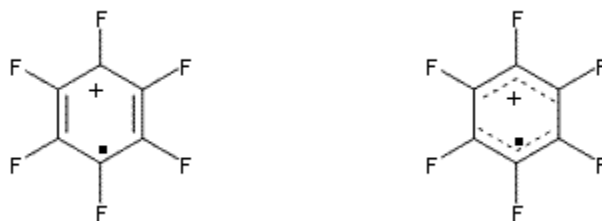
Seppelt and coworkers suggests that the hexafluorobenzene radical cation

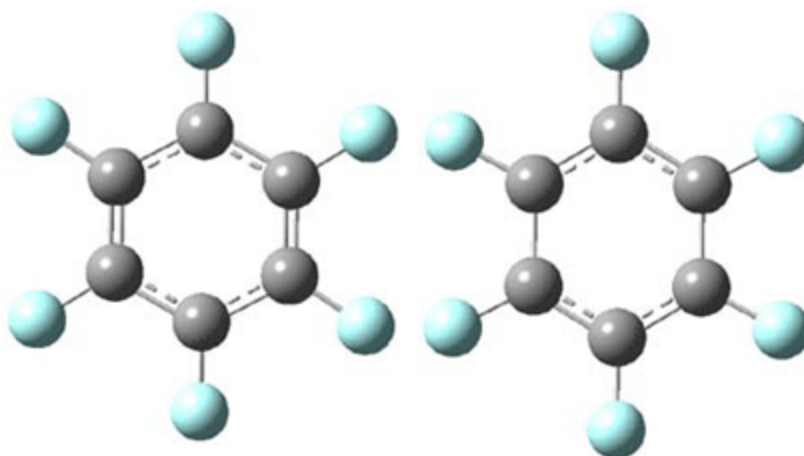
$C_6F_6^{\cdot+}$  exhibits bond-stretch isomerism.<sup>1</sup>

The oxidized  $C_6F_6$  with  $O_2^+SbF_{11}^-$  and obtained  $C_6F_6^{\cdot+}Sb_2F_{11}^-$  as a crystalline solid.

X-ray diffraction identified 2 structures. B3LYP/TZPP computations confirmed the identity of two isomers, a “quinoid” form **1** and a “bisallyl” form **2**, shown in

Figure 1. The two structures are nearly degenerate, with **1** predicted to be 0.09 kcal mol<sup>-1</sup> more stable than **2**. The computed two unique C-C bond lengths are 1.371 and 1.427 Å in **1** and 1.449 and 1.389 Å in **2**, and these distance agree well with the X-ray experimental values.





**1** – quinoid

**2** – bisallyl

**Figure 1.** UB3LYP/6-311+G(d) optimized structures of **1** and **2**. Note once again the article and supporting materials lacked the full description of these structures!)

The potential energy surface in the neighborhood of these two isomers is like that of a sombrero. The two isomers lie in the circular trough and movement around this trough is nearly flat. The peak of the sombrero is the  $D_{6h}$  structure, which is a transition state interconverting **1** and **2**, with a barrier of 3 kcal mol<sup>-1</sup>.

**1** and **2** are clear examples of bond-stretch isomerism, though it is likely that the complexation with the counter ion is what freezes out the rapid interconversion of the two.

Source: <http://comporgchem.com/blog/?p=369>