

## Grasping Carbon – Bonding Nature of Penta- and Hexacoordinated Carbon by Experimental Electron Density Distribution Analysis

Carbon is a central element of chemistry. It enjoys a limitless molecular diversity in millions of molecules, and yet, for new students of chemistry and experienced researchers alike, the structures of carbon compounds are typically understood in terms of the very simplest of bonding concepts. Whether di-, tri-, or tetracoordinate, carbon obeys the octet rule with great predictability and has four 2-electron covalent bonds. In another words, carbon has four hands to grasp neighboring atoms. On the reaction path, however, most organic molecules take intermediate structures, in which the carbon atom of the reaction center forms more than four bonds. A hypervalent compound has bonds exceeding the number of bonds expected from the octet rule. Because the reaction intermediate has additional bonds, hypervalent compounds are considered to be models of intermediate states.

The pentacoordinated carbon compound is synthesized aiming at the model of the intermediate state of  $S_N2$  reaction. The central carbon atom of the compound has an  $sp^2$ -hybridization state, which is the same as the very famous intermediate of the  $S_N2$  reaction. The carbon atom forms three covalent bonds. The carbon atom and the bonding three atoms lie on the same plane. The empty  $p$ -orbital is orientated perpendicular to the plane. Oxygen atoms form two hypervalent bonds with the central carbon atom by donating the lone pair electron to the empty  $p$ -orbital of the carbon. Then, three-center four-electron bonds are formed.

The hexacoordinated carbon compound is an extension of making the pentacoordinated compound. The central carbon atom has an  $sp$ -hybridization state. The carbon atom forms two covalent bonds with linear geometry. Four oxygen atoms coordinate to the central carbon atom by donating lone pairs to empty  $\pi^*$ - or  $p$ -orbitals. Then, two three-center four-electron bonds are formed.

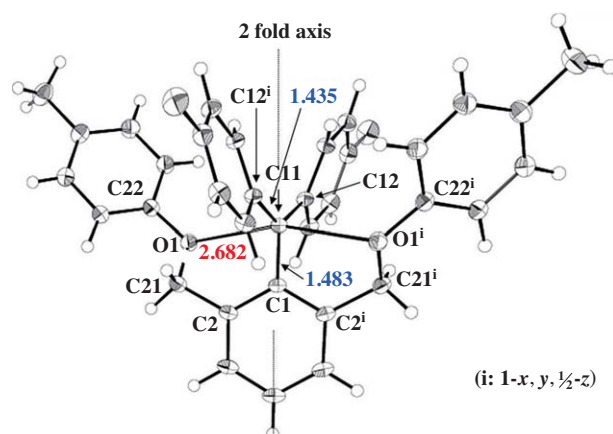
Since the hypervalent bond, in general, is weaker than the coordination bond, and shows a shallow and broad energy minimum, the evaluation of their bonding nature by theoretical calculations is sometimes difficult. X-ray diffraction, on the other hand, gives the total electron density distribution in crystal. If highly accurate and precise data were obtained, we can see all the chemical bonds in the molecule as they are. To understand the detail of the bonding nature, the electron configurations of hypervalent carbon compounds as models for reaction

intermediates were clarified experimentally by electron density distribution analyses using single-crystal diffraction data [1,2].

The diffraction data of both crystals were measured at beamline **BL04B2** using a MacScience imaging plate diffractometer. In order to reduce absorption and extinction effects, we use small crystals and high-energy X-rays (37.8 keV) for measurements. The data were collected with some different crystal orientations to ensure high redundancies. The electron density distributions of valence electrons were derived by a multipole expansion method, following normal crystal structure analyses using spherical atom models.

**Figure 1** shows the molecular structure of the pentacoordinated carbon compound. The compound lies on the crystallographic twofold axis through C1 and C11, which is a hypervalent carbon. The atom C11 is placed on the  $sp^2$ -plane, that is formed with by C1 and C12, and symmetry related C12. The atoms O1 and its twofold axis related atom coordinate to C11 from both sides of the  $sp^2$ -plane. The distance of C11-O1 is short enough to form a bond. Thus, the geometry of the hypervalent carbon atom is trigonal bipyramid. Because of the symmetry, two apical C-O bonds are identical. **Figure 2** shows an isosurface static model map, and bond paths and bond critical points of hypervalent bonds. In the map, one of the two lone pairs in the  $sp^3$ -orbital on each oxygen atom is oriented towards the empty  $p$ -orbital of the central carbon atom. Such geometry of the orbital indicates the dative nature of the hypervalent bonds.

