

HEXACOORDINATE CARBON

The search for the elusive hypervalent carbon atom took an interesting turn for the positive with the report of the synthesis and characterization of **1** and especially its dication **2**.¹ The x-ray structure was obtained for both compounds along with computing their B3PW91/6-31G(d) geometries. These computed geometries are shown in Figure 1.

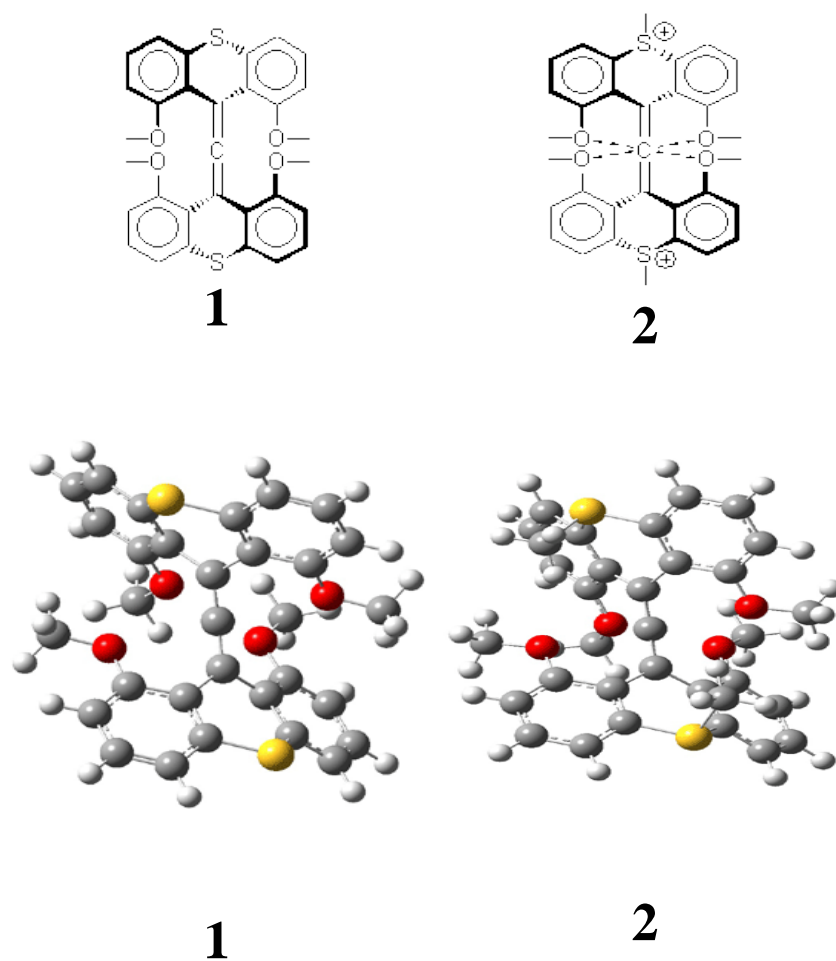


Figure 1. B3PW91/6-31G(d) optimized geometries of **1** and **2**.¹

The allene fragment is bent in both structures: 168.5° (169.9° at B3PW91) in **1** and 166.8° (172.7° at B3PW91) in **2**. The distances between the central carbon atom of the allene and the four oxygen atoms are 2.66 to 2.82 Å, and computed to be a little longer. Interestingly, these distance contract when the dication **2** is created; ranging from 2.64 to 2.75 Å (again computed to be a little longer). These distances, while significantly longer than normal covalent C-O bonds, are less than the sum of the C and O van der Waals radii. But are they really bonds?

This is not a trivial answer to solve. The authors opt to employ topological electron density analysis (Bader's atoms-in-molecules approach). Using the electron density from both the high resolution x-ray density map and from the DFT computations, bond paths between the central allene carbon and each oxygen are found, though with, as expected, low values of ρ . The Laplacian of the density at the critical point are positive, indicative of ionic interactions. So according to Bader's model, the existence of a bond path in a ground state molecule is the necessary and sufficient condition for bonding.

The others conclude by proposing that $O^{\cdots}C$ intermolecular interactions with separations of around 2.6 to 2.8 Å may also suggest hypervalent cases.

Source: <http://comporgchem.com/blog/?p=70>