**Figure 3** shows the molecular structure of the hexa-coordinated carbon compound. The bond



**Fig. 1.** Molecular structure of the pentacoordinated carbon compound. Bond distances are given in Å.

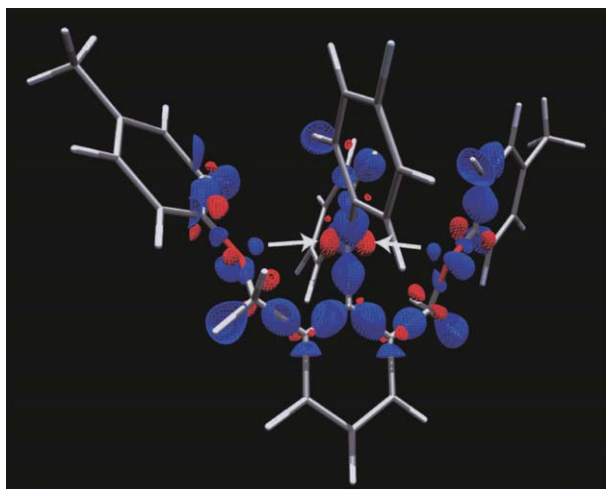


Fig. 2. Isosurface static model map of the penta-coordinated carbon compound. The isosurfaces are drawn in red and blue for electron-poor and electron-rich regions, respectively.

distance for both C17-C9 and C17-C26 is 1.3 Å, which indicates the double bond formations rather than single bonds. The C9-C17-C26 is slightly bent. The angle is 167°. The oxygen atoms are placed on the equatorial positions, and they are in contact with the central carbon atom. The distances were not identical. The O-C-O angles largely deviated from those of regular octahedral geometry. Figure 4 shows the isosurface Laplacian map of electron density distribution and bond paths. In the equatorial plane, the atom C17 has no charge concentration. This is well consistent with the consideration from orbital arrangements; in this region, the empty  $\pi^*$ -orbitals should be arranged. The bond paths start from the electron rich oxygen atoms to the central carbon,

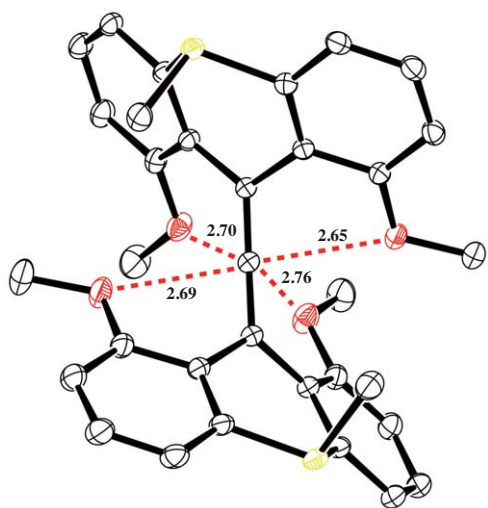


Fig. 3. Molecular structure of the hexacoordinated carbon compound. Bond distances are given in Å.

passing through the electron depression region around the carbon. These indicate that dative character of the bonds. All the C-O bond paths are curved. This indicates poor orbital overlapping of the hypervalent bonds for this compound.

The total electron densities of the compounds were analyzed quantitatively using Bader's "Atoms in Molecule" theory. They also reveal the dative character of the hypervalent bonds in both compounds.

In conclusion, the detailed bonding nature of hypervalent bonds can be derived by experimental method. Therefore, if some conditions are satisfied, the electron configuration of reaction intermediate can be analyzed by this method, and valuable chemical information can be derived in chemistry.

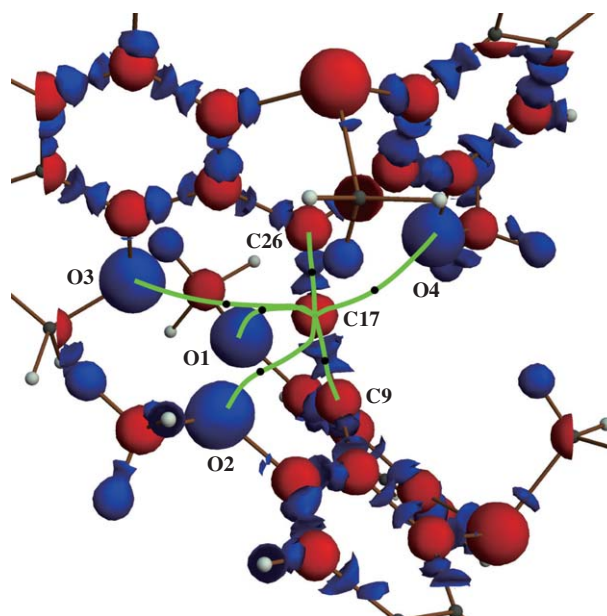


Fig. 4. Isosurface Laplacian distribution plot of the hexacoordinated carbon compound with six bond paths to C17 (green lines). The isosurfaces are drawn in red and blue for electron depressed and electron-concentrated regions, respectively.

Daisuke Hashizume

Advanced Technology Support Division, RIKEN (Wako)

E-mail: hashi@riken.jp

#### References

